Chem. Rev. **2002,** *102,* 4191–4241

Reactions of Ground State and Electronically Excited Atoms of Main Group Elements: a Matrix Perspective

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Received March 13, 2002

Contents

> *By convention there is color, by convention sweetness, by convention bitterness, but in reality there are atoms and space.*
>
> Democritos, fragment 125, ca. 4000 B.C.

I. Introduction

Instinct may suggest that atoms are reagents second to none, for, the noble gases apart, the atoms of an element must be thermodynamically superior as synthons to the element in bulk. Yet this thermodynamic advantage fails to reflect the substantial kinetic barriers that oppose many reactions of atoms in their electronic ground state, which are far from spontaneous. Here we survey the reactions of atoms of the main group elements, with particular reference to how they may be generated and studied through the medium of matrix isolation, the importance of excitation of the atoms, and the contrasting fortunes of the atoms and their reaction products under the restraining influence of a solid matrix, as compared with the freedom of the gas phase. We go on to elaborate some of the more significant findings, and the review concludes with a table summarizing some of the research that has been carried out in this field with literature coverage extending up to late 2001 and occasionally into 2002.

Plainly there is a degree of arbitrariness in a choice that excludes, first, the atoms of d-block and f-block elements and, second, ions as opposed to neutral atoms and molecules, at least as primary reagents. The choice has been dictated partly on the grounds of our own experience and of keeping the review to manageable proportions. We have discounted monatomic ions as precursors while admitting that ionization is one of the courses that a neutral atom may take, either spontaneously or on excitation, in as-

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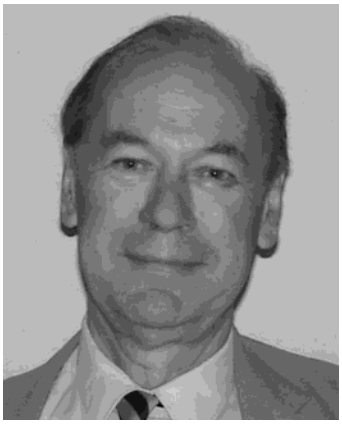
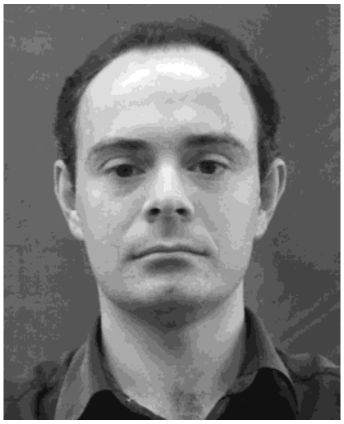
10.1021/cr020405x CCC: $39.75

Hans-Jörg Himmel studied chemistry in Heidelberg, Germany, where he received his diploma in 1994. In that year he started work for his Ph.D., first in Heidelberg and then in Bochum under the supervision of Prof. Dr. Christof Wöll at the Institute of Physical Chemistry; this work, completed in 1998, was in the field of surface science. From 1998 to 2000 he joined the group of Prof. Tony Downs at the Inorganic Chemistry Laboratory in Oxford, U.K., with funding from the Deutsche Forschungsgemeinschaft (DFG), and received a D.Phil. degree from the University of Oxford in 2000. Since October 2000 he has been working on his Habilitation at the Institute of Inorganic Chemistry of the University of Karlsruhe, receiving a Habilitanden-Stipendium from the DFG since 2001. His research interests center on reaction mechanisms in inorganic chemistry, with vibrational and UV–vis spectroscopy as the major methods of experimental inquiry, the matrix isolation technique as a primary tool for forming and retaining intermediates, and extensive use of quantum chemical modeling.



Tony Downs gained his first degree and Ph.D. from the University of Cambridge, U.K., where his research, concerned with perfluoroorgano derivatives of sulfur, was supervised by the late Professor H. J. Emeléus and by Dr. (now Professor) E. A. V. Ebsworth. Prior to his move to Oxford, he held a Salter's Fellowship (1961–1962) at Cambridge and was appointed a Senior Demonstrator (1962–1963), then Lecturer (1963–1966), in inorganic chemistry at the University of Newcastle upon Tyne. At the University of Oxford he was appointed first (1966) a Senior Research Officer, then (in 1971) a Lecturer, and latter (1996) a Professor in inorganic chemistry; he has been concurrently a Tutorial Fellow of Jesus College. His current research interests focus on reactive intermediates in the shape of hydrido and organo derivatives of both typical and transition elements. Characteristic of this research has been the alliance of synthetic studies (often requiring peculiarly rigorous exclusion of impurities) with a variety of physical techniques, including matrix isolation, vibrational spectroscopy, and electron as well as X-ray diffraction.



Tim Greene obtained his M.A. and D.Phil. degrees from the University of Oxford, the latter in 1995 for studies of reactive hydrido- and organometallic compounds under the supervision of Professor Tony Downs. In 1997, he was awarded an EPSRC Advanced Fellowship, which he held at Oxford until being appointed to a lectureship in inorganic chemistry at the University of Exeter in September 2001. His current research interests involve using the technique of matix isolation to study how small molecules may be activated by their interaction with a metal center. In addition, he is interested in the structure and reactivity of a range of main group hydrido- and organometallic compounds, most notably those involving metals from group 13.

sociation with a suitable partner. The reactions of ions in the gas phase have attracted many studies, as the research literature will testify. Such ions have also featured in matrix isolation experiments, but mostly as the products of reactions occurring within the matrix. It is true that some high-energy sources of atoms (q.v.) and molecules may give rise to a significant fraction of ions, but the competing claims of atoms and ions on a given substrate are apt to be hard to distinguish, certainly by the methods of interrogation normally at the disposal of the matrix isolationist.

The present paper is to our knowledge the first attempt to summarize the current state of knowledge about the reactivity of atoms of the main group elements in their electronic ground or excited states as revealed by matrix isolation experiments. Many more studies have sought to identify the atoms and their response to a potential reagent in the gas phase. Certain aspects of this reactivity have been discussed in previous reviews. For example, Perutz has reported on the reactions of atoms in matrices, but with examples usually involving main group or transition metal atoms generated in situ as intermediates.[1] The reactivity of an atom found in these circumstances will often differ significantly from that of the free atom in its electronic ground state. Moreover, many new reactions involving the atoms of main group elements have come to light in the 16 years since Perutz's review appeared. Reviews by Almond and Downs,[2] Almond and Orrin,[3a] Almond,[3b] and Almond and Wiltshire[3c] include sections dealing with atomic reactions in matrices, but most of the examples quoted relate to transition metal atoms. In a survey of the spectroscopic identification and characterization of matrix-isolated atoms, Gruen[4] has emphasized the role of UV−vis spectroscopy as an analytical technique, but transition metals again dominate the chemical action. Contemporary with this account are two reviews taking in specific reactions of main group metal atoms, also studied by matrix isolation methods. The first deals with alkali metal atoms;[5] the second, which is concerned with atoms of other main group metals, reports on their reactions with O_2, O_3, and CO.[6] The results available at this time shed little light on the mechanisms of the reactions. A much more recent article treats in some detail the production, detection, and photophysics of metal atoms in rare gas complexes, clusters, and matrices, but offers no commentary on the *chemistry* of these species.[7] On the other hand, the specific case of matrix-isolated Hg atoms has been discussed with regard not only to their spectroscopy and dynamics but also to their photochemistry.[8] McClinchey and Skell[9] and Klabunde[10] have also surveyed the use of the vapors of main group elements in organometallic and organic synthesis. In this case, however, the reactions take place not in solid matrices at high dilution and low temperatures or in the gas phase, but following the co-condensation of the vapors of the element and the organic substrate at relatively high temperatures ($\geq$77 K and often near 300 K). The final products of these reactions are often organic compounds, for example, saturated organic molecules produced by the reduction of alkenes by Al atoms and H_2O and proceeding, it is claimed, with 95% stereospecificity. Other reviews have been concerned specifically with the preparation and reactions of carbon,[11] silicon,[12] and selenium and tellurium atoms.[13] In addition, there exists a more or less complete bibliography of matrix studies, relating to atomic as well as polyatomic species, over the period 1950−1997.[14]

The myriad studies of atomic behavior in the fluid phases defy compendia or overviews. Breckenridge and Umemoto are among the few to have attempted anything along these lines, with reviews on the quenching of electronically excited gaseous atoms by physical and chemical means that date back to 1982−1983.[15,16] A more recent book, *Gas-Phase Metal Atom Reactions*,[17] is mainly preoccupied with techniques, the only allusion it makes to main group chemistry concerning the interaction of Mg atoms with CO_2. Yet research activity in this mature field has burgeoned with the exploitation of new or improved techniques. For example, crossed-beam studies[18] have progressed through the use of laser excitation or electrical discharge to generate supersonic beams of transient species with a flux sufficient to allow for the study of many reactions of practical interest. To laser-induced fluorescence (LIF), time-of-flight (TOF) mass spectrometry, and other well-tried methods of detecting and interrogating atoms and/or the products of their reactions have been added numerous alternatives. These include, for example, resonantly enhanced multiphoton ionization (REMPI),[19] Penning ionization,[20] coherent antistokes Raman spectroscopy (CARS),[21,22] ion imaging,[23] IR absorption[22,24] and emission,[25] Doppler profile analysis,[26] cavity ring-down spectroscopy,[27] real-time femtosecond studies,[28] scattering state[29] and transition state[30] spectroscopy, and zero electron kinetic energy (ZEKE) spectroscopy.[31] Concentrations range from the rarefied of the interstellar medium,[32] through those of planetary atmospheres,[33] to the relatively dense state of liquid helium solutions.[34] Thermal energies meanwhile run the gamut from the ultrahot (in plasmas,[35] for instance), through the less hot (as in typical combustion processes[36]) and the 3−30 kJ regime of normal, controlled laboratory conditions, to the ultracold (achieved, for example, by laser cooling[37]). Moreover, atomic encounters may be with either neutral or charged[38] participants. The final outcome depends intimately on the nature of the aggregate initially created by the coming together of the protagonists. More often than not, a reactive encounter has its origins in an aggregate that is in effect a loosely bound van der Waals molecule, a factor that has stimulated a wealth of research on the structures, energies, photochemistries, and dynamic behaviors of such molecules.[39]

The foregoing survey, brief and selective as it is, makes plain the immensity and diversity of gas-phase studies in particular. The results derived from this source have established and illuminated much of our understanding of major subjects, each with a life and literature of its own. Among these we may cite (i) flames and combustion,[36] (ii) plasma diagnostics,[35] (iii) atmospheric science (in which, for example, atoms such as O, Cl, and Na influence in various ways and degrees the composition and properties of the earth's atmosphere),[33] and (iv) the chemistries of stars, comets, and the interstellar medium.[32] It is surely a sign of the pivotal role of gas kinetics, and not merely of individual ingenuity, that Nobel prizes have come to investigators of reactions such as $Cl + Cl \rightarrow Cl_2$,[40] $H + Cl_2 \rightarrow HCl + Cl$,[41] $Cl + O_3 \rightarrow ClO + O_2$,[33] and $Na + I \rightarrow ?$.[28]

To attempt in a modest review such as this any sort of commentary on the fate of main group atoms in the gas phase would be to steer for some "false impossible shore". Our ambitions are altogether more limited in the course we take. In considering the possible changes that may arise from the initial atomic encounter, we are not primarily concerned with the intimate *physical* details of energy transfer. Attention is certainly directed to the relative virtues and limitations of the gas and matrix phases as media for investigating the chemistry of atoms. The sort of matrix that a solid noble gas provides is often portrayed as a pseudo-gaseous environment with regard to its effect on a species entrained within it. Where chemical reactivity is concerned, however, there are fundamental differences between the gas and matrix phases. The matrix necessarily inhibits severely the mobility of the atomic and molecular guests while also acting like a solvent in its capacity to absorb any excess of energy that may arise from physical or chemical excitation and to stabilize potential products. It may also have more subtle functions, for example, in modifying the photophysical and spectroscopic properties of the guests. There follows (in section V) a discussion of the reactivity of the atoms of selected main group elements with particular reference, as appropriate, to the reactions with small molecules such as H_2, O_2, CH_4, $HC{\equiv}CH$, H_2O, and NH_3. As noted already, we restrict ourselves to neutral atoms and molecules as reagents, with ionization featuring only as a means of detection and analysis, or as a possible reactive outcome. Gas-phase studies are considered, therefore, not systematically but here and there for the counterpoint they provide to the main theme of matrix studies. Overall runs the motif of reactivity in a confined space.

II. Experimental Techniques

In this section we outline some of the techniques needed to generate and detect the atoms of main group elements and to monitor any reactions in which they engage.

A. Atom Generation

The atoms may be generated in at least four different ways, namely, (i) by thermal evaporation of the solid element, (ii) by laser ablation of the solid element, (iii) by bombardment of the solid element with ions (sputtering), and (iv) by thermolysis, photolysis, or discharge of a suitable precursor molecule. From the standpoint of the matrix experiment, it is necessary also to distinguish methods in which the atoms are generated *externally* and then co-condensed with the prospective reagent and an excess of the matrix gas from those in which the atoms are formed *internally*, that is, within the matrix deposit. These external and internal categories will now be used as a framework for a brief outline of the different routes, due attention being paid to their merits and demerits.

1. Formation of Gaseous Atoms: External Methods in Matrix Experiments

(i) Thermal Evaporation.[10,42,43] The thermal evaporation of metal or other atoms can be carried out either by resistive heating or by electron bombardment, where electrons emitted from a filament are accelerated under a potential gradient toward an appropriate metal target. Resistive heating is the easier and more widely applicable method. The element of interest can be heated either directly, for example, by passing the current through it in the form of a thin wire, or indirectly by heating a wire or container made from another, more refractory material in thermal contact with the element to be evaporated.

Direct heating has the practical disadvantage that the electrical contact can be lost if the element has to be heated above its melting point or if it evaporates so quickly that the solid source becomes insupportably thin. Further complications may arise from the properties of the solid element, for example, brittleness or inadequate electrical conductivity. For these reasons, direct heating is mainly employed only if very high temperatures are needed to evaporate the element, for example, for the evaporation of carbon.[11]

Indirect heating is mostly favored for evaporation temperatures between about 200 and 1500 °C. It too is limited by a number of factors.

- Evaporation of the furnace material has to be avoided so that appropriately refractory materials need to be chosen. The furnace should not normally be heated to a temperature more than two-thirds of the melting point of the support (because at this point the surface starts to melt).
- The support should not react with the element to be evaporated. Another potential problem is etching of the support by the element because this is liable to damage the furnace (e.g., Al in a Ta-lined furnace).
- The currents needed for evaporation are higher than those needed for direct heating.

As a furnace material tantalum is often the best choice because it can sustain high temperatures and is a soft, relatively inert material that is easily formed into a container.

One handicap of the thermal evaporation technique is that the vapor is liable to contain not only atoms but also dimers and higher clusters, the chemistry of which is often quite different from that of the atoms themselves (compare, for example, the reactions of Ga and Ga_2 with H_2 in a solid noble gas matrix,[44] section II.B). One obvious way to solve this problem would be to produce the desired species as a mass-selected ion or molecular beam. Despite formidable technical problems, such mass selection is now feasible in conjunction with the matrix isolation principle,[45,46] but studies carried out to date have concentrated on the polyatomic clusters (which are likely to replicate more closely small particles or solid surfaces) rather than their monatomic parents.

(ii) Laser Ablation.[46,47] A pulsed, focused laser beam can be used to eject atoms from a solid target. The advantage of this method is that most elements which are solids can be evaporated without any problems. The vapor consists almost entirely of atoms because the high energy of the laser-induced plasma results in decomposition of any dimers or larger clusters. There are further advantages of efficiency and cleanliness stemming from the fact that each laser pulse causes only a minute amount of the sample to be instantaneously heated to a very high temperature and so vaporized. On the other hand, however, the high energy of the atoms so produced is apt to make them unselective in the reaction paths they follow. In these circumstances it may be difficult to judge the photolysis behavior of the atoms, and some of the products, for example, loosely bound adducts, may well escape detection. Further complications may arise from the production by laser vaporization of not only neutral species but also electrons and ions. It has been shown, for example, that in the plasma created by the vaporization of magnesium or calcium >10% of the atoms are likely to be ionized.[48] Although laser ablation may thus be quite an efficient source of ions,[46] identification of all the different reagents, products, and reaction pathways can be problematic. In addition, the plasma acts as a powerful radiation source with the capacity to excite atoms and molecules alike. Such excitation probably accounts for the cleavage of the strong N≡N bond when laser-ablated Al,[49] Ga,[50] or In[50] (M) atoms are co-condensed with N_2; the IR spectra of the resulting matrices then reveal the formation of such products as MN and NMN.

(iii) Sputtering with Ions.[51] A third possibility originally developed by Bass and others in the 1960s is the bombardment of a target of the solid element with ions such as Ar^+ possessing high kinetic energy (typically ~1 keV). The kinetic energy of the impinging ions is used to eject atoms and clusters from the target. It is of course a condition that the ions must be chemically inert in order to prevent reactions from occurring between them and the target atoms. Using a reactive gas for sputtering denies any sight of the target atoms but may be useful in matrix experiments, for example, as a means of generating species such as AlH[52] and BO.[53]

(iv) Molecular Sources of Atoms.[1] Activation of a suitable molecular precursor by the action of a discharge, of heat, or of photolysis offers another well-trodden path to main group atoms.

(a) Discharge Methods.[42,54] Certain compounds of a given element can be made to decompose with the formation of atoms of that element under the action of a discharge. A case in point is provided by O atoms, which can be generated from dioxygen by passage through a microwave discharge (see ref 55, for example). The disadvantage of the method is that the other fragments produced in the discharge process, which may well include ions, represent impurities with the potential to confuse by their spectra and to act as precursors to unwanted products. A further source of impurities is the glass or quartz apparatus in which the discharge is struck, and which leads inevitably to the presence of Si-containing products. Discharge methods are most popular for generating the nonmetal atoms H, N, O, F, Cl, Br, and I and are featured in some of the earliest matrix isolation experiments carried out by Pimentel and others.

(b) Thermal or Photolytic Dissociation. Alternatively a precursor can be decomposed by supplying it with thermal or, more often, photolytic energy to produce atoms of one of the constituent elements. For example, flash pyrolysis of a gaseous mixture of Br_2, O_2, and Ar provides a means of forming Ar matrices doped with both Br atoms and O_2 molecules.[56] The low concentrations of molecules in the gas phase make photolysis a relatively inefficient method of producing atoms under these conditions, and for the purpose of matrix isolation more is to be gained by irradiating the molecules *during* deposition so as to take advantage of the increased molecular concentrations and relative mobilities of both atoms and molecules during this phase of the experiment. More often, however, photolysis is used to form atoms by dissociation of a suitable molecular precursor once it has been isolated in a matrix.

2. Atom Formation in Situ in Matrix Experiments

Photodissociation of a molecular precursor entrained within a transparent matrix is a well-trodden route to atomic products.[1,2,14] The approach is exemplified by the photochemical decomposition of matrix-isolated OCS, leading to the creation of S atoms and CO.[1] Although the S atoms may thus be formed not only in an excited electronic state but also with a significant excess of energy, their freedom to migrate from the site of their formation is severely restricted by the matrix environment (see section IV). That some diffusion can occur is evidenced by the luminescence characteristic of S_2, which can be observed on annealing such a matrix,[1] but in other cases the photogenerated atom may have little opportunity to exit the matrix cage in which it and its coproduct have been formed. In these circumstances, the reactive options are effectively prescribed by the cage, with regeneration or isomerization of the parent molecule as the most likely outcome; the photochemistry of matrix-isolated ICN illustrates well this situation.[57]

Caution is also necessary in interpreting the results of this sort of experiment because the atoms may be passed on from the precursor to the reagent without any clearly defined stage at which they can be regarded as "free". A good example is provided by the UV photolysis of ozone, which is a well-known source of O atoms. When ozone is isolated together with phosphine in a solid argon matrix, however, it forms a complex $H_3P\cdot O_3$, which dissociates under the action of visible light to H_3PO and O_2, at least in the primary step.[58] Hence, O atom transfer has occurred through what might be termed an "inner sphere" mechanism because the O atom is never free from the perturbing influence of either the O_2 or the PH_3 molecule. Accordingly, the reaction cannot strictly be classified as one involving O atoms.

Photolysis of a molecular precursor in situ is particularly important for the generation of nonmetal atoms such as H, C, N, O, F, and S under matrix conditions.[1,2] The ideal precursor should be small and should perturb other species only weakly; furthermore, it should be dissociated by low-energy irradiation to produce the requisite atom and the minimum number of unreactive coproducts. No precursor fulfills all of these requirements, and so some compromise has to be struck. Many sources give rise to atoms in electronically excited states; we may compare, for example, the following reactions:[59]

$$\mathrm{SCS} \xrightarrow{h\nu} \mathrm{CS}\ (\mathrm{A}\ ^3\Pi) + \mathrm{S}\ (^3\mathrm{P})\ \text{(photolysis at 8.4 eV)} \tag{1}$$

$$\mathrm{OCS} \xrightarrow{h\nu} \mathrm{CO}\ (^1\Sigma^*) + \mathrm{S}\ (^1\mathrm{S})\ \text{(photolysis at 8.4 eV)} \tag{2}$$

Although the lifetimes of these states are typically very short and are not appreciably affected by the medium, decay to the ground state may often be forestalled by chemical reaction, and the range of such reactions is likely to be considerably greater than that open to the ground-state atom. For example, S atoms in the excited ^{1}D state, but not in the ^{3}P ground state, insert characteristically into the C−H bonds of alkanes,[60] and similarly O (^{1}D), but not O (^{3}P), adds to N_2 to form N_2O.[61]

B. Atom Detection

An essential general feature of the studies reviewed here is that the atoms, once formed, should somehow be detected; numerous systems purporting to involve the intermediacy of atoms lack this basic test. UV−vis absorption and emission and EPR offer the principal spectroscopic means of detecting the atoms themselves.[1] An alternative strategy is to introduce a specific molecule that reacts with the atoms to form a characteristic molecular product; this in turn may be identified by its vibrational, UV−vis, or EPR spectrum.[1] Sometimes, too, dimerization of the atoms may give rise to characteristic UV−vis absorption or emission (q.v.). The methods most widely applied in matrix studies involve UV−vis or EPR measure-

Table 1. Characteristic Electronic Transitions of Some Main Group Atoms for Which Wavelengths Are Known in the Gas and Solid Matrix Phases

	electronic transition, λ/nm			
atom	gas phase	solid matrix	assignment	ref
H	121.6	Ar 117.4	$2p\ ^{2}P \leftarrow 1s\ ^{2}S$	302
D	121.5	Ar 117.2	$2p\ ^{2}P \leftarrow 1s\ ^{2}S$	302
Li	671.0	Ar 634.0−678.0[a]		
		Kr 632.5−684.0[a]	$2p\ ^{2}P \leftarrow 2s\ ^{2}S$	63, 64
		Xe 654.5−697.5[a]		
Na	589.2, 589.8	Ar 553.0−596.5[a]		
		Kr 559.0−603.5[a]	$3p\ ^{2}P \leftarrow 3s\ ^{2}S$	64, 65
		Xe 548.5−598.0[a]		
K	766.7, 770.1	Ar 688.0−778.0[a]		
		Kr 707.5−775.5[a]	$4p\ ^{2}P \leftarrow 4s\ ^{2}S$	65
		Xe 744.0−809.5[a]		
Rb	780.2, 795.0	Ar 656.6−798.1[a]	$5p\ ^{2}P \leftarrow 5s\ ^{2}S$	66, 67
Cs	852.3, 894.6	Ar 726.0−845.0[a]	$6p\ ^{2}P \leftarrow 6s\ ^{2}S$	67
Be	234.9	Ne 232.0		
		Ar 235.0−237.0[a]	$2p\ ^{1}P \leftarrow 2s\ ^{1}S$	68
		Kr 240.5		
Mg	285.3	Ne 274.6		
		Ar 279.9−283.2[a]		
		Kr 281.9−285.4[a]	$3p\ ^{1}P \leftarrow 3s\ ^{1}S$	69, 70
		Xe 292.9−295.5[a]		
		N_2 283.3		
Ca	422.7	Ne 412.2		
		Ar 417.5, 407.3		
		Kr 428.8, 422.5	$4p\ ^{1}P \leftarrow 4s\ ^{1}S$	70, 71
		Xe 433		
		N_2 404, 415		
	457.7	Ar 453.1, 448.7		
		Kr 459.2, 452	$3d\ ^{1}D \leftarrow 4s\ ^{1}S$	
		Xe 461		
		N_2 453		
Sr	460.9	Ne 442.3	$5p\ ^{1}P \leftarrow 5s\ ^{1}S$	70
		Ar 466.2		
	496.3	Ar 484.1−497.2[a]	$4d\ ^{1}D \leftarrow 5s\ ^{1}S$	
Ba	553.7	Ar 513.0−542.5[a]		
		Kr 531.0−555.0[a]	$6p\ ^{1}P \leftarrow 6s\ ^{1}S$	72
		Xe 553.4−573.0[a]		
Zn	213.9	Ar 206.9		
		Kr 212.5	$4p\ ^{1}P \leftarrow 4s\ ^{1}S$	73−75
		Xe 220.2		
	307.7	Ar 297	$4p\ ^{3}P \leftarrow 4s\ ^{1}S$	
		Kr 301		
Cd	228.9	Ar 221.0		
		Kr 226.6	$5p\ ^{1}P \leftarrow 5s\ ^{1}S$	74, 75
		Xe 235.4		
	326.2	Ar 312.4		
		Kr 316.0	$5p\ ^{3}P \leftarrow 4s\ ^{1}S$	
		Xe 322.8		
Hg	184.9	Ar 178.5		
		Kr 183.5	$6p\ ^{1}P \leftarrow 6s\ ^{1}S$	74
		Xe 189.8		
	253.7	Ar 245.8		
		Kr 248.9	$6p\ ^{3}P \leftarrow 6s\ ^{1}S$	
		Xe 253.2		
Al	308.2	Ne 292.2		
		Ar 291.8, 287.6	$3d\ ^{2}D \leftarrow 3p\ ^{2}P$	76, 77
		Kr 298−310[a]		
		Xe 324		
	394.4	Ne 320.0		
		Ar 339.0	$4s\ ^{2}S \leftarrow 3p\ ^{2}P$	
		Kr 368, 363		
		Xe 368		
Ga	287.4	Ne 248.0−292.0[a]		
		Ar 255.3−274.7[a]		
		Kr 270.0−308.5[a]	$4d\ ^{2}D \leftarrow 4p\ ^{2}P$	76
		Xe 274.0−302.5[a]		
	403.3	Ne 327.5		
		Ar 343.0		
		Kr 366.7−398.0[a]	$5s\ ^{2}S \leftarrow 4p\ ^{2}P$	
		Xe 372.0−410.0[a]		
In	167.6, 164.9	Ne 164.0−166.4[a]		
		Ar 167.1, 169.2	$5s5p^{2}\ ^{2}P \leftarrow 5s^{2}5p\ ^{2}P$	78, 79
		Kr 170.6−172.4[a]		
		Xe 178.9−183.9[a]		
	175.7, 202.5	Ne 174.3, 197		
		Ar 176.9, 197	$5s5p^{2}\ ^{2}D \leftarrow 5s^{2}5p\ ^{2}P$	
		Kr 179.8, 203		
		Xe 187.5, 214		
	285.9, 277.6	Ne 264.4, 269.6		
		Ar 277.4, 286.4	$5s5p^{2}\ ^{4}P \leftarrow 5s^{2}5p\ ^{2}P$	
		Kr 295.0		
		Xe 301.0		
	304.0	Ne 324.7, 329.4		
		Ar 326.0, 329.4	$5d\ ^{2}D \leftarrow 5p\ ^{2}P$	
		Kr 358.4		
		Xe 378.0		
Tl	377.7	Ar 321.5, 326.8		
		Kr 353.1	$7s\ ^{2}S \leftarrow 6p\ ^{2}P$	79, 80
		Xe 358.7		
Si	252.0/251.5/250.3	Ar 232.6	$4s\ ^{3}P \leftarrow 3p\ ^{3}P$	81
Ge	267.0/265.2/255.6	Ar 228.2, 237.7	$5s\ ^{3}P \leftarrow 4p\ ^{3}P$	81
Sn	224.3/224.7/226.5	Ar 218.1, 230.1	$5d\ ^{3}D \leftarrow 5p\ ^{3}P$	82
	254.7	Ar 246.5−261.0[a]	$6s\ ^{1}P \leftarrow 5p\ ^{3}P$	
	286.4, 288.7	Ar 278.0, 279.4	$6s\ ^{3}P \leftarrow 5p\ ^{3}P$	
Pb		Ar 244.9		
		Kr 261.4	$7s\ ^{3}P \leftarrow 6p\ ^{3}P$	83
		Xe 264.8		
N	346.7	Ar 347.8[b]	$2p^{3}\ ^{2}P \rightarrow 2p^{3}\ ^{4}S$	84
	520.2, 520.0	Ar 521.4−524.0[a,b]	$2p^{3}\ ^{2}D \rightarrow 2p^{3}\ ^{4}S$	
Bi	461.7	Ne 458.2	$6p^{3}\ ^{2}P \leftarrow 6p^{3}\ ^{4}S$	85
	647.8	Ne 644.0, 644.4	$6p^{3}\ ^{2}D_{5/2} \leftarrow 6p^{3}\ ^{4}S$	
	875.7	Ne 871.1	$6p^{3}\ ^{2}D_{3/2} \leftarrow 6p^{3}\ ^{4}S$	
O	630.2	N_2 636.7−650.0[b]		
		555.0−565.7[b]	$2p^{4}\ ^{1}S \rightarrow 2p^{4}\ ^{1}D$	84
		494.0−502.5[b]		
S	450.8	Ar 456[b]	$3p^{4}\ ^{1}S \rightarrow 3p^{4}\ ^{3}P$	86
	772.7	Ar 775[b]	$3p^{4}\ ^{1}S \rightarrow 3p^{4}\ ^{1}D$	

[a] Multiplet pattern observed. [b] Measured in emission; wavelengths otherwise relate to absorption spectra.

ments on the atoms themselves, but trapping experiments may sometimes afford the only useful criterion. At best, EPR spectra are sensitive and highly informative with regard to the electronic state of a paramagnetic atom and even the geometry of the matrix site in which it is trapped. However, potential problems also lurk: the interpretation of the EPR spectra is often relatively complicated; anisotropic matrix fields tend to broaden the resonances; and multispin atoms with $S > 1/2$ cannot be guaranteed to give a detectable signal.

1. UV–Vis Absorption[1,2,4,14,43,62]

One of the most direct and sensitive ways of characterizing atoms in matrices hinges on their electronic absorption spectra. Table 1 lists the electronic transitions of some of the atoms of main group elements that have been investigated in both the gas and the solid matrix phases.[63−86] The group 1 elements have been extensively studied[63−67] on this basis because the associated np ← ns transitions give relatively simple spectra.

Although a close relationship to the spectrum of the gaseous atom is usually evident, the matrix environment is liable to cause significant changes. Thus, the transitions shift in energy, usually by only a few percent but sometimes by as much as 10−20%, with the switch from the gas to the matrix phase, the shift varying from matrix to matrix in a more or less predictable manner. The sharp features that characterize the spectrum of the gaseous atom are also broadened, sometimes to give line widths up to 200 cm^{-1} or more for an individual transition. The width is in fact governed (a) by the atom-cage potentials for the two atomic states linked by that transition and (b) by the Franck−Condon principle as applied to the lattice phonons.[62] Accordingly, the line widths of the matrix spectrum are often found to vary with temperature. The envelope associated with a particular atomic transition may reveal a multiplet pattern that reflects the occupancy of different matrix sites or the splitting of a degenerate level by the crystal field associated with a specific site. In addition, there may be significant changes in oscillator strength, and the presence of impurities in the matrix may even cause the appearance of transitions that are otherwise forbidden. Just how marked the change of intensity can be is shown by the $5s^26s^1$ ($^2S_{1/2}$) ← $5s^25p^1$ ($^2P_{1/2}$) transition of In atoms, which is clearly visible in absorption by the vapor, yet quenched apparently when the atoms are trapped in a noble gas matrix.[78] An explanation is to be found in the overlap of the noble gas wave functions with the rather expansive orbital of the 6s electron ($r_{nl} = 8.5a_0$), resulting in an unusually strong interaction between the matrix and the excited state, such that there is substantial quenching of intensity.

Despite the complications, electronic absorption spectra are able to report not only on identity but also on the atomic concentration prevailing in a matrix. This concentration cannot necessarily be assumed to reflect accurately the composition of the gaseous flux falling on the deposition surface because not all species will have the same sticking probability and aggregation of the atoms may well occur in the act of condensation. In addition, the absorption spectra may reveal through the appearance of additional absorptions the presence of dimers and/or higher aggregates. For example, optical absorptions sometimes betraying signs of a vibronic progression have been observed for the matrix-isolated dimers Mg_2 (near 400 nm and corresponding to the A $^1\Sigma_u^+$ ← X $^1\Sigma_g^+$ transition)[69] and Pb_2 (near 230, 485 and 605 nm).[83] The bands can often be assigned on the basis of how the spectrum responds to changes of concentration (achieved, for example, where the atoms come from a thermal source, by changing the furnace temperature) or to annealing of the matrix, which tends to favor aggregation and also to shift atomic transitions toward the gas-phase frequencies. Knowledge of aggregation is vital because the reactivities of atoms and their aggregates may differ widely, as exemplified by the behaviors of Ga and Ga_2.[44] Thus, matrix-isolated Ga atoms react with H_2 to give the Ga(II) insertion product HGaH, but only after photoactivation. Under similar conditions, however, Ga_2 dimers react spontaneously (i.e., upon deposition) with H_2 to form the dihydrido-bridged species Ga(μ-H)$_2$Ga.

2. Electronic Transitions in Emission[1,2,14,43,62]

Distinctive atomic autographs are also provided by UV−vis emission spectra, whether spontaneous or optically induced (fluorescence). Indeed, the very first experimental evidence that highly unstable species could be trapped in a solid at low temperatures came in all probability from the luminescence spectra of solid N_2 or O_2 that had been bombarded with positive ions or electrons;[87] hence, the presence of excited N or O atoms was established. These early studies clearly foreshadow the way in which spontaneous emission has been used subsequently to identify the excited electronic state of an atom or molecule generated by physical or chemical means. So it has been proved with the S (^1S) atoms formed by vacuum-UV photolysis of matrix-isolated OCS (eq 2) and which can be recognized by their emission signatures at 775 nm (^1S → ^1D) and at 465 nm (^1S → X ^3P).[86] Elaboration of those early experiments has also shown that N atoms produced by the action of a microwave discharge or of low-energy electrons on dinitrogen and trapped in a solid matrix display emissions centered near 520 and 1040 nm attributable to N (^2D) → N (^4S) and N (^2P) → N (^2D) transitions, respectively.[88]

Fluorescence methods offer considerable advantages of sensitivity in the detection of both atoms and their molecular products because the intensity of emission is proportional to that of the exciting radiation—which can be varied at will. The narrow line width of this radiation, as delivered by a laser source in laser-induced fluorescence, makes for characteristically sharp, well-resolved spectra capable of revealing for gaseous samples not only vibrational but also rotational detail. However, the method is not without its limitations; sensitive it may be, but self-absorption of the fluorescence is liable to become an increasing problem as the sample concentration rises.

A solid noble gas matrix, transparent from the far-IR to the vacuum-UV, offers a very favorable medium for the observation of stimulated emission.[62] There are several factors facilitating the establishment of a population inversion and increasing the gain in these conditions as compared with the gas phase. Furthermore, the absence of rotational dilution and the sharpness of the transitions make stimulated emission an exceptionally sensitive, space- and time-specific method of interrogating molecules. Hence, there is much information to be gained about both the excited and ground electronic states of atoms and molecules, including the dynamics of relaxation. Illustrative of such studies is the laser-induced fluorescence observed for Tl atoms isolated in Ar, Kr, or Xe matrices and which, in concert with the corresponding absorption spectra, has been exploited to elucidate the interaction potentials between the metal guest and its matrix cage.[80b] Such luminescence is very sensitive to the presence of foreign species. In the event that an interacting molecule makes a marked distinction between the ground and excited states of an atom, as with NH_3 and Hg,[89] there is likely to be a demonstrable change in the emission characteristics of the atom.

Electronic transitions associated with most atoms and closed-shell molecules are confined to the UV–vis region, but radicals often possess low-lying electronic states, which offer the possibility of transitions that appear in IR absorption or emission. Thus, the gaseous radicals PH, AsH, and SbH, made by the reaction of H atoms with the heated elemental solids, have been identified and characterized by the IR emission corresponding to the $^1\Delta \rightarrow X\,^3\Sigma^-$ transition.[90] An oven flow reactor has also been adapted to study the IR chemiluminescence of reaction 3, resulting from the $A\,^1\Sigma^+ \rightarrow X\,^1\Sigma^+$ and $A'\,^1\Pi \rightarrow X\,^1\Sigma^+$ transitions of the MO products.[25]

$$M + N_2O \xrightarrow[M = \text{Ca or Sr}]{} MO + N_2 \qquad (3)$$

3. Magnetic Circular Dichroism (MCD)[2,14,43,91]

The scope of UV–vis absorption measurements can be extended very substantially, in principle, by appealing to the technique of magnetic circular dichroism. In ideal circumstances, MCD experiments can be particularly instructive with regard to the assignment of electronic transitions and the identification of electronic states. The method is especially apposite for paramagnetic systems with an even number of electrons or with high orbital angular momentum and which are therefore ill suited to EPR measurements (q.v.). Although some elegant MCD studies have been carried out on a handful of matrix-isolated atoms, they have seldom been exploited to track the *chemical* fate of these atoms.

4. EPR Measurements[1,2,14,43,92]

As noted already, the EPR technique has great potential in the investigation of paramagnetic species. Because EPR transitions depend only on the properties of the electronic ground state of a paramagnet, because they can result in relatively narrow lines for the matrix-isolated species, and because they are very sensitive to small changes of environment, the method should be ideally suited to studies designed to clarify the nature of that environment. Various matrix-isolated atoms have certainly been characterized in this way by appropriate components of their g and A tensors. For example, a detailed analysis of the EPR spectrum of either Al or Ga atoms trapped in noble gas matrices implies that the atom invariably occupies an axially distorted substitutional site in the host lattice.[76] On the other hand, there are but few cases of matrix-isolated atoms with nonzero orbital angular momentum for which EPR spectra have been reported, probably because of the anisotropy of the matrix fields which broadens the resonances beyond recognition. Nevertheless, EPR studies have enjoyed considerable success in charting the course and products of certain atomic reactions, taking place typically in a matrix environment. Representative systems include Li + NH_3,[93] Li + HCl,[94] M + C_2H_2 (M = Li, Na, or K),[95] M + H_2 (M = Al[96] or Ga[97]), M + CH_4 (M = Al[98] or Ga[97]), M + CO (M = Al,[99] Ga,[100] or In [101]), and Al + HCl or Cl_2.[102]

5. Vibrational Spectroscopy[1–3,14,42,43,103]

Pre-eminent among the methods of investigating the fate and identity of a *molecular* reagent or product is IR spectroscopy. This reflects not so much the sensitivity but the comparative ease with which the IR spectrum of a sample can be measured and—more especially—the capacity of such a spectrum to reveal the identity, likely structure, and concentration of an unknown molecule. High-resolution studies of vapor samples may reveal rotational detail with the additional information about symmetry, structure, and even precise dimensions contained therein. Such rotational structure is missing from the spectra of matrix-isolated molecules. Nevertheless, positive information about the stoichiometry and structure of a new molecule may still be gained from the effects of changing the isotopic composition of the molecule and from comparisons with the spectrum simulated on the basis of appropriate quantum chemical calculations.

In the absence of stimuli other than the thermal energies of normal or low temperatures, molecules inhabit principally only the lowest vibrational states, so that transitions need to be from lower to higher states. Accordingly, IR measurements are normally made in absorption. On the other hand, the molecular products of atomic reactions in the gas phase often carry an excess of vibrational energy, which may give rise to IR emission.[25] The advent of modern FT-IR equipment has greatly facilitated IR emission measurements, which have played a notable part in the exploration of atomic reactions. There is no better example—and a Nobel Prize-winning example[41]—than the IR chemiluminescence associated with the HCl molecules formed in reaction 4 and which give

$$H + Cl_2 \rightarrow HCl + Cl \qquad (4)$$

access to vital information concerning the distribution of their vibrational and rotational energy. Such measurements made at high resolution have also provided the first detailed structural characterization of the molecule HOI as formed, for example, in reaction 5.[104] Quite aside from its importance in

$$C_2H_5I + O(^3P) \rightarrow HOI + C_2H_4 \qquad (5)$$

fundamental studies of chemical dynamics, IR emission has proved invaluable for the monitoring of such molecules as OH and O_3 in the earth's atmosphere[33] and also for the detection of various molecules in astronomy.[25] Matrix-isolated molecules give less scope for IR emission, but laser excitation may give rise to vibrational emission, as with WO isolated in solid neon at 6 K.[105]

Offering an alternative view of vibrational transitions, Raman spectroscopy has been much less widely exploited.[106] The main drawback is the inherent weakness of the normal Raman effect. There are other practical difficulties too, associated with light scattering by the solid host material in matrix experiments, and with the risks of heating, photolysis, or fluorescence under the action of the exciting radiation. Perhaps the most spectacular successes have come with the resonance enhancement, which can be achieved under appropriate conditions, as in the cases of matrix-isolated Sn_2,[107] Pb_2,[108] Bi_2,[85,109] Bi_4,[109] and Te_3,[110] that is, products of aggregation reactions of the relevant atoms. Electron-transfer reactions involving metal atoms and either O_3 or I_2 lead to the products $M^+O_3^-$ (M = Mg, Ca, Sr, or Ba)[111] or $M^+I_2^-$ (M = alkali metal),[112] which have also been characterized under matrix conditions by their resonance Raman spectra.

6. Submillimeter, Microwave, and Radiowave Methods

Beyond EPR studies, the absorption or emission of radiation in the submillimeter to radiowave range has played little part in matrix isolation experiments in the characterization of atoms or of molecules with little or no degree of rotational freedom. A quite different situation prevails in the gas phase. Thus, the field of astrochemistry is built almost entirely on centimeter and millimeter wave emission spectroscopy of species in astronomical sources that range from stellar envelopes to comets.[25,32] Rotational transitions of molecules that can be observed in these or neighboring regions of the electromagnetic spectrum give access, in principle, to precise information about the dimensions and finer spectroscopic details of simple molecules,[113] such as Ng·HX (Ng = noble gas; X = halogen),[39] which may be formed as a result of an atom–atom or atom–molecule encounter. Some examples will be given in sections V and VI. Astronomy has benefited enormously from the 21-cm emission line of the H atom, which corresponds to the transition from the parallel to the antiparallel state of the proton and electron spins. This line has probably revealed more about the properties of the interstellar medium than has any other feature or method. It has also been exploited to investigate the spiral structure and rotation of the Milky Way and other galaxies.

7. Mass Spectrometry and Other Ionization Methods

Although ionization methods have been used extensively to study reactions in the gas phase, they do not lend themselves readily to matrix experiments.[2] Time-of-flight (TOF) mass spectrometry in particular has proved to be highly informative for the simultaneous monitoring of reaction products and precursors, having the special merit of imposing no restrictions on the number of different species. For example, tunable laser ionization with mass spectrometric detection has been exploited to investigate $Mg(NH_3)_n$ clusters ($n = 1-36$),[114] and the anionic aluminum–nitrogen clusters $Al_xN_y^-$ ($x = 2-9$; $y = 1-3$) formed by laser ablation of aluminum in the presence of a helium carrier gas and a small percentage of nitrogen can be mass-selected with a quadrupole mass analyzer and subsequently detected with a channeltron electron multiplier.[115] Combination of the crossed molecular beam method with mass spectrometric detection has led, moreover, to clear evidence that cyclic borirene $(CH)_2BH$ is a primary reaction product when ground-state B (^2P) atoms interact with C_2H_4 under collision-free conditions (see Figure 1).[116] Other examples include the tracking of the reactions of K atoms with CH_3I,[117] of N (^2D) atoms with D_2,[118] of O atoms with CH_3OH[119] or SiH_4,[120] and of Cl atoms with D_2,[121] isoprene,[122] or CH_3I.[123] On the other hand, mass spectrometry is of itself primarily a means of detection and quantitative assay; structural and other information can be gained only indirectly, for example, on the basis of fragmentation patterns.

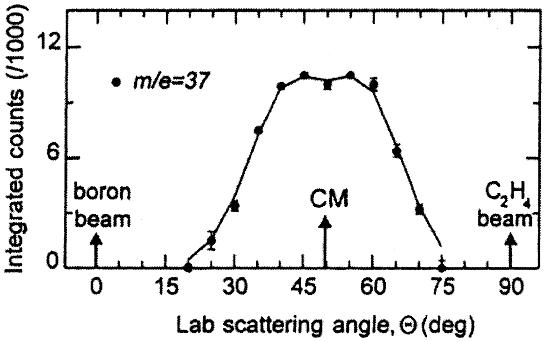


Figure 1. Laboratory angular distribution of the product C_2H_3B (m/e 37) of the crossed molecular beam (CMB) reaction B (^2P) + C_2H_4 (X ^1A_g) at a relative collision energy of 4.2 kcal mol^{-1}. The solid line represents the angular distribution obtained from the best-fit CM angular and translational energy distributions. (Reprinted with permission from ref 116. Copyright 2000 American Chemical Society.)

Multiphoton ionization techniques have become standard tools in the elaboration of chemical reaction dynamics in the gas phase.[19] In this case, irradiation of an atom or, more often, a molecule with an intense laser source results in absorption of two or more photons and, if the total energy absorbed exceeds the ionization potential, an electron is ejected. The products may then be analyzed by ion current measurements, TOF mass spectrometry, or photoelectron kinetic energy measurements. When the initial absorption occurs via specific electronic states of the neutral target, the condition of resonantly enhanced multiphoton ionization (REMPI) is achieved. Among the range of applications that multiphotoionization spectroscopy has found we may note the quantum-state-specific detection of reactants and products and the preparation of quantum-state-selected reactants in fundamental studies of chemical reactivity. A typical example is provided by a recent REMPI-based analysis of the vibrational and rotational state distributions of the HD formed in the reaction between H and D_2.[124] Similar means have been used to demonstrate both bond selectivity and mode specificity in the reaction of Cl atoms with vibrationally excited CH_4 molecules.[125] In one of several important developments, the use of position-sensitive detectors has made possible the recording of two-dimensional images of photofragments, REMPI measurements providing, for example, for state-selective detection of the products.[23] These ion images reflect both the velocity distribution and alignment of the ionized reaction products, and their analysis gives access to the full three-dimensional velocity distributions of these products. Ion imaging in one form or another is now well established as a particularly revealing way of exploring many chemical reactions in the gas phase.

The collision of an electronically excited atom with a second atom or with a molecule may result in so-called Penning ionization, as represented formally in eq 6.[20] Most widely explored have been the cases

$$A^* + B \rightarrow A + B^+ + e^- \qquad (6)$$

where A is a noble gas atom, and particularly He, in what are nearly always associative processes proceeding via appropriate metastable atom−atom or atom−molecule pairs. Some of these intermediates are so-called "Rydberg molecules", having no stable ground state but being based on the introduction of an electron into a Rydberg orbital of a bound ion core. Examples include the hydrides NgH (Ng = Ar, Kr, or Xe) [126] and the celebrated excimer molecule ArF, which have been characterized by their emission spectra. Molecular beam experiments have exposed a wealth of new detail on the dynamics of Penning ionization, with mass and various kinds of electron spectroscopy being used to analyze the products and with angle-resolved measurements communicating data on the scattering of both reagents and products.

Multiphoton ionization is closely related to what is conventionally understood to be photoelectron spectroscopy, and this indeed represents another possible method of investigating reactions in the gas phase, notably in the form of time-resolved studies.[127] A relatively newly developed approach employs a scanning photon source, much as in photoionization efficiency studies, that separates the ions thus formed from high-lying Rydberg states by introducing a delay and then ionizes these states with an extraction pulse. In essence we then have the technique of zero electron kinetic energy (ZEKE) spectroscopy,[31] which has major advantages of resolution and selection rules over conventional photoelectron spectroscopy, relying as it does on photoionization at a fixed wavelength and then analysis of the kinetic energy of the photoelectrons emitted. Examples of transients that have been characterized by their ZEKE spectra include $Na{\cdot}OH_2$,[128] $Na{\cdot}NH_3$,[128] ND_4,[129] Ar_2,[130] and $Ar{\cdot}NO$.[131]

8. Chemical Trapping[1,14,42,43,62,103,132]

If the atom itself is in an electronic state that carries no convenient spectroscopic tag, then its presence may have to be inferred from the results of a chemical trapping experiment. This requires the doping of the medium with a reagent known to interact spontaneously with the atom to give a well-authenticated molecular product having a distinctive spectroscopic signature. Detection by proxy has the merit of convenience, but it clearly results in destruction of the atoms and does not easily lend itself to estimates of atomic concentration, at least under conditions other than those of the trapping experiment itself. For nonmetal atoms such as H and Xe, which lack electronic transitions in a readily accessible region of the electromagnetic spectrum, however, chemical trapping may be one of the few devices at hand. H atoms are often recognized as a result of scavenging by CO to give the radical HCO, most easily identified by its characteristic IR spectrum.[133] A convenient method diagnostic of ground-state S atoms depends on the reaction with O_2 and the observation of the IR absorption or UV emission spectrum of the SO_2 so generated.[134] Some products, such as HCO, are photolabile, and unless the sample can be efficiently screened from radiation capable of inducing dissociation, the sensitivity of the method is liable to be seriously impaired.

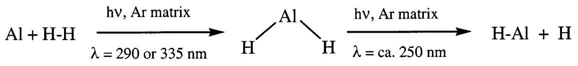
C. Atom Activation

Simple addition reactions apart, atoms seldom experience reactions with little or no activation barrier, and even some addition reactions are by no means spontaneous. Some of the methods of generating atoms, such as laser ablation, described in section IIA, give rise to highly energetic atoms, sometimes in excited electronic states and/or possessing high translational energies. In these cases the ensuing reactions may be spontaneous and indiscriminate, making it difficult to assess properly the pathways taken. For example, an intermediate such as a weakly bound adduct between the atom and substrate, which normally precedes insertion or other reactions, is liable to be decomposed so quickly and effectively as to escape detection under these conditions.

In practice, atoms may be activated and thereby induced to enter into reaction in at least five ways, namely, (i) by photolysis, (ii) in gaseous discharge processes, (iii) by laser ablation, (iv) by the chemical reaction giving rise to them, and (v) by thermal means.

1. Photolysis[1]

The most effective and controlled way of inducing an atomic reaction involves photolysis, ideally with radiation at a well-defined wavelength that enables the nature of the excitation to be appraised. In practice, a high- or medium-pressure Hg arc is still most commonly used as the radiation source emitting broad-band UV−vis light, normally restricted to the range $200 \leq \lambda \leq 800$ nm by the optical windows of the apparatus and by a water filter designed to shield the sample from the heating effects of IR radiation. Many experiments depart from the ideal in depending on the action of this broad band of radiation and so give little clue to the exact mode of activation. Altogether more revealing are experiments involving selective photolysis achieved, say, by using an appropriate filter or monochromator to limit the wavelengths of the radiation falling on the sample, or by employing radiation of closely defined wavelength, for example, as emitted from a laser source. With an appropriate knowledge of the UV−vis absorption spectrum of the sample, it may then be possible to determine the electronic states of the reacting species. Thus, studies of argon matrices containing Al atoms and H_2 show that HAlH is formed on irradiation with UV light, but selective photolysis (λ = ca. 290 or 335 nm) is needed to establish that excited ^2S or ^2D Al atoms are essential prerequisites to this reaction.[135] Subsequent photolysis with light having still shorter wavelengths ($\lambda = \sim$250 nm) results in dissociation of the HAlH (eq 7).



(7)

As may be anticipated in part from the changes in the electronic spectra brought about by exchanging the gas for the matrix phase (see section IIB), atoms and molecules trapped in matrices are liable to differ from their gaseous counterparts in their response to irradiation. Nowhere is this difference more conspicuous than in photoionization. The ability of a solid noble gas host to solvate and so stabilize a cation reduces significantly the adiabatic ionization energy of a neutral guest species, and the more polarizable the noble gas the more stable the cationic state becomes.[136] The point is clearly made by the discovery that the adiabatic ionization energy of the H atom is lowered from the gas-phase value of 13.595 eV to about 8.4 or 7.8 eV when it is trapped in a solid Kr or Xe matrix, respectively. There is now persuasive IR evidence that H atoms produced by photodissociation of HX molecules (X = Cl, Br, or I) trapped in an Xe matrix ionize under UV irradiation to form the vibrationally bound, linear $[XeHXe]^+$ ion.[137] In this process photoionization is undoubtedly facilitated by the favorable electron affinity of the halogen atom. Much earlier precedents for such photoionization were in fact set by Kasai,[138] who pointed out that the energy, ΔE, required to transfer an electron from an electron donor D to an electron acceptor A trapped together within a solid matrix is given by eq 8. Here

$$\Delta E = E_{\mathrm{IP}}(\mathrm{D}) - E_{\mathrm{EA}}(\mathrm{A}) - \frac{e^2}{4\pi\epsilon_r\epsilon_0 R} \qquad (8)$$

E_{IP} (D) and E_{EA} (A) are the ionization energy of D and the electron affinity of A, respectively, ϵ_r is the relative permittivity of the solid, R is the separation between D^+ and A^-, e is the electronic charge, and ϵ_0 is the vacuum permittivity. Working along these lines, Kasai showed that UV irradiation of an Ar matrix containing Cd atoms and HI yields Cd^+, which could be identified by its EPR spectrum.[138]

These examples testify to the profound influence a solid matrix environment and a matrix dopant may have on the photochemical behavior of a guest species. Recent studies have demonstrated that the matrix may also operate in other ways to bring about photolytic changes that would not otherwise be possible,[139] the effects being most marked in the case of a matrix composed of the heaviest, most polarizable noble gas atoms, viz., xenon. For example, two-photon excitation of the xenon may occur, and the excitons $Xe_n{}^*$ thus formed are capable of transferring their energy to the guest species which, if it is a molecule, may suffer dissociation. Moreover, through the operation of the "heavy atom" effect, the xenon matrix favors intersystem crossing, and this may result in significant population of an excited electronic state, which is otherwise debarred to the guest under the rules that normally govern optically induced electronic transitions. Associated with this state is the possibility of photochemical changes quite distinct from those achievable by direct means.

2. Discharge Methods[42,54,132]

The conditions prevailing within an electric discharge are likely to generate high-energy products, including neutral and charged species with high kinetic energies and often in excited electronic states. Atoms produced in this way are liable to be highly reactive (as with so-called "active" nitrogen, for example), but the reactions they undergo within, or downstream from, the discharge zone are largely uncontrollable and effectively open to investigation only by the products they yield.

3. Laser Ablation[46,47]

As noted previously, laser ablation also produces highly energetic atoms. By employing a cold carrier gas to cool and quench the vaporization products, and LIF typically to detect them, numerous molecular species (Be_2,[140] Sn_2,[141] and SiC_2,[47] for example) have been detected in the gas phase. Alternatively, the products can be trapped, with or without a potential reagent, in a suitable low-temperature matrix and interrogated there at greater leisure, usually by means of IR spectroscopy. However, it is with the *novel products* more than the mechanisms of the reactions that these studies are mostly concerned, the atoms being able by virtue of their excess energy to enter reaction channels from which they would normally be debarred.

4. Chemical Methods

Photogeneration from molecular sources may deliver at the outset atoms in specific electronically excited states, for example, S (^{1}S) and O (^{1}D).[1] Although reaction may have to compete with physical modes of relaxation, we have already noted how this activation may open the way to insertion and other reactions with activation barriers too large to be overcome by the ground-state atoms under similar conditions.

5. Thermal Activation

Although atoms are sometimes produced with high thermal energies, controlled thermal activation in the gas phase is likely to result in changes in the rate more than the pathway of reaction. Solid matrices offer less scope for thermally induced changes, although annealing encourages the diffusion of small atoms, for example, H,[136] or molecules, for example, CO,[142] and so may induce simple aggregation or addition reactions, provided that the activation barrier is minimal. Thermally induced diffusion certainly appears to favor reaction 9 because the yield of the

$$\mathrm{N} + \mathrm{AlN} \rightarrow \mathrm{NAlN}\ (^4\Pi_u) \qquad (9)$$

linear NAlN molecule increases when a solid matrix containing laser-ablated Al atoms and N_2 is annealed.[49] However, it is not always clear that thermal diffusion is all that is involved. Diffusion of atoms during photolysis, for example, is difficult to assess because it depends on the energy acquired by the atom during reaction and how quickly this energy is transferred to the matrix, as well as competition from recombination to regenerate the precursor (reflecting the role of the cage effect). Larger atoms, for example, Br, are effectively immobile over the relatively narrow range of temperatures allowed by normal matrix conditions. Hence, the very rigidity of the matrix medium, so important to the preservation of labile species, becomes a distinct disadvantage when thermal reactions of the species are to be explored.[132]

D. Apparatus

Studies of atomic reactions call for significantly different types of apparatus according to the medium in which they take place and/or in which the products are sampled.

1. Matrix Isolation[2,14,42,43,46,61,103,136]

The essence of this method is the co-condensation of one or more vapor species with an excess of an inert, spectroscopically transparent gas (e.g., Ar) on a suitable support at low temperatures (typically 4−30 K). The atoms may be introduced in the vapor, or they may be generated photolytically within the matrix (see section IIA). Apart from the need for low pressures ($\leq 10^{-6}$ Torr), the key element of the apparatus is the cryogenic system, which may be either a liquid helium cryostat or, more often, a closed cycle refrigerator using helium as the working fluid. This is not the place, however, for technical details of the sort of apparatus used in matrix experiments, which are amply covered in books and other review articles.[2,43,46,62,103,136]

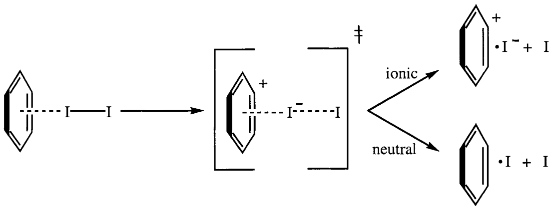
2. Gas-Phase Studies

Details of the experimental methods applied to the study of atomic reactions in the gas phase are also to be found elsewhere.[132,143] Of the techniques reporting directly on such reactions, that involving a fast flow reactor has been the principal source of information about reactions with time scales in the millisecond range.[143] This reactor typically consists of a quartz tube with an internal diameter of ~5 cm and a length of ~1 m. A carrier gas, for example, He, transports the atoms (generated, for example, by a discharge) from one end of the tube to the reaction zone, where they are mixed with an excess of the reagent. The time between initiation and reactant or product detection at some point downstream in the flow tube, and hence the reaction rate, can be calculated if the velocity of the gas mixture is known. Enclosure of the tube within a suitable oven allows the temperature in the reaction zone to be varied. Detection and monitoring of some or all of the species can be effected by various techniques, for example, resonance fluorescence, LIF, laser magnetic resonance, mass spectroscopy, and EPR and IR spectroscopy.[143] Resonance fluorescence is a particularly well-tried method for detecting atoms and estimating their concentrations.

Some atomic reactions have also been studied in real time by flash photolysis. For example, dissociation of HBr (eq 10a) by a pulse of radiation from an ArF laser ($\lambda = 193$ nm) gives Br atoms that can then be monitored by time-resolved resonance fluorescence as they react with SiH_4 (eq 10b).[144] The same principle has been adopted with striking success not in the gas phase but in supercritical fluid samples to follow the reaction of a noble gas atom Ng (= Ar, Kr, or Xe) with an unsaturated metal carbonyl $M(CO)_5$ (M = Cr, Mo, or W) to form the transient Ng·$M(CO)_5$;[145] in this case the molecular reagent and product have been tracked by time-resolved IR measurements. With an ultrafast laser giving femtosecond pulses it has even been possible through REMPI to detect free I atoms formed in the dissociative charge-transfer reaction of the benzene−iodine complex (eq 11).[146] Hence the dynamics and mechanism of this and other reactions implicating I atoms have been charted in unprecedented detail.

$$HBr \xrightarrow{h\nu} H + Br \tag{10a}$$

$$Br + SiH_4 \xrightarrow{h\nu} HBr + SiH_3 \tag{10b}$$



(11)

Another method of attack is to exploit the very high temperatures developed in a shock tube to bring about the dissociation of a precursor molecule such as C_3O_2 (eq 12) and then follow the reaction of the transient species (C atoms in this case) with an added reagent by absorption or other spectroscopic means.[143] For example, the reaction of C atoms with NO (eq 13) has been studied in this way.[147] However, the method of initiation lacks selectivity, and a complicated array of reactions will often be set in motion.

$$C_3O_2 \rightleftharpoons C + 2CO \tag{12}$$

$$C + NO \rightarrow N + CO \tag{13}$$

III. Reaction Pathways

Addition of an atom A to a notional triatomic molecular substrate X−Y−Z is likely to be the primary step in the reactions of A, certainly at low energies. The resulting atom−substrate pair varies hugely in character from a very weakly bound complex A···X−Y−Z, with minimal perturbation of A and XYZ, through a relatively tightly bound complex A·X−Y−Z, with appreciable mutual perturbation of the partners, to a molecular product A−X−Y−Z featuring a strong covalent bond between A and XYZ. Adducts of the first class, which are by their nature hard to detect and characterize, are formed by nonpolar substrates low in polarizability and acid−base potential, for example, H_2 or CH_4. Adducts of the second class, having binding energies in excess of ~10 kJ mol^{-1}, are identifiable at low temperatures by their distinctive IR, UV−vis, or EPR spectra. Representative of this class is the Al atom complex

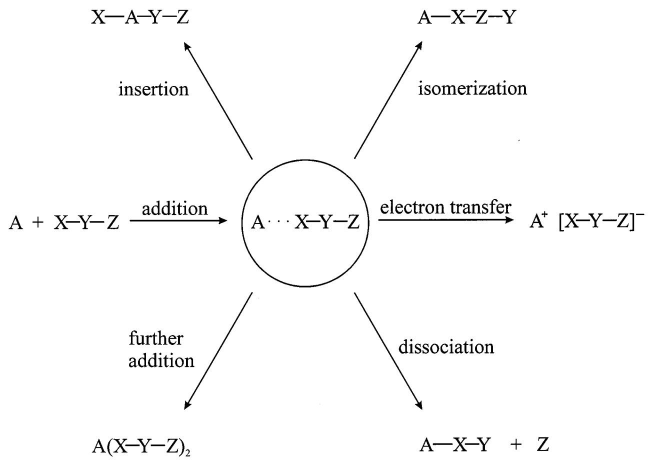
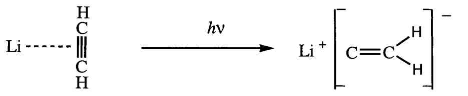


Figure 2. Reaction scheme showing the possible products of the reaction between an atom A and a molecule XYZ.

$Al{\cdot}NH_3$, with a binding energy calculated to be ~60 kJ mol^{-1}.[148,149] In an addition product of the third kind, for example, ClCO or N_2O, however, a strong bond is established, with an energy typically exceeding 100 kJ mol^{-1}, between the atomic and molecular reagents (Cl + CO [150] or O + N_2,[151] respectively). While the energy available to the system is kept to a minimum, no radical change in the geometry of the X−Y−Z unit, for example, with cleavage of an X−Y or Y−Z bond, is to be expected. Thus, an insertion reaction of an atom in its electronic ground state into a covalent bond is rarely encountered at low temperatures, for example, under matrix conditions. Subsequent reactions that may be more or less spontaneous, even under low-energy conditions, but are strongly concentration-dependent, may follow two courses, either addition of a *second* A atom or X−Y−Z molecule to the primary A·X−Y−Z pair or aggregation of the would-be reagents and/or their primary product A·X−Y−Z.

The initial atom−substrate pair, A·X−Y−Z, whether loosely or tightly bound, is likely to be pivotal to any ensuing reactions that may be induced once the energy stakes are raised. As represented in Figure 2, there are four possibilities, namely, (i) insertion of A into an X−Y or Y−Z bond, (ii) isomerization of the X−Y−Z unit, for example, A−X−Y−Z → A−X−Z−Y, (iii) electron transfer between A and X−Y−Z, and (iv) dissociation with rupture of one or more bonds in the X−Y−Z unit, resulting possibly in displacement of a Y or Z atom. None of these reaction types is necessarily exclusive, it should be understood. In practice, it is not always easy to distinguish one from the other, and a given reaction may well involve more than one of these processes. It is clear from Figure 2, for example, that the products of reactions i−iii are still *addition* products of A and X−Y−Z, that the products of reactions i and ii are *both* isomers of the precursor, and that the electron-transfer product from reaction iii may differ from the precursor only in its electronic distribution. Nevertheless, the reaction types illustrated formally in Figure 2 provide a useful framework for the following discussion, which seeks to exemplify, and elaborate upon, them.

Contact pairs characterized by weak atom−substrate interactions will become only short-lived transients with the thermal energy available in the gas phase at normal temperatures, amounting perhaps to little more than "sticky" collisions, and thereby being a relatively inefficient means of advancing any reaction. In the more restricted environment of the condensed phases, and particularly in solid matrices at low temperatures, they are likely to be highly influential. The capacity of the medium to hold the pair in place and also to retain the reaction products, for example, within the enclosure of the matrix cage, creates opportunities for reaction that arise very seldom in the gas phase at elevated temperatures. The weak interaction of the ground state may give place to a strong interaction when one of the components is raised by photolysis to an excited electronic state. This is the basis presumably of the insertion reactions that are observed to take place between Al, Ga, and In atoms isolated together with H_2 or CH_4 in solid argon matrices at low temperatures[98,135,152] and yielding the divalent metal compounds RMH (R = H or CH_3). As the atom−substrate interaction strengthens, spectroscopic signs of the complex become evident, for example, through changes in the vibrational or UV−vis spectrum of the substrate molecule or through the appearance of a charge-transfer band in the UV−vis spectrum. Such is the case with the addition products $M{\cdot}NH_3$,[148] $M{\cdot}PH_3$,[153] and M·CO (M = Al,[154] Ga,[155] or In[155]). Again, photolytic activation may be largely localized within one of the interacting species, but there is now the possibility of excitation by charge transfer, as in eqs 14 and 15, where electron transfer is accompanied by isomerization of an ethyne to a vinylidene derivative,[95] or of a dicarbonyl to form a derivative of the radical anion $[OC{\cdot}CO]^{\bullet-}$.[155] With metal atoms having low ionization energies, for example, the alkali metals, and/or molecules with high electron affinities, for example, the dihalogens, electron transfer may occur spontaneously. A contact pair, which can be regarded as a more or less strongly bound molecule, will have its own characteristic photochemistry. A good example is provided by the reaction of I atoms with O_2. Co-deposition in a solid matrix at low temperature leads to the formation of the radical I−O−O.[156] This is not photostable but decomposes to form the angular O=I=O molecule when it is irradiated with light at wavelengths near 254 nm. The detection of O_3 implies that the change proceeds via photodissocia-



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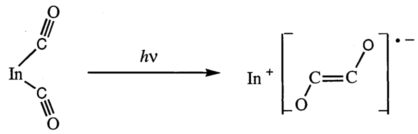

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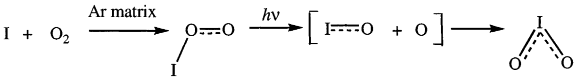


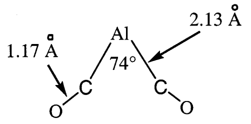
(16)

tion of the I−O−O followed by recombination of the IO molecule and O atom thus released (eq 16).

A. Simple Addition Reactions

Examples of substrate molecules that enter into more or less specific interactions with atomic reagents to give spectroscopically identifiable products include NH_3, PH_3, CO, unsaturated hydrocarbons, N_2, H_2O, and O_2. Some of these will be discussed individually in section V.

That main group metal atoms are capable of binding CO came as a matter of surprise in the 1970s, for carbonyl derivatives had been widely believed for many years to be the exclusive preserve of metals of the d-block. Nevertheless, matrix isolation experiments make it quite clear that atoms as diverse as Al,[154] Si,[157] and Sn[158] are all capable of binding CO quite specifically, although the products are short-lived under normal conditions. Thus, the matrix formed by co-condensing Al vapor with CO and an excess of noble gas displays IR bands that can be attributed only to the ν(CO) fundamentals of the molecules AlCO and $Al(CO)_2$.[154] The wavenumbers of these fundamentals are 150−250 cm^{-1} red-shifted with respect to ν(CO) of the free CO molecule, and not dissimilar from those of a late transition-metal carbonyl such as $Ni(CO)_4$. The implication of relatively strong Al−CO binding is reinforced by DFT calculations, which impute binding energies of 81 and 176 kJ mol^{-1} to the molecules AlCO and $Al(CO)_2$, respectively.[155] Hence coordination of the first CO molecule appears to encourage the addition of a second, and $Al(CO)_2$ is indeed the dominant product at all but the lowest CO concentrations. An intriguing feature of $Al(CO)_2$ brought to light by the calculations is its angular structure, **1**, with a tight C−Al−C angle of ~74° and Al−C−O arms that are not linear but slightly bent so that the two carbon atoms appear to be drawn toward each other. Further experimental and theoretical studies along these lines reveal a similar response to CO by Ga and In atoms.[155]



1

As in the case of CO, unsaturated hydrocarbons such as C_2H_4, C_2H_2, and C_6H_6 do not form lastingly stable compounds with main group metals. Yet there is now ample evidence that specific complexes with distinctive spectroscopic properties are often formed by the addition of the metal atom to such a molecule at low temperatures. For example, various matrix studies show that Li atoms add severally to C_2H_2,[95,159,160] C_2H_4,[160] and C_6H_6[160] to form (η^2-C_2H_2)-Li, (η^2-C_2H_4)Li, and (η^2-C_6H_6)Li, respectively, although binding energies on the order of only 10 kJ mol^{-1} are anticipated by quantum chemical calculations. In the gas phase such contacts are short-lived and serve merely to provide a means of energy transfer. Al atoms also add to C_2H_2[161,162] and C_2H_4[162−164] to form complexes with geometries similar to those of the corresponding Li compounds, but now with binding energies estimated to be 50−90 kJ mol^{-1} and with considerable potential for activation to induce metal insertion and other significant changes.

When there is appreciable interaction between the atom and the molecule, electron transfer must occur in some degree, as a result of delocalization of occupied orbitals or population of vacant orbitals that are bonding or antibonding, respectively, in the electronic makeup of the molecule. Thus, the IR spectra of the adducts (η^2-C_2H_2)Al[161] and (η^2-C_2H_4)-Al[164] indicate that metal coordination causes the C_2H_2 and C_2H_4 molecules each to suffer a marked reduction in the C−C stretching force constant (by ~33% in the case of C_2H_4, consistent with a bond lengthening of ~0.12 Å). On this sort of evidence, the products are not very different from the familiar π-type complexes formed by transition metals. In the same way Li atoms have been shown by EPR studies to form 1:1 adducts with HCl and HF having binding energies estimated to be 75 and 84 kJ mol^{-1}, respectively.[94] With Li·HCl the unpaired electron occupies what is essentially an antibonding σ-orbital of an elongated H−Cl moiety; this is coordinated side-on to the Li atom, to which a substantial positive charge (+0.47e) is thereby imparted. Intriguingly, though, the HF complex has a linear structure Li···F−H with the unpaired electron in an s−p hybridized orbital of the Li and directed away from the F atom; there appears to be dative interaction of the valence electrons of the F atom with the vacant Li orbitals to afford a significant *negative* charge (−0.18 e) on the metal atom. With the readily oxidizable metal atoms of the s-block and oxidizing molecules such as dioxygen or a dihalogen, electron transfer is likely to proceed to the point where the product approximates to an ion pair, for example, $M^+O_2^-$ (M = Li, Na, K, Rb, or Cs),[165] $Ca^{2+}O_2^{2-}$,[166] and $M^+X_2^-$ (M = Li, Na, K, Rb, or Cs; X = F,[167] Cl,[168] Br,[112,169] or I [112]). The progressive reduction of the O_2 substrate in the products LiO_2 and CaO_2 is clearly evident from the frequency of the ν(OO) mode, which decreases from ~1550 cm^{-1} in free O_2 to 1097 cm^{-1} in LiO_2[165] and still further to ~740 cm^{-1} in CaO_2.[166]

With saturated hydrocarbons, as with H_2, contact pairs including atoms in their electronic ground states involve interactions too weak to permit spectroscopic detection, despite numerous attempts to do so in matrix and other experiments.[170] Whereas CH_4 gives no such signs, however, the more polarizable SiH_4 molecule appears on co-deposition with Al atoms in a noble gas matrix to form a loosely bound complex having a distinctive UV−vis and EPR spectrum;[171] quantum chemical calculations argue for η^2-coordination of the metal by the slightly distorted SiH_4 tetrahedron in the resulting adduct.

Even the least reactive atoms are not excluded from addition, provided always that the molecular substrate is a sufficiently powerful acceptor and that the medium does not introduce unwanted competition. Such is the extraordinary acceptor power of the unsaturated metal carbonyl $M(CO)_5$ (M = Cr, Mo, or W) that it will form an adduct with a heavier noble gas atom, for example, Xe, which takes up the vacant sixth site left by the square-pyramidal coordination of the metal atom. This was first brought to light by photolysis studies of matrix-isolated $M(CO)_6$ molecules.[172] IR measurements on a liquid xenon solution indicate that the adduct $Xe\cdots Cr(CO)_5$ has a half-life of ~2 s at 175 K,[173] and time-resolved measurements have led to the detection of this and related species as transients in supercritical fluid solutions at room temperature.[145,173] The reaction of $Xe\cdots W(CO)_5$ with CO under these conditions has an enthalpy of activation of 34 kJ mol^{-1}, representing a lower limit to the $W\cdots Xe$ bond enthalpy. On this evidence, the bond is roughly twice as strong as a conventional hydrogen bond.

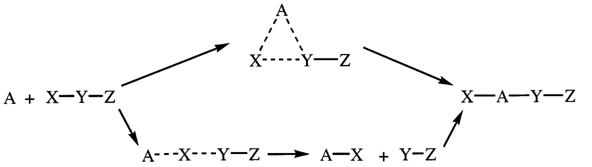
Competition with atom−molecule addition may sometimes arise from aggregation reactions of the individual atoms or their aggregates, although these can be largely suppressed by working at low concentrations and in matrix experiments where, as noted previously, there is little opportunity for diffusion and the action is almost entirely confined to the matrix cage. With the lighter group 14 atoms, which form strongly bound clusters, for example, C_n[174] and Si_n,[175] however, there seems to be little potential barrier to aggregation, which becomes therefore a serious alternative to other potential atom−molecule reaction channels.

B. Insertion

Unlike addition, insertion of an atom into the bond of a molecule, as in eq 17 (see Figure 2), so as to

$$A + X{-}Y{-}Z \rightarrow X{-}A{-}Y{-}Z \tag{17}$$

create two new bonds (A−X and A−Y) at the expense of the one that has been ruptured (X−Y), is seldom spontaneous, irrespective of any thermodynamic advantage that the process may offer. The product X−A−Y−Z can be formed in one of two ways (eq 18).



(18)

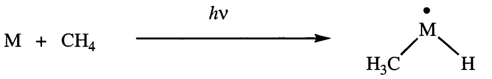
One involves concerted addition of the X−Y bond to A, the other dissociation of the X−Y bond at an early stage. A concerted mechanism operates if the atom A interacts simultaneously with *both* atoms X and Y; the bonding thus achieved is at the expense of the X−Y bond, which is thereby weakened. By contrast, the dissociative route is likely to be favored when the atom A interacts with just one atom of X−Y−Z, say X, to form an A−X bond with a concomitant weakening of the X−Y bond to the point of dissociation. This affords the fragments A−X and Y−Z, which may combine under appropriate conditions to generate the notional product X−A−Y−Z (see eq 16, for example). Information about the pathway taken may be gained with the help of experiments in which the molecular reagent is a mixture of two different isotopomers, for example, X−Y−Z and X′−Y′−Z. Thus, the reaction between a metal atom M and H_2 probably follows a dissociative course if HMD is formed in addition to HMH and DMD in experiments with an H_2/D_2 mixture, whereas a concerted mechanism is implied by the finding that HMH and DMD are the only products to be formed. Doubts will inevitably arise, however, if the product is labile and open, through dissociation and recombination, to atom-scrambling.

Notable examples include the insertion of a metal atom into a strong, relatively inert bond, such as that presented by H_2, CH_4 or O_2. It makes no difference that reaction 19 between a metal atom M in its

$$M + H{-}H \rightarrow H{-}M{-}H \tag{19}$$

electronic ground state and H_2 has an estimated enthalpy change of ca. −160, −60, and +32 kJ mol^{-1} for M = Be,[176,177] Al,[177] and Zn,[178] respectively: in no case does the reaction occur without significant activation. This may be provided under matrix conditions by photoexcitation of the metal atoms (to the ^2S or ^2D state in the case of Al[135] and to the ^1P or ^3P state in the case of Zn[178]) to give either angular, photolabile HAlH or linear, photostable HZnH. In the gas phase, however, the reaction between $Zn(^3P_1)$ and H_2 takes quite a different turn; the product is now ZnH, probably formed via decomposition of a bent, electronically excited HZnH intermediate.[179,180]

Similar in strength to the H−H bond is the C−H bond of an alkane, activation of which by insertion of a metal atom, whether naked or precoordinated, has for many years stimulated intense interest. None of the experiments carried out to date gives any hint of significant interaction between CH_4 and any metal atom in its electronic ground state.[170] Photoexcitation is invariably needed to induce a reaction. Transition[181] and group 12[182] metal atoms (M) have been shown to insert into a C−H bond of CH_4 only after s → p excitation, the σ-bonding orbitals of the CH_4 interacting repulsively with an atomic S state but attractively with a P state. It might be expected therefore that a group 13 metal atom in its ^2P electronic ground state would be capable of reacting spontaneously with CH_4. In fact, such a reaction is symmetry-forbidden, and matrix studies have shown that only after np → (n + 1)s or np → nd excitation of the atom does insertion occur, as in eq 20, to give



(20)

CH_3MH (M = Al,[98] Ga,[152] or In[152]) featuring the divalent metal and an angular C−M−H skeleton. In keeping with the behaviors of the corresponding dihydrides, the methyl hydrido derivatives of the group 12 metals Zn, Cd, and Hg are photostable, whereas the corresponding molecules formed by the group 13 metals decompose on exposure to broadband UV−visible radiation to give the univalent species CH_3M.[152] The few studies that have been carried out on larger hydrocarbons imply that the stronger C−H bond is more susceptible to insertion than is the weaker C−C bond, possibly because of the greater steric barrier opposing attack of the latter. Hence, the only detectable product of the matrix reaction between photoexcited Hg atoms and C_2H_6 is CH_3CH_2HgH; of CH_3HgCH_3 there is no sign.[182]

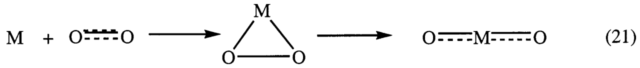
Table 2. Geometries and Vibrational Wavenumbers of Oxide Molecules of the Types OMO and Cyclic (η^2-O_2)M Trapped in Solid Matrices at Low Temperatures[a]

		wavenumber, cm^{-1}		
M	geometry/symmetry	ν(O−O)	ν(M−O)	ref
^6Li	cyclic/C_{2v}	1097.4	743.8, 507.3	165a
Na	cyclic/C_{2v}	1094	390.7, 332.8	165b
K	cyclic/C_{2v}	1108	307.5	165b,c
Rb	cyclic/C_{2v}	1111.3	282.5, 255.0	165c,d
Cs	cyclic/C_{2v}	1115.6	268.6, 236.5	165d
Be	cyclic, $^1A_1/C_{2v}$ O−Be−O angle ~74°		1264.1/1212.1,[b] 928.9[b]	184, 185
	linear, $^3\Sigma_g^-/D_{\infty h}$		1413.2	
Mg	cyclic, $^1A_1/C_{2v}$ O−Mg−O angle ~40°		681,[b] 426[b]	184, 185
	linear, $^3\Sigma_g^-/D_{\infty h}$		767.7, 723.6[b]	
Ca	cyclic, $^1A_1/C_{2v}$	739.2, 742.1[b]	555.7,[b] 505.5[b]	184, 185
	bent, $^3B_2/C_{2v}$		515.7, 497.0[b]	
Sr	cyclic, $^1A_1/C_{2v}$	729.9, 729.8[b]	509.2, 473.1[b]	184, 185
	bent, $^3B_2/C_{2v}$		532.4, 496.0[b]	
Ba	cyclic, $^1A_1/C_{2v}$	754.5	468.3	166, 184
	bent, $^3B_2/C_{2v}$		570.2	
Zn	linear, $^3\Sigma_g^-/D_{\infty h}$		748.2/744.4/740.9	203
Cd	linear, $^3\Sigma_g^-/D_{\infty h}$		626.6/625.4	203
B	linear, $^2\Pi_g/D_{\infty h}$		1347.6/1299.3	188
Al	cyclic, $^2A_2/C_{2v}$		496.3	200
	linear, $^2\Pi_g/D_{\infty h}$		1129.5	
Ga	cyclic, $^2A_2/C_{2v}$		380.9	201
	linear, $^2\Pi_g/D_{\infty h}$		912.7/908.6	
In	cyclic, $^2A_2/C_{2v}$	1084.2	332.0	201
	linear, $^2\Pi_g/D_{\infty h}$		755.4	
Tl	cyclic, $^2A_2/C_{2v}$	1082.0	295.2	202
	linear, $^2\Pi_g/D_{\infty h}$		698.0	
C	linear, $^1\Sigma_g/D_{\infty h}$		2344.8, 1383.7[c]	189
Si	linear, $^1\Sigma_g/D_{\infty h}$		1416.4	190
Ge	linear, $^1\Sigma_g/D_{\infty h}$		1061.6, 870.1	190, 191
Sn	linear, $^1\Sigma_g/D_{\infty h}$		860.1−866.1[d] 874.8−881.0[b]	192
Pb	cyclic/C_{2v}	728.7	437.3	193
	linear, $^1\Sigma_g/D_{\infty h}$		659, 764.8−765.3	
P	bent/C_{2v}		1319.0	194
O	bent/C_{2v}		1039.7, 1105	195
S	bent/C_{2v}		1147.1, 1351.1	196
Se	bent/C_{2v}		922.1, 964.4	197
Te	bent/C_{2v}		822.6, 839.4	198
Cl	bent/C_{2v}		941.1-948.5 1100.8−1108.2	199
Br	bent/C_{2v}		791.2−794.1 842.8−846.6	56
I	bent/C_{2v}		766.1−768.0 795.4−800.3	156

[a] Data refer to Ar matrices except where indicated otherwise. [b] N_2 matrix. [c] Value affected by strong Fermi resonance. [d] Kr matrix.

The ease of such insertion depends not only on the strengths of the bonds being formed in relation to the bond being broken but also on the degree of prior interaction between the atom in its electronic ground state and the reagent molecule. Quantum chemical calculations forecast that insertion into an Si−H bond of SiH_4 is opposed by a smaller activation barrier than is the corresponding insertion into a C−H bond of CH_4.[183] The results of matrix experiments investigating the reactions of excited Hg atoms with CH_4 or SiH_4 are indeed consistent with this prediction.[183] As in all such experiments, the initial contact pair Hg (^1S)···EH_4 (E = C or Si) plays an essential role in the ensuing photochemistry, and there is every reason to believe that the ground-state (^1S) Hg atom interacts more strongly with SiH_4 than with CH_4. Unmistakable evidence of such interaction is certainly to be found in the corresponding reactions of a group 13 metal atom with NH_3, and the resulting adduct M·NH_3 (M = Al, Ga, or In) has its own distinctive photochemistry;[148] irradiation into the characteristic absorption maximum near 440 nm results in highly efficient insertion of the metal into an N−H bond of NH_3, with the formation of the divalent metal species $HMNH_2$ (cf. reaction 20). In the case of M = Al, it has been shown that a second NH_3 molecule is taken up to form $Al(NH_3)_2$, which is also photolabile, but at wavelengths near 550 nm (cf. Al·NH_3).[148b]

Insertion of an atom into a multiple bond is likely to proceed in stages, with the initial formation of a tricentered cyclic intermediate. Thus, the insertion of a metal atom into the O—O bond of dioxygen will usually evolve through the formation of a superoxo or peroxo intermediate (q.v.) before rupture of the O—O bond is finally brought about, to give a dioxo derivative OMO (eq 21). Some vibrational properties of these different product types are listed in Table 2.[56,156,165,166,184−203] The behavior of the group 2 metal atoms Be, Mg, and Ca (M) under matrix conditions is typical.[166,184,185] The ground-state (^1S) atoms add spontaneously to O_2 to yield the cyclic peroxo molecules (η^2-O_2)M: in the excited ^3P state, by contrast, they insert into the O—O bond to generate the triplet dioxo products OMO, namely, linear OBeO and OMgO ($^3\Sigma_g^-$) and angular OCaO ($^3B_2$). Intriguingly, the outcome may be influenced by the choice of the matrix host, according to its ability to quench the excited metal atoms.[184] A similar pattern is found with the cyclic products (η^2-O_2)M′ formed without the need for significant activation of the corresponding group 13 metal atoms (M′ = Al,[200] Ga,[201] In,[201] or Tl[202]), whereas excitation of the atoms to the ^2D state is evidently a prerequisite to insertion, giving linear OM′O molecules.



(21)

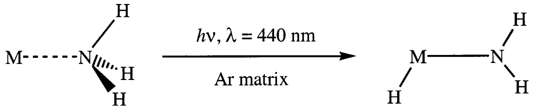
The properties of N_2 make it unusually resistant to insertion of an atomic reagent. It is surprising therefore that, even allowing for the extra energy imparted to atoms by laser ablation, the group 13 atoms B,[204] Al,[49] Ga,[50] or In [50] (M) should appear to react with dinitrogen on co-condensation to give, among other products, the linear ($^4\Pi_u$) NMN molecule. However, experiments with mixtures of $^{14}N_2$ and $^{15}N_2$ make it quite clear that N atoms are in fact implicated, these being formed by photodissociation of N_2 under the action of the radiation from the focused laser plume at the M target. Typical of the reactions of the heavier M atoms in a solid N_2 matrix are the following:

$$\begin{aligned} M + N &\rightarrow MN \\ N + MN &\rightarrow NMN \\ N + N_2 &\rightarrow NNN \\ M + N_3 &\rightarrow MN_3 \end{aligned} \tag{22}$$

in which *addition* rather than insertion is the rule.

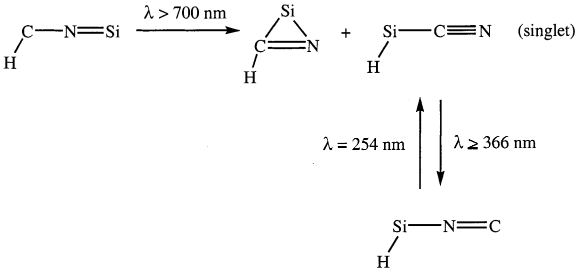
C. Isomerization

A polyfunctional molecule inevitably offers to an atomic reagent a variety of reaction sites and access accordingly to different isomeric products. Although these products may vary widely in their energies, both thermodynamically and kinetically, the additional energy that is often imparted to an atom to induce reaction is likely to be retained, at least in part, by the initial product. By this means or by supplementary activation, rearrangement of the product becomes a real possibility. Where addition of an atom to a molecule leads to a distinct, identifiable product, which can be shown to function specifically as the precursor to insertion, the reaction can of course equally well be described as isomerization, as in the cases represented by eq 23 (where M = Al, Ga, or In).[148] Photoexcitation may give rise to more than one isomer. For example, irradiation of the adduct M·PH_3 under conditions similar to those outlined in eq 23 affords not only $HMPH_2$ but also a second product, H_2MPH.[153] According to quantum chemical calculations, the latter differs little in energy from the former, whereas H_2MNH lies at substantially higher energy than $HMNH_2$.[149]



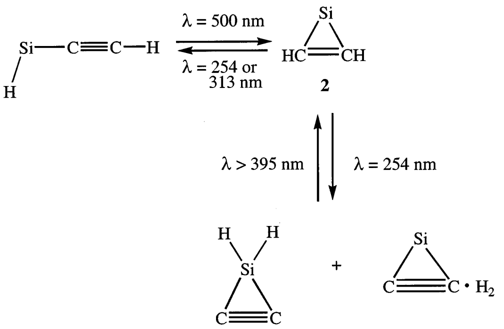
(23)

The HCN molecule illustrates well the way in which isomeric products may arise. Matrix studies have established that laser-ablated Be atoms react with HCN to give both HBeCN and HBeNC, as well as the decomposition products BeNC and BeCN.[205] The primary pathway appears to involve insertion of an excited (^3P) Be atom into the H—C bond to give [HBeCN]†, a "hot" product, which can either relax and be trapped in the matrix or rearrange to the more stable isomer HBeNC. By contrast, thermally generated Si atoms add to the lone pair on the nitrogen atom of HCN with the formation of HCN=Si on codeposition in an argon matrix.[206] This product, (silaisocyano)carbene, is itself photolabile and rearranges under the stimulus of visible or UV radiation to one of no less than three alternative isomers (eq 24).

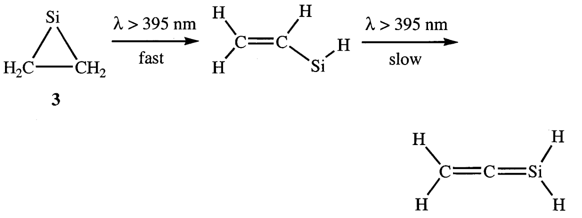


(24)

Mention has already been made of the ethyne → vinylidene isomerization brought about by irradiation of the lithium complex (η^2-C_2H_2)Li (eq 14).[95] Ground-state Si atoms also add initially to the multiple bonds of ethyne,[207] ethene,[207] and formaldehyde [208] to give the cyclic products **2**, **3**, and **4**, respectively. These give rise to quite a rich photochemistry in which, as revealed in eqs 25−27, isomerization plays a con-



(25)[207]



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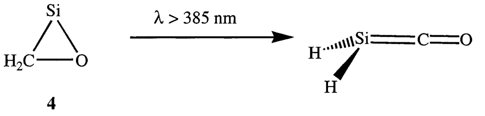

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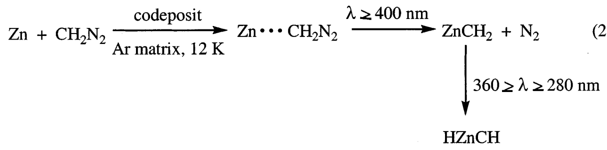
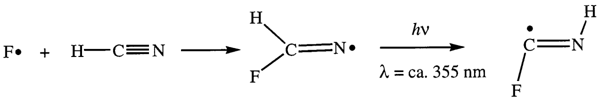


(28)[209]

spicuous part. Carbene → carbyne rearrangement can also be engineered, as witness the case of matrix-isolated $ZnCH_2$, albeit one step removed from the initial atom-molecule reaction (eq 28).[209]

In quite different chemical territory, we note that F atoms add to HCN in an argon matrix to produce $H(F)C{=}N^{\bullet}$ radicals in concentrations sufficient for IR and EPR detection and that these undergo photoisomerization at wavelengths near 355 nm to *trans*-$F\dot{C}{=}NH$ (eq 29).[210] Moreover, Cl atoms combine with ClO_2 when trapped together in a solid matrix to give the isomers $ClClO_2$ and ClOClO;[211] the only products of this reaction normally detectable in the gas phase are Cl_2 and O_2. To $ClClO_2$ and ClOClO there needs to be added a third, known isomer, ClOOCl. All represent potential, photolabile products from the dimerization of ClO, arguably linked to the fate of stratospheric ozone.[33] NO_2 is another molecular reagent offering the choice of more than one site of attack to a halogen atom. Co-deposition of F atoms with NO_2 in an N_2 matrix gives rise to the hypofluorite FONO, and only on UV photolysis does this rearrange to the more familiar nitryl fluoride, FNO_2.[212] Under similar conditions Br atoms form *first* $BrNO_2$, access to BrONO requiring photoexcitation in the near-UV region,[213] whereas Cl atoms react spontaneously to give both $ClNO_2$ and ClONO, as well as a third isomer OClNO formed, it is believed,[214] by insertion of a "hot" Cl atom into one of the N−O bonds of NO_2.

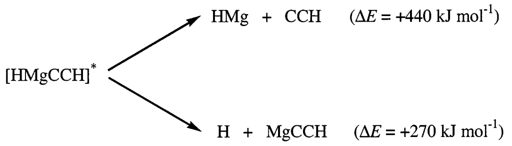


(29)

D. Decomposition

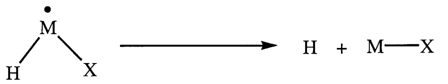
Implicit in all the primary processes considered so far has been the constancy in the overall composition of the molecular assembly from its inception as an atom−molecule adduct, despite subsequent changes of bonding or geometry. Yet another outcome entails break-up of the molecule at some stage, with the rupture of one or more bonds and the separation of discrete atomic or molecular fragments. Any surplus energy the molecule may carry as a consequence of the mode of its formation is perfectly capable of providing the driving force for decomposition, making it a pervasive feature of atom−molecule reactions in the gas phase, but distinctly less common when the same reagents are confined to a solid matrix environment at low temperatures. Decomposition may result simply in rupture of whatever bond has been established between the atom and the molecule to regenerate the starting materials. For example, Hg atoms in the excited $^3P_0$ state interact with NH_3 in the gas phase to give an exciplex product $Hg{\cdot}NH_3{}^*$, the decay of which to Hg ($^1S_0$) + NH_3, to the accompaniment of emission at $\lambda = 345$ nm, affords an effective exit channel in the quenching of the excited metal atoms.[15] Alternatively, decomposition may proceed through the rupture of another bond in the intermediate. This is exemplified by the photodecomposition of I−O−O leading primarily to IO + O (eq 16);[156] under similar conditions there are two decay channels open to Br−O−O, one leading back to Br + O_2 and the other leading to BrO + O.[56]

In the condensed phases, the liquid or solid host is able to act as a sink for energy transfer, thereby facilitating the relaxation of a "hot" molecule. With a solid matrix in particular, there is also the physical constraint of the cage surrounding the molecule, which impedes the separation of would-be dissociation products. Spontaneous or photoinduced decomposition remains a serious option, however, and especially when at least one of the products is a small atom or molecule, for example, H, F, or N_2, having appreciable mobility even in a solid matrix at low temperatures.[136] A good illustration is provided by the case of the excited HBeCN molecules believed to be the primary product of the matrix reactions between laser-ablated Be atoms and HCN.[205] In addition to relaxation and isomerization (q.v.), the molecules also have access to dissociation channels yielding H + BeCN or H + BeNC. In analogous studies with other group 2 or group 13 atoms, decomposition predominates to the exclusion of insertion, at least in the final analysis, with MNC (M = Mg, Ca, Sr, or Ba)[215] or MCN + MNC (M = Al, Ga, In, or Tl)[216] being the only products detectable by their IR spectra. The reactions of laser-ablated metal atoms with ethyne follow a similar pattern: whereas Be inserts into a C−H bond to give HBeCCH, in addition to a number of other products, Mg gives rise to only MgCCH, MgH, and CCH.[217] Presumably the Mg insertion product is not relaxed but decomposes immediately via one of the two channels in eq 30.



(30)[217]

Photolysis may also result in decomposition of the first product of an atom−molecule reaction, as represented in eq 27 [208] and by the behaviors of insertion products of the type HMX featuring a divalent group 13 metal, M = Al, Ga, or In, and various substituents, X = H,[135] CH_3,[152] or NH_2[148] (eq 31).



(31)

The difference between the matrix and gas phase is starkly but typically exemplified by the reaction of B atoms with O_2. Trapping of laser-ablated B atoms with O_2 in a noble gas matrix gives rise to both BO and OBO,[188] whereas BO is the exclusive product in the gas phase.[218] The situation is as set out in eq 32. The insertion product OBO is formed initially in

$$\begin{aligned} B + O_2 &\xrightarrow{\Delta E = -860\ \text{kJ mol}^{-1}} OBO \\ OBO &\xrightarrow{\Delta E = +560\ \text{kJ mol}^{-1}} O + BO \end{aligned} \tag{32}$$

a reaction so exothermal that, unless the large excess of energy is quenched by a third body, decomposition to O + BO is an inevitable sequel. It is generally the case that third bodies are in short supply in the gas phase, and so decomposition to form a strongly bound diatomic fragment or to regenerate the starting materials is the normal outcome of a reactive atom−molecule encounter under these conditions. The gaseous B/O_2 system exemplifies a common format, and many are the kinetic studies that have been carried out on atom−molecule reactions resulting in displacement. These include the two processes central to the “chlorine catalytic cycle” (eq 33) and other primary processes (e.g., eq 34) of crucial importance in atmospheric chemistry,[33] as well as a host of reactions involving metal atoms and molecules such as a dihalogen or N_2O (e.g., eqs 35 and 36).[219,220]

$$\begin{aligned} Cl + O_3 &\rightarrow ClO + O_2 \\ ClO + O &\rightarrow Cl + O_2 \end{aligned} \tag{33}$$

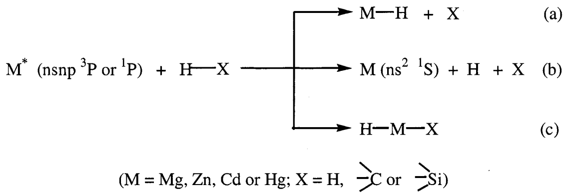
$$O + H_2O \rightarrow 2OH \tag{34}$$

$$M\ (^1S) + Cl_2 \rightarrow MCl + Cl\ (M = Ca\ \text{or}\ Sr) \tag{35}$$

$$Pb\ (^3P_0) + N_2O \rightarrow PbO + N_2 \tag{36}$$

Regarding the intervening stages of these changes, that is, the nature and lifetime of the activated complex, information is apt to be oblique. Some vital clues may be gained, nevertheless, by analyzing the electronic states and energies of the products in relation to the corresponding properties of the reagents.[15,179] For example, the distribution of translational energy may be analyzed as a function of scattering angle in mass spectrometric studies with molecular beams, whereas the rotational and vibrational energies of molecular products may be probed, notably through the medium of chemiluminescence or LIF.

Such methods have featured prominently in studies of the interactions of excited group 2/12 metal atoms with H−H, ⩾C−H, or ⩾Si−H bonds.[179] There are three possible pathways, as represented in eq 37; which of these is favored depends on M and its excited state, as well as X. Accurate quantum-state-resolved distributions have been determined for the vibrational and rotational energy of the MH (v,N)



(37)[179]

products in exit channel 37a on the basis of laser pump−probe techniques. Ab initio calculations of appropriate potential surfaces have also served as a mechanistic guide. The absence of significant vibrational excitation of MH implies a “late” release of potential energy, whereby the M−H bond is essentially formed in the regions of the M*−HX potential surface where energy release occurs to produce the MH + X products. In the reactions of M (^3P) atoms with H_2 or SiH_4, moreover, the rotational energy distribution in MH points to a mechanism in which the excited M atom inserts into the H−X bond (X = H or SiH_3) with little or no activation barrier to form a triplet intermediate [H−M−X]* with an M−H bond distance calculated to be very similar to that in the free M−H product molecule. The vibrational and rotational distributions observed in MH are then presumed to reflect the moderately anisotropic decomposition of the *bent* [H−M−X]* intermediate, which is too short-lived for statistical population of all degrees of freedom and may in fact decompose within one H−M−X bending vibration. According to ab initio calculations on the M (^3P)/H_2 system, a C_{2v} ($^3B_2$) approach with only slight H−H bond stretching is initially favored; the potential energy drops continuously as M approaches H_2, leading to a local minimum in the PE surface at fairly short M···H_2 separations (1.8−2.0 Å). There is then a slight rise in PE before the H−H bond suddenly breaks, and the H−M−H bond angle increases sharply to ∼70°, yielding another local PE minimum in which the H−H bond has essentially been broken. Another slight rise in PE then opposes the decomposition of this intermediate into H + MH. A similar local PE surface topology is believed to apply to the M (^3P)/SiH_4 system. Laser excitation of jet-cooled M/CH_4 mixtures (M = Cd or Hg) gives rise to spectroscopic transitions consistent with bound M ($^3P_1$)···CH_4 van der Waals complexes with well depths on the order of 8 kJ mol^{-1}.[221] However, there is little to suggest significant perturbation of the CH_4 molecule, leaving a substantial barrier to C−H bond activation (see Figure 3). This accords with the experience of numerous gas-phase studies that the reactions of M (^3P) atoms with CH_4 are quite inefficient.[179] Curiously, though, $^3P \leftarrow {}^1S$ excitation of M atoms trapped together with CH_4 in a solid argon matrix affords the insertion product CH_3MH (M = Zn, Cd, or Hg).[182]

The reluctance of gaseous M (^3P) atoms to react with alkanes is not shared by the same atoms in the more energetically excited ^1P state.[179] All the available experimental and ab initio evidence is consistent with efficient, indiscriminate attack and cleavage of all alkane C−H bonds studied, with no activation barriers, by both Zn ($^1P_1$) and Mg ($^1P_1$). This is probably because the singlet state offers M (np) orbitals having a better energy match, and hence

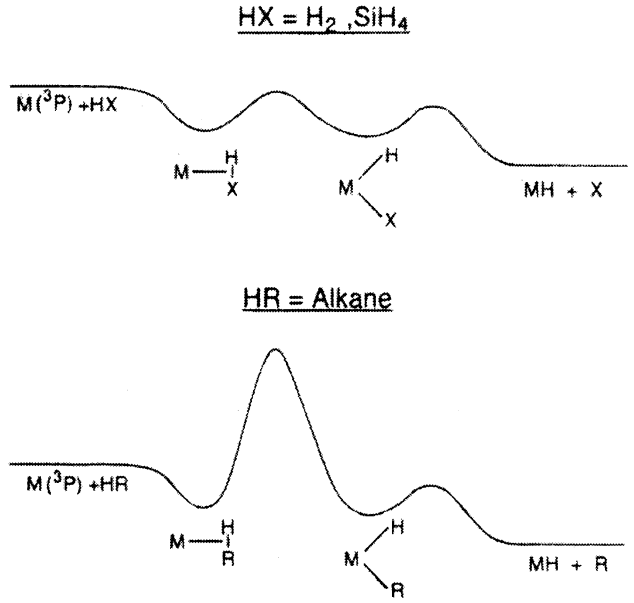


Figure 3. Schematic potential energy curves for the reactions of M(nsnp ^3P) excited states with H_2 or SiH_4 (top) and an alkane (bottom). (Reprinted with permission from ref 179. Copyright 1996 American Chemical Society.)

better overlap, with the localized C−H (σ*) orbitals, thereby offsetting the electron−electron repulsion from neighboring bonds or from C−H (σ)···M (ns) overlap. However, the two metals differ in the events that follow. Mg ($^1P_1$) attack appears to involve prompt C−H bond-breaking because the quantum-state distributions of the MgH (v,N) products do not vary significantly with the strength of the C−H bond or the complexity of the alkane molecule containing it. Although the bimodal rotational-state distribution of the MgH suggests that two microscopic mechanisms are involved, any R−Mg−H intermediate formed does not appear to survive more than about one bending vibration without transferring energy to the R component. So it is believed that the Mg atom never really “inserts” into the C−H bond in a true sense. Yet we note that the insertion product CH_3-MgH can be identified following $^1P \leftarrow {}^1S$ excitation of Mg atoms isolated in a solid methane matrix.[222] By contrast, the Zn (^1P)/RH interaction involves the formation of long-lived, ground-state $[R−Zn−H]^\dagger$ intermediates even in the gas phase, with lifetimes that increase with the complexity of the alkyl group R. The two types of dynamic behavior characterizing the Mg (^1P)/RH and Zn (^1P)/RH systems are also to be found in the analogous reactions of excited O ($^1D_2$) atoms with alkanes;[16,179] in this case the formation of long-lived $[ROH]^\dagger$ complexes is favored by the simpler but not by the larger alkanes.

IV. Comparison between Gas-Phase and Matrix Isolation Studies

Whether in a gas at low pressure or in a solid inert matrix at low temperature, reactive intermediates or products are well isolated not only from one another but also from other potentially reactive molecules. With an appropriate method of interrogation, therefore, both sets of conditions offer the opportunity to monitor and characterize such species as they arise in atomic reactions. As indicated by various examples cited in the preceding sections, however, there are in reality major differences between the two types of experiment in what they reveal. In summary and as indicated in Table 3, these are as follows.

(i) The matrix outstrips the gas environment in its ability to quench excited products and disperse the energy liberated in exothermic processes, which is likely otherwise to induce decomposition. Hence, a photochemical reaction is typically arrested immediately after the primary change has taken place. The energies and lifetimes of atoms and molecules in excited *electronic* states are not markedly affected by a matrix environment.[1] Radiative decay is essentially temperature-independent, and although some nonradiative processes are suppressed by the matrix, others are accelerated. Very occasionally it is evident that the relative energies or lifetimes of excited states vary from one matrix to another. This appears to be the case, for example, with Mg (^3P), which is quenched sufficiently rapidly in solid N_2, but not in solid Ar, to forestall reactive interaction with O_2 molecules (q.v.).[184] Far more often, however, such effects are of marginal concern.

(ii) Atomic and molecular species are held rigidly in the matrix unless steps are taken deliberately to anneal the solid sample. Even then, only very small species are free to diffuse within the matrix so that there is invariably a strong *cage effect*.[136] Not only does this inhibit the separation of atom−molecule or molecule−molecule pairs created by photodissociation, it also tends to restrict to such pairs the opportunity for insertion, isomerization, or other changes. Indeed, the bulk of two-body reactions occurring in matrices require the sustained proximity of the reactants; reactions calling for mobility over a longer range are confined to small and/or highly energetic atoms and molecules. Because of the cage effect, photolysis of a matrix sample may appear to be without effect for the simple reason that the products recombine, either spontaneously or under the action of the photolyzing radiation, to restore the status quo. To be taken into account is also the possibility that the cage effect may influence the way in which a compound decomposes. For example, the photodecomposition of CH_3GaH isolated in an Ar matrix gives $CH_3Ga + H$ but not $GaH + CH_3$, probably because H atoms, but not CH_3 radicals, are sufficiently mobile to be able quickly to escape from the site of their formation.[152]

In summary, the matrix cage may give rise to no fewer than five possible events.[136]

(a) It may permit a photoexcited guest species simply to relax into its ground electronic state.

(b) A matrix-trapped molecule may dissociate transiently, but the photofragments, being unable to escape from the cage, recombine to form either the parent molecule or an isomer, as with ICN [57] (see section II.A).

(c) Photodissociation of such a molecule may also occur, but the fragments are unable to exit the cage and any form of recombination is opposed by an activation barrier that cannot be surmounted under the prevailing conditions. In this case, the fragments

Table 3. Atomic Reactions: Comparison between Gas-Phase and Solid Matrix Studies

gas phase	solid matrix at low temperature
• rotational transitions give information about dimensions	rotation is quenched by the matrix environment
• heat of exothermic reactions can cause decomposition of primary product	heat of reactions is removed by the matrix environment
• no interaction with environment	different matrix sites can lead to matrix-splitting of spectroscopic transitions; confinement of primary products
• loosely bound complexes are too unstable to be detected under normal conditions	loosely bound complexes are preserved in the matrix environment and can be studied at leisure
• thermodynamically unstable compounds, e.g., rare gas compounds, are often too short-lived for normal studies	thermodynamically unstable compounds, e.g., compounds such as HXeH, can be generated and preserved
• a large number of analytical methods are available (including rotational, IR, UV−vis, EPR, mass, UPS, and XPS spectroscopies and electron diffraction) for interrogation of compounds	only a few experimental techniques are readily applicable in practice (e.g., IR, UV−vis, and EPR)
• kinetic measurements are possible over a wide temperature range	kinetic measurements are largely ruled out; the temperature range is narrow

are trapped together in the same cage, often disclosing spectroscopic signs of mutual perturbation.

(d) One of the photofragments may succeed in exiting the cage, and so result in permanent dissociation of a molecular precursor, as with CH_3GaH.[152]

(e) The species or a dissociation product of a molecular guest may react with the matrix, as with H^+ ions in an Xe matrix.[137]

The mobility of atomic or molecular guests within a solid matrix is plainly an issue vital to the understanding of the physical and chemical fates of an atom in these conditions. To what degree an atom is free to exit its initial matrix site is, however, difficult to assess and is likely in any case to depend on the energy possessed by the atom; for example, a photogenerated atom may be released with sufficient kinetic energy to force its way out of the cage where it has been formed. Photogenerated H atoms with an energy excess of ~2.6 eV have been shown to propagate over distances of ≥10 nm through an Xe matrix before disposing of their kinetic energy. Likewise, O and especially F atoms may have mean lengths of travel varying from a few nanometers up to ~50 nm. The unusual mobiltity of H atoms is partly a matter of size, but it also reflects the fact that photodissociation of an X−H bond typically imparts most of the energy to the light atom, which is then slower to lose this energy to its environment than are heavier fragments. In addition, quantum mechanical tunneling may be a significant factor.[136,223] The diffusion of certain atoms in thermal equilibrium with the host lattice can be studied by the luminescence resulting from the formation of molecules such as S_2, SO, or O_2 on controlled annealing of the deposit.[1,136] The activation barrier to thermally activated diffusion of H atoms in solid Kr at ~22 K has been estimated to be 6.4 kJ mol^{-1}, with the corresponding barrier in solid Xe at ~33 K being 11.9 kJ mol^{-1}.[224] By contrast, proton diffusion in a noble gas (Ng) matrix is effectively a ligand exchange reaction, with the $[Ng\text{-}HNg]^+$ entity trading one of its Ng atoms for a neighboring atom in the matrix cage; computed barriers to this exchange range from 10 kJ mol^{-1} in He and Ne to 30−35 kJ mol^{-1} in Kr and Xe, that is, considerably greater than for diffusion of neutral H atoms.

(iii) So rigidly are all but the very smallest molecules held in a solid matrix that they do not rotate, and the cage effect combines with the low temperature to halt dynamic processes leading to the interconversion of conformers. Even a barrier of 5 kJ mol^{-1} appears as a mountain at 10 K when $kT = 0.08$ kJ mol^{-1}. These features have two important consequences. First, we lose the information carried by rotational transitions reporting particularly on the precise dimensions of the molecule, as well as its history, which form a substantial element of gas-phase studies.[15,179] Second, the possible existence of more than one conformer complicates the vibrational and other spectra of matrix-isolated molecules. Spectroscopic transitions are likely also to be multiplied by the occupancy of different trapping sites within the matrix and by interaction with an atom or another molecule contained within the same site.[2,43,103] However, these complications are not without benefit in the light they may shed, when accurately interpreted, on a variety of weak interactions not easily gauged in the majority of gas-phase studies.

Hence the matrix technique has been particularly instructive in the spectroscopic access it has given to loosely bound complexes, which may act as precursors to insertion and other reactions. Examples include $M{\cdot}NH_3$ and M·CO (M = group 1[93,225226] or group 13 metal[148,154,155]), $M{\cdot}PH_3$ (M = Al, Ga, or In),[153] $Al{\cdot}SiH_4$,[171] and $Zn{\cdot}CH_2N_2$.[209] One of the few ways in which species such as these can be detected and characterized at first hand in the gas phase is by spectroscopic analysis of jet-cooled mixtures. Many such studies have indeed been carried out on van der Waals complexes composed of an atom and a molecule both in their electronic ground states. Ar·HCl typifies the bulk of these species in featuring a partnership of distinctly limited potential for significant chemical change.[227] More insight into the mechanism of photochemical change is likely to be gained by fluorescence studies of short-lived complexes such as M $(^3P_1){\cdot}CH_4$ involving electronically excited atoms (M = Cd or Hg)[220] or of longer lived but highly reactive molecular products such as CH_3M (formed from M atoms and a methyl source such as $Sn(CH_3)_4$, where M = Li,[228] Na,[229] Mg,[230] Ca,[231] Sr,[232] Ba,[233] or Al[234]).

Some matrix reactions have no established counterparts in the gas phase. Nowhere is this better illustrated than by the formation of the divalent noble gas compounds HKrX and HXeX (X = H,[235,236]

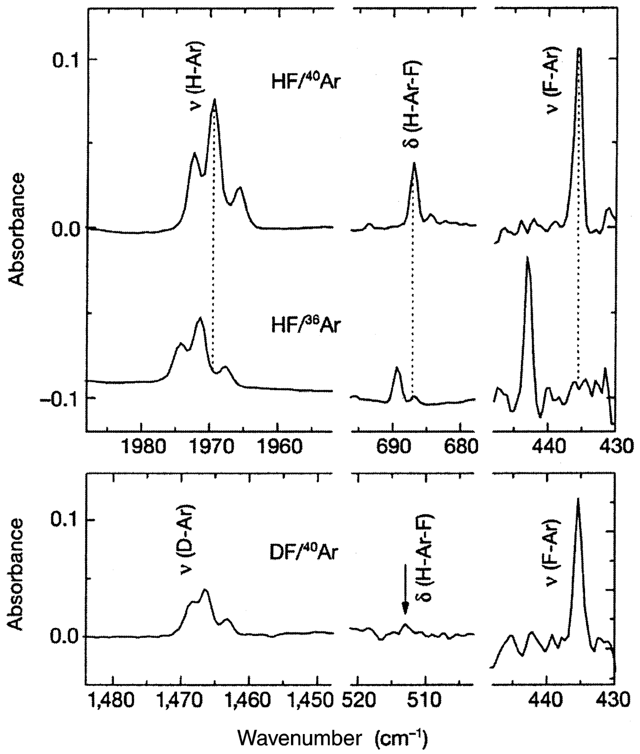


Figure 4. Infrared absorptions of HArF isolated in a solid Ar matrix at 7.5 K. The effects of isotopic substitution (^{40}Ar/^{36}Ar and H/D) are shown (see ref 243a).

halogen,[237,238] OH,[238,239] SH,[240] CN,[241] or NCO [242]), all of which are highly unstable with respect to decomposition into the elemental noble gas and HX. Most striking of all has been the very recent sighting of what is arguably the first authenticated argon compound HArF.[243] Yet these molecules can be generated by photolysis, typically with vacuum-UV radiation, and subsequent annealing of a matrix made up of the relevant noble gas and doped with HX (see Figure 4, for example). The conditions result in cleavage of the H−X bond and addition of the fragments to the noble gas atom. That argon is indeed capable of forming weakly covalent bonds is also implied by the properties deduced for the gaseous complexes Ar•CuX[244] and Ar•AgX [245] (X = F, Cl, or Br) identified in a pulsed jet by their microwave spectra. Unlike Ar•Hg [246] and Ar•NaCl,[247] which are true loosely bound, highly flexible van der Waals complexes featuring long Ar−metal distances, Ar•CuX and Ar•AgX are linear, relatively rigid species in their vibrational ground states, with Ar−metal distances measuring 2.22−2.30 and 2.56−2.64 Å, respectively. According to quantum chemical calculations, the Ar−metal bond energy is quite substantial, namely, ca. 23 and 47 kJ mol^{-1} for the AgF and CuF complexes, respectively.[244,245]

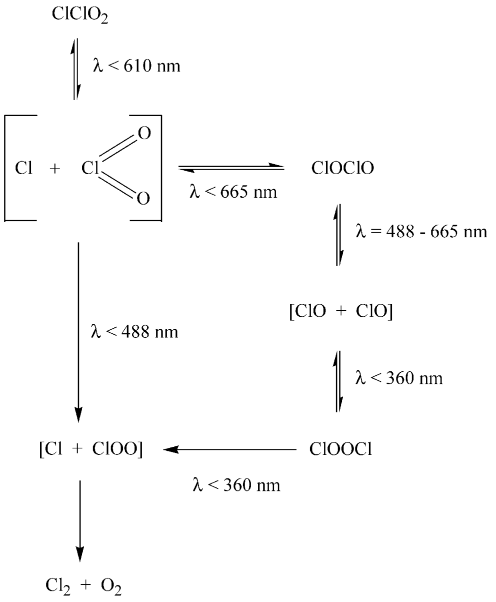


Figure 5. Scheme showing the photochemically induced reactions of Cl_2O_2 isomers in a solid Ar matrix.

The ability of a matrix to confine reagents and so favor reaction pathways that might otherwise be avoided is also underscored, albeit less exotically, by the photochemistry of the chlorine oxides ClOOCl, $ClClO_2$, and ClOClO (q.v.).[211] All of the isomers are photolabile and dissociate to give the products Cl + ClO_2, Cl + ClOO, or 2ClO. When trapped in the same matrix cage, these can be made under appropriate photoactivation to follow the pathways shown in Figure 5:[211] the gas phase offers no such control with the result that photodecay leads only to Cl_2 + O_2. In this ability to direct reactivity, matrix cages show in a primitive way some of the characteristics of zeolite, micelle, and other cavities that, by the act of confinement of the reactive species, are able to dictate both the kinetics and selectivity of chemical reactions.[248]

(iv) From a purely practical point of view, solid noble gases are seldom perfectly transparent to photolyzing radiation, and the problem becomes increasingly acute at short wavelength; only rarely are appreciable photochemical yields to be had, for example, under vacuum-UV irradiation of a matrix sample. Absorption coefficients of the matrices in the vacuum-UV region are typically high, and any products formed in the surface layers of the deposit shield the inner layers from the photolyzing radiation. The problem can be circumvented to some extent by concurrent deposition and irradiation[249] (see section II.A).

V. Selected Reactions of Atoms of Main Group Elements

In this section we review some of the reactions that occur through the interaction of main group atoms with various molecules. For one element selected as being representative of each group, the characteristic reactions of its atoms are illustrated diagrammatically, with salient features being adumbrated briefly in the following account. Matrix experiments provide the mainstay of the experimental results, although reference will be made, where appropriate, to gas-phase and theoretical investigations.

A. Li Atoms

The Li atom is better adapted than any other in group 1 to covalent bonding, primarily because of the accessibility and potential for overlap of its valence

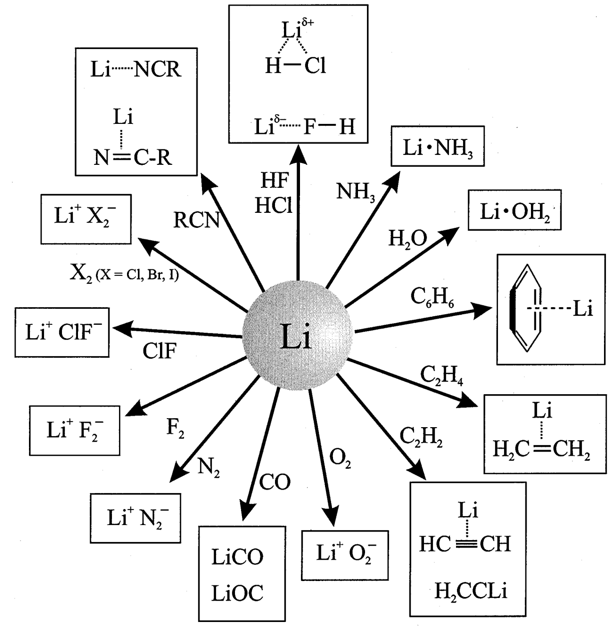


Figure 6. Overview of some of the reactions of Li atoms that have been studied.

p-orbitals. Figure 6 summarizes some typical reactions that it has been shown to undergo. Characteristic features are (i) the spontaneity of many of the changes (reflecting the relatively low ionization energy of the single 2s valence electron) and (ii) the predominance of metal-to-molecule electron transfer as a working principle. Even with a molecule as resistant to reduction as N_2 there is a spontaneous reaction to give a product that approximates to the formulation $Li^+N_2^-$ on the evidence of an unusually low ν(NN) frequency (1800 cm^{-1}).[250] As might be expected, products of the type $Li^+X_2^-$ result through the interaction with a dihalogen molecule X_2;[112,167–169] this is but a short-lived stage in the "harpoon" mechanism that delivers LiX + X in the gas phase.[143] As already noted, HF and HCl each form a 1:1 complex, but with very different structures, under matrix conditions; the HF complex appears to be an exception to the normal rule in having an Li atom carrying a partial *negative* charge.[94] Complexes are also formed severally with NH_3[93,225] and RCN (R = H or CH_3),[251] with metal–ligand charge transfer as the principal agent of binding; in the case of RCN, this leads to two types of complexes, one linear, R–C≡N·Li, and the other linked side-on to the C≡N bond, (η^2-R–C≡N)Li. With ethene,[160,252] ethyne,[95,159,160] and benzene,[160,253] symmetrical π-type complexes are formed, with the charge transfer reducing markedly the barrier to ethyne → vinylidene isomerization (eq 14).[95,254]

The thermal reaction with NH_3 evidently proceeds further in the gas phase because monomeric $LiNH_2$ has been synthesized very recently[255] by the interaction of Li and NH_3 vapors in the presence of argon as a carrier gas. The molecule has a lifetime estimated to be <1 s under these conditions, but not so short as to prevent its pure rotational spectrum from being measured in absorption in the millimeter/submillimeter ranges (see Figure 7), with results clearly pointing to a planar structure.

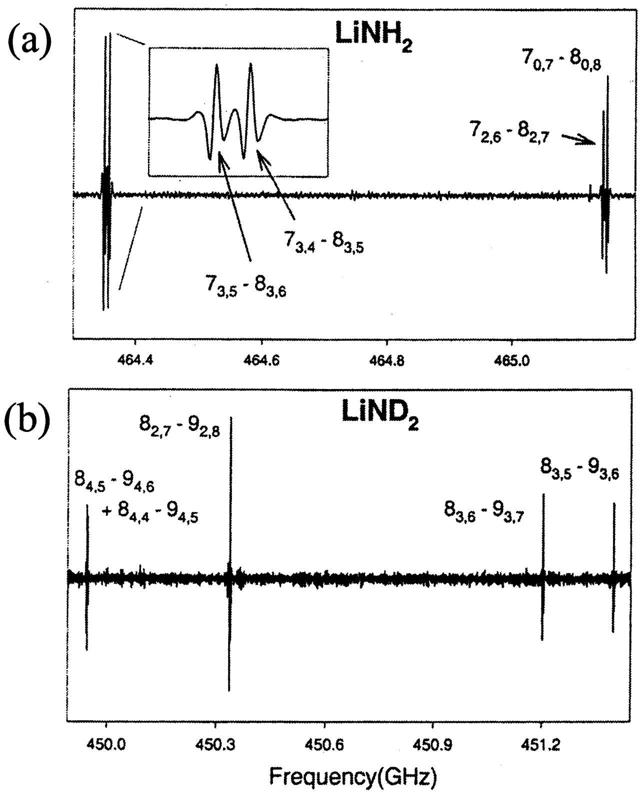


Figure 7. Spectra of a section of the J = 7–8 transition of $LiNH_2$ and part of the J = 8–9 transition of $LiND_2$ near 465 and 451 GHz, respectively. The quantum number labeling is $J_{K_aK_c}$, K_a and K_c being projections of the total angular momentum J (exclusive of nuclear spin) onto the symmetry axis of the molecule in the respective prolate and oblate symmetric top limits. In the $LiNH_2$ spectrum, the K_a = 0 and 3 components are present, as well as one component of the K_a = 2 doublet. In the inset, the asymmetry splitting of the K_a = 3 component near 464.4 GHz is shown. For $LiND_2$, one line for the K_a = 2 doublet is visible but both components for K_a = 3 and 4 are present. The effect of nuclear spin statistics, coupled with the Boltzmann factors, is evident in the data. For $LiNH_2$, the K_a odd lines are stronger than the K_a even ones; in the $LiND_2$ spectrum, the opposite occurs. Both spectra are composites of 9–16 100 MHz scans, each lasting ~1 min in duration. (Reprinted with permission from ref 255. Copyright 2001 American Chemical Society.)

B. Mg Atoms

A group 2 metal atom such as Mg is much less likely than a group 1 metal atom to interact spontaneously with a molecule to form more than a loosely bound adduct. This reflects partly the increased ionization energy, but more especially the character of the ^1S ground state, which interacts repulsively with the bonding orbitals of simple molecules such as H_2 and CH_4.[179] Ab initio calculations reveal that C_2H_4···Mg (^1S) is a van der Waals complex with a binding energy of ~3 kJ mol^{-1} and minimal perturbation of the ethene molecule.[256] On similar grounds, CO_2 is judged to form a *metastable* complex with Mg (^1S) approximating in its formulation to the ion-radical pair $Mg^+CO_2^-$.[256] With the Mg bridging the two terminal O atoms of a bent CO_2 fragment, this product may be amenable, as has been claimed, to stabilization in a solid CO_2 matrix. Mg atoms also form a weakly bound 1:1 complex with H_2O identifi-

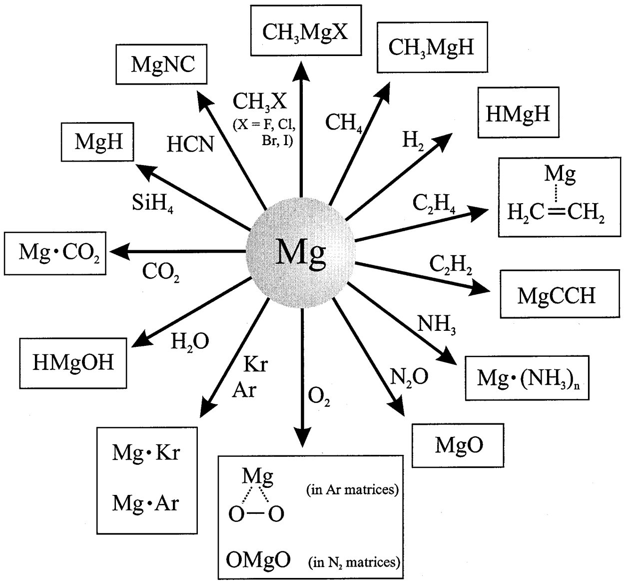


Figure 8. Overview of some of the reactions of Mg atoms that have been studied.

able in an Ar matrix by a red shift of 15.5 cm^{-1} in the wavenumber of the ν_2 fundamental of the H_2O molecule.[257] For more eventful progress, however, photoexcitation of one of the valence 3s electrons of Mg is necessary, typically to attain the $^3P_1$ or $^1P_1$ excited state;[179] less selective population of these states also occurs when Mg atoms are generated by laser ablation. Matrix studies have shown that such activation results, as shown in Figure 8, in insertion reactions with the following molecules to give the products identified in parentheses: H_2 (HMgH),[186] O_2 (OMgO),[184,185,258] CH_4 (CH_3MgH),[222,259] CH_3X (CH_3MgX, where X = F, Cl, Br, or I),[260] and H_2O (HMgOH).[257] Where comparisons are possible, the corresponding gaseous reactions involve displacement with the formation of a diatomic derivative of the metal, for example, MgH (from H_2 or RH)[179] and MgO (from O_2).[15,16,261] Even the quenching action of a matrix is not efficient enough to prevent the decomposition of the "hot" insertion products [HMgCN]* (to MgNC + H)[205] and [HMgCCH]* (to MgCCH + H).[217] As might be expected, the reactivity of the Mg atom varies from one excited state to another. Although this leads to changes of rate or energy distribution in the gaseous products, for example, MgH (v,N), only in the case of the Mg/O_2 system under matrix conditions do we find any suggestion of a change in the *product* of the reaction (see section III).[184,185,258]

C. Zn Atoms

Whatever the differences in reactivity between the bulk metals, Zn and Mg are much alike in the atomic state. The ^1S ground state is distinctly passive, with the diazomethane complex $CH_2N_2{\cdot}Zn$ [209] offering a rare example of the sort of weak interaction that Zn (^1S) may experience. Again, electronic excitation of the atom, usually to the ^1P or ^3P state, is a precondition to significant interaction, and insertion has been shown then to take place with H_2,[178] CH_4,[182] and O_2[203] in solid matrices at low temperatures (see Figure 9). Somewhat unexpectedly, the reaction with O_2 yields only the linear dioxide OZnO, with no sign of a cyclic product (η^2-O_2)Zn (cf. the behavior of the group 2 metals). Excited Zn atoms do not normally differ from excited Mg atoms in the chemical *outcome* of gaseous reactions, but detailed analysis of the products implies that Mg ($^1P_1$) and Zn ($^1P_1$) do differ significantly in the microscopic mechanisms of their attack of C−H bonds (q.v.).[179] The apparent ability of the Zn atoms truly to insert into the C−H bonds under these conditions may depend, it has been suggested, on the smaller size of the Zn (4s) compared with the Mg (3s) "core". According to ab initio analysis,[187] the Zn (^3P) + SiH_4 reaction is quite different from the Zn (^3P) + CH_4 reaction, proceeding through a completely attractive surface that leads to a very shallow potential well (>80 kJ mol^{-1} below the initial reactants), where a stable $^3A'$ $HZnSiH_3$ exciplex is found. The activation barrier toward the ZnH + SiH_3 exit channel is estimated to be only ~8 kJ mol^{-1}, so that, in keeping with experimental results,[262] these products are readily formed. Simple alkenes open another major exit channel for the quenching of Zn (^3P);[263] there is considerable evidence of triplet−triplet energy transfer—more especially from Cd (^3P) and Hg (^3P)—to the organic substrate, leading to efficient isomerization, for example, of ethene-d_2 and *cis*-butene.

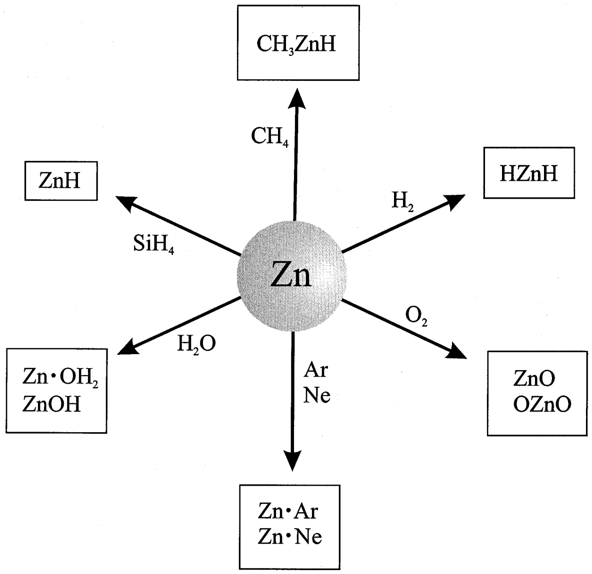


Figure 9. Overview of some of the reactions of Zn atoms that have been studied.

D. Ga Atoms

With the group 13 metal atoms come unfulfilled expectations of reactivity, as noted previously in section III. Matrix experiments give ample evidence that Al and Ga atoms in their $^2P_{1/2}$ ground state form 1:1 adducts with a variety of molecules, viz., N_2,[264] O_2,[201,265] CO,[100,155] C_2H_2,[161,162] C_2H_4,[162−164] H_2O,[266] NH_3,[148] and PH_3.[153] According to DFT calculations, the binding energies of some of these range from 8.4 kJ mol^{-1} for $Ga{\cdot}N_2$ to 61 kJ mol^{-1} for Ga·CO.[149] With a total binding energy of ~125 kJ mol^{-1} for Ga(CO)$_2$,[155] it is thus evident that CO binds quite

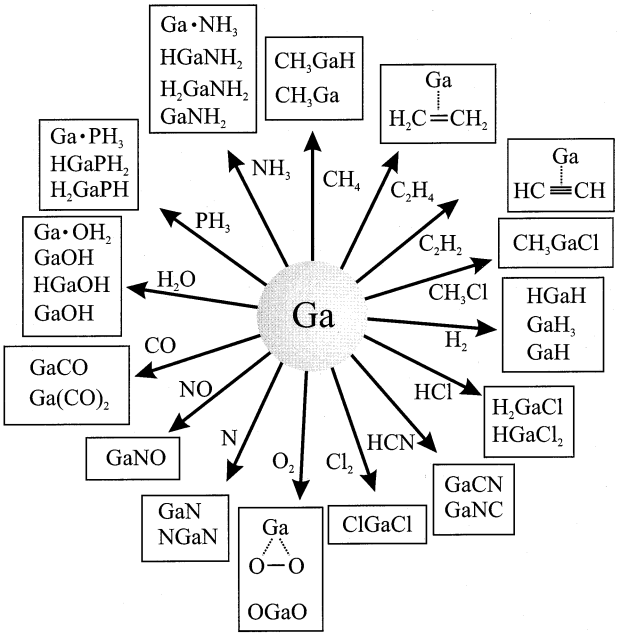


Figure 10. Overview of some of the reactions of Ga atoms that have been studied.

strongly to the metal, as attested experimentally by a mean ν(CO) wavenumber which is appreciably *lower* for $Ga(CO)_2$ ($\sim$1970 cm^{-1}) than for $Ni(CO)_4$ ($\sim$2076 cm^{-1}). To proceed further with the activation of the interacting molecule, however, requires $^2S \leftarrow {}^2P$ or $^2D \leftarrow {}^2P$ excitation of the metal atom. As indicated in Figure 10, insertion then takes place with the following reagents to deliver the products given in parentheses: H_2 (HGaH),[135,267] CH_4 (CH_3GaH),[152,267,268] H_2O (HGaOH),[266] NH_3 ($HGaNH_2$),[148] and PH_3 ($HGaPH_2$).[153] Each of these gallium(II) derivatives is itself photolabile and decomposes under UV irradiation, usually with the formation of a gallium(I) compound, for example, GaH,[135] CH_3Ga,[152] or $GaNH_2$[148] (see eq 31).

The reaction of Ga atoms with NH_3 trapped in an argon matrix proceeds spontaneously with the formation of an adduct $Ga{\cdot}NH_3$ identifiable (i) by its IR spectrum, which shows a distinctive blue shift of the symmetric NH_3 deformation mode with respect to uncoordinated NH_3, and (ii) by a strong absorption near 440 nm in the UV–vis spectrum.[148] Photolysis into this absorption band brings about the decay of the signals due to the adduct and the simultaneous appearance of a new set of IR signals belonging to the radical $HGaNH_2$. However, this species is itself photolabile; photolysis with broad-band UV–vis light ($200 < \lambda < 800$ nm) leads to decomposition to the univalent gallium amide $GaNH_2$. Additionally, the evolution of another product, H_2GaNH_2, is observed, presumably through the reaction of H atoms with unchanged $HGaNH_2$ molecules. The likely reaction scheme is set out in Figure 11, and the corresponding IR spectra are reproduced in Figure 12.

The matrix reactions of laser-ablated Ga atoms with O_2 are quite complicated, the products apparently including cyclic (η^2-O_2)Ga and the linear insertion product OGaO (see section III), as well as the cyclic anion $[(\eta^2\text{-}O_2)Ga]^-$.[201,202]

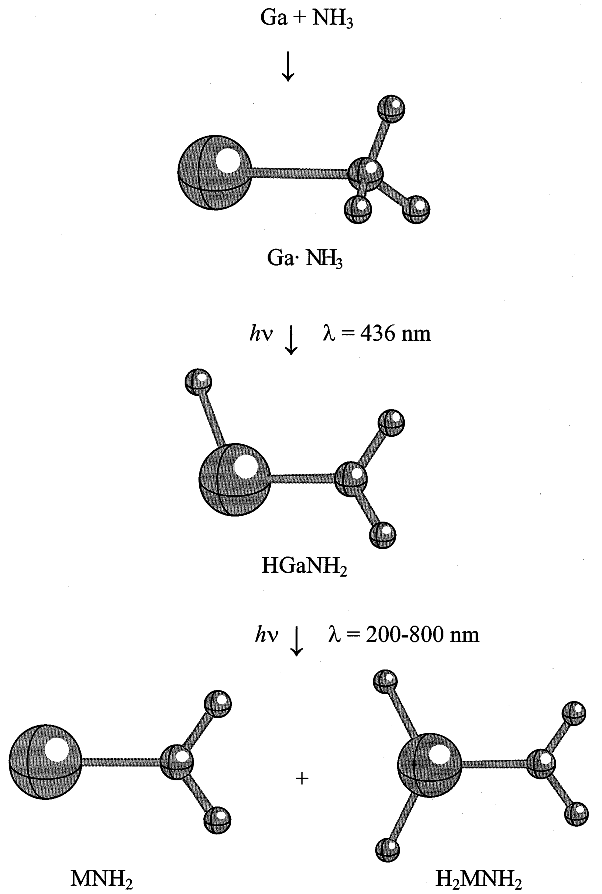


Figure 11. Scheme summarizing the thermally and photolytically activated reactions of Ga atoms with NH_3 in a solid Ar matrix.

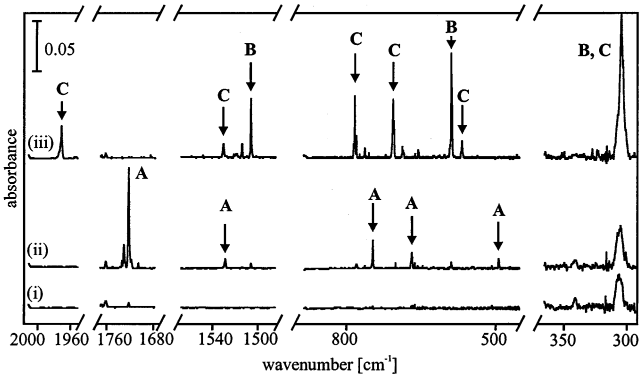


Figure 12. IR spectra showing the reactions initiated by photolysis of Ga atoms isolated in a solid NH_3-doped Ar matrix: (i) spectrum recorded immediately after deposition; (ii) spectrum recorded following a period of photolysis at λ = 436 nm; (iii) spectrum recorded following broad-band UV–vis photolysis ($200 < \lambda < 800$ nm). Products are as follows: **A**, $HGaNH_2$; **B**, $GaNH_2$; and **C**, H_2GaNH_2. (Reprinted with permission from ref 148a. Copyright 2000 American Chemical Society.)

E. Si Atoms

Although the evidence is somewhat fragmented, Si atoms in their ^3P ground state appear to be distinctly more reactive than their group 13 counterparts. As illustrated in Figure 13, addition to H_2O occurs to give a weakly bound charge-transfer complex Si···

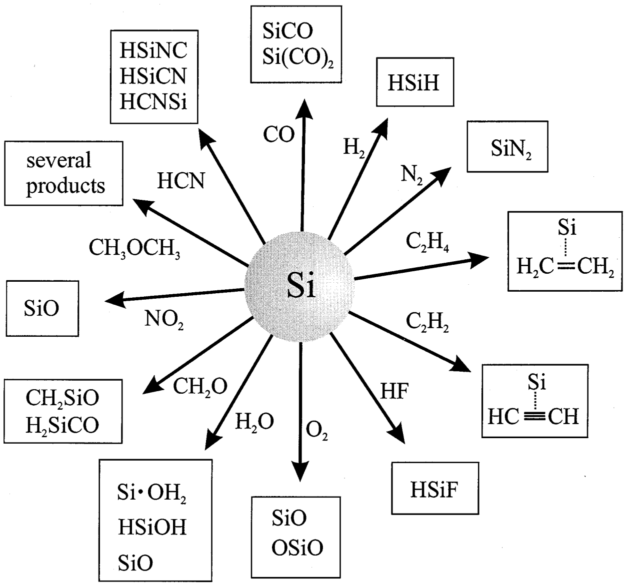


Figure 13. Overview of some of the reactions of Si atoms that have been studied.

OH_2 recognizable in an Ar matrix by an 18.3 cm^{-1} red shift in the ν_2 fundamental of the H_2O molecule.[269] Much more strongly bound addition products are formed with CO and N_2 in the linear $^3\Sigma$ molecules SiCO and SiNN, and SiCO readily takes up a second CO molecule (for example, on annealing of an Ar matrix) to give linear $Si(CO)_2$, an analogue of "carbon suboxide".[157] However, the most striking feature of the H_2O complex is that it is reported to rearrange spontaneously with insertion to produce HSiOH; the finding that photolysis is needed to bring about the corresponding change for $Si\cdots OD_2$ has led to the invocation of a hydrogen tunneling mechanism.[269] Further matrix experiments indicate that ground-state Si atoms also react spontaneously with H_2[270] and HF[271] to give the insertion products HSiH and HSiF, respectively. The signs are that HSiH is initially formed in its excited $^3B_1$ state, which then has access to a reaction channel involving a second molecule of H_2 and leading to SiH_4. Physical quenching competes with this channel to deliver HSiH in its $^1A_1$ ground state, and this in turn has the ability to insert into an Si−H bond of SiH_4 (yielding Si_2H_6) without encountering a significant activation barrier. It is probable that Si (^3P) also inserts into the O_2 bond, but the involvement of laser-ablated Si atoms in the matrix experiment identifying the formation of the linear SiO_2 molecule raises doubts about the electronic state or states of the reacting atoms.[190] On the other hand, photoexcitation is certainly needed to bring about insertion of an Si atom into a C−H bond and other changes following the initial formation of cyclic silylene addition products with HCN,[206] C_2H_2,[207] C_2H_4,[207] and H_2CO [208] (see section III, eqs 24−27).

F. S Atoms

The elemental vapors of the heavier members of groups 15 and 16 are composed of oligomers with but a small fraction of atoms, even at high temperatures. Group 15 atoms are particularly problematic: there are no clean sources, and the high energy conditions needed to generate them in useful concentrations are not conducive to control of any reactions that ensue. The problems are not much less acute with the heavier group 16 atoms. Only very recently, for example, has UV photolysis of H_2Te enabled Te atoms to be produced under (matrix) conditions lending themselves to chemical exploration; the strongly bound monotellurium analogue of CO_2, OCTe, has already been shown to result from facile addition to CO.[272]

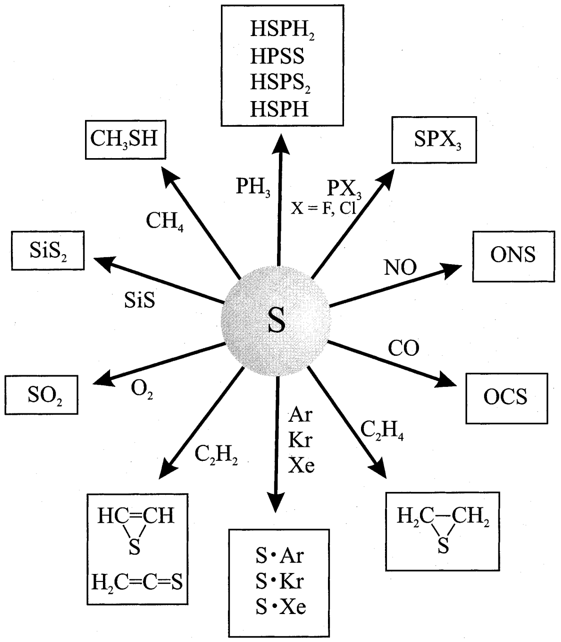


Figure 14. Overview of some of the reactions of S atoms that have been studied.

Decomposition of a suitable precursor either by photolysis (of OCS, for example)[1] or by the action of a discharge (on S_n or H_2S, for example)[42] can also be engineered to create sulfur atoms, usually populating one or more excited electronic states, as well as the ^3P ground state. For example, vacuum-UV irradiation ($\lambda = 147$ nm) causes matrix-isolated OCS to dissociate into CO + S (^1S), as evidenced by luminescence near 780 and 465 nm associated with decay of the S atoms to the ^1D and ^3P states, respectively.[86] Photolysis at wavelengths >200 nm gives CO + S (^3P, ^1D), and annealing of the matrix then results in thermoluminescence in the visible region attributable to the formation of excited S_2 molecules.[59] The existence of different atomic states and competition from recombination of the atoms tend to complicate the detailed interpretation of experiments with S atoms, representative reactions of which are displayed in Figure 14. Thus, there is sometimes doubt about the electronic state of the reacting atom. The ground-state atom certainly inserts spontaneously into O_2, as witnessed by the luminescence that develops near 440 nm arising from SO_2 in the excited $^3B_1$ state.[273] By contrast, S atoms in the excited ^1D state but not in the ground state insert characteristically into the C−H bonds of alkanes.[60] With the following molecular substrates addition occurs to give the strongly bound addition products identified in parentheses: CO (OCS),[274] SiS (SiS_2),[275] NO (SNO),[276] PX_3 (SPX_3; X = F or Cl),[274] C_2H_4 ($\overline{CH_2CH_2S}$),[274] and C_2H_2 ($\overline{CH{=}CHS}$, and $H_2C{=}C{=}S$).[274] At the other extreme, very weak interaction characterizes the complexes Ng·S formed by excited S (^1S) with the noble gas atoms Ng = Ar, Kr, or Xe and detectable by their characteristic emission spectra.[277]

G. Br Atoms

Br atoms lack the thermodynamic drive and matrix mobility of F atoms but are still significant electrophiles. Unlike F atoms, moreover, they have some potential, at least formally, to insert into the bond of a strongly oxidizing molecule such as O_2 or F_2. However, the modest strengths of bonds to bromine make reactions such as that in eq 38 endothermic

$$Br + R{-}H \rightarrow R{-}Br + H \tag{38}$$

by ca. 70 kJ mol^{-1} for R = H and 136 kJ mol^{-1} for R = CH_3.[278] Hence excitation of one or the other of the interacting partners is often necessary to induce a chemical change. Whereas the reaction with H_2 is slow under normal conditions, it becomes fast when the Br atoms are spin−orbit excited ($^2P_{1/2}$) and the H_2 is vibrationally excited ($v = 1$).[279] In other cases, as indicated in Figure 15, addition is commonly observed or implied. Matrix studies bear witness to the formation of loosely bound complexes of Br atoms with C_6H_6,[280] H_2O,[281] and HCl.[281] The Br acts as an acid with respect to each of the first two of these molecules interacting, for example, with the O atom of H_2O, but as a base with respect to HCl, to which it is weakly hydrogen-bonded. According to the results of gas-phase and matrix experiments, dihalogen molecules such as Br_2[282] and ICl[283] give more strongly bound triatomic complexes. Reaction with the radicals NO and NO_2 is fast and normally leads in BrNO [284] and $BrNO_2$ [213] to products with relatively strong N−Br bonds. IR monitoring of the reaction of Br with NO_2 in the gas phase at temperatures between 215 and 300 K shows that the major product is in fact the cis isomer of BrONO (see Figure 16).[285] At room temperature this reverts rapidly to $Br^{\bullet} + NO_2$, but at low temperatures isomerization to $BrNO_2$ sets in. Rapid reactions appear also to take place between Br atoms and both BrONO and $BrNO_2$ with the formation of $Br_2 + NO_2$.

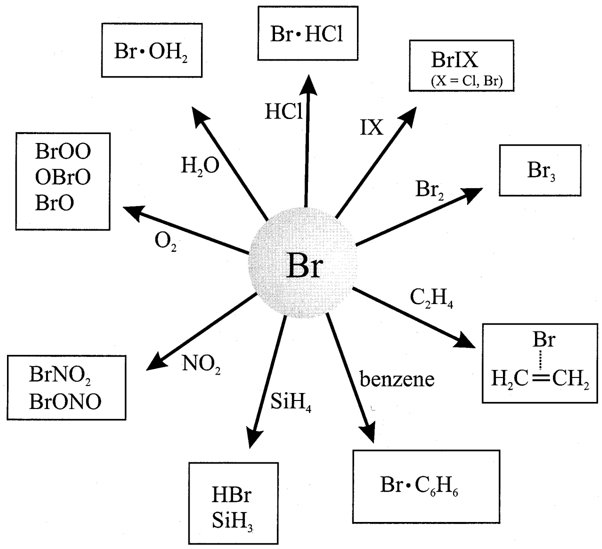


Figure 15. Overview of some of the reactions of Br atoms that have been studied.

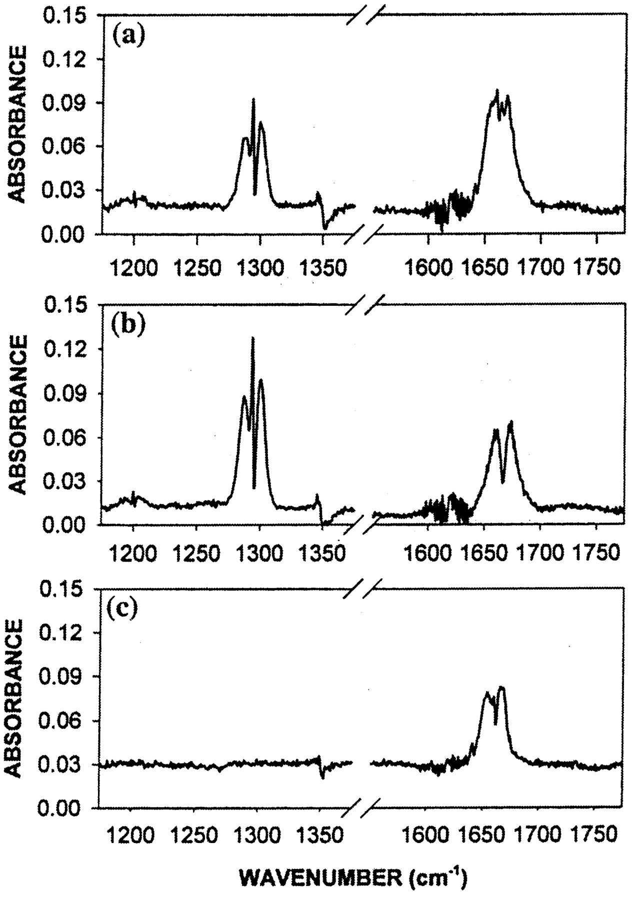


Figure 16. IR spectra showing the reaction of Br atoms with NO_2 in the gas phase: (a) spectrum recorded following the photolysis of a mixture of Br_2, NO_2, and N_2 at 228 K; (b) spectrum recorded following the dark decay of the gas mixture; (c) difference spectrum obtained by subtraction of the $BrNO_2$ features from spectrum a and attributable to *cis*-BrONO. (Reprinted with permission from ref 274. Copyright 2000 American Chemical Society.)

However, it is the reactions with O_3 and O_2 that have attracted most notice on account of their stratospheric significance.[33,286] Minimal activation is needed to bring about the exothermic reaction of ground-state Br atoms with ozone in accordance with eq 39

$$Br + O_3 \rightarrow BrO + O_2 \tag{39}$$

(cf. eq 33).[284] Under stratospheric conditions, the resulting BrO radicals are able to interact with other oxygen-bearing radicals, for example, O, BrO, NO_2, or HO_2, in catalytic cycles compassing the conversion of O_3 to O_2. The atmosphere may carry a comparatively small load of bromine (compared, say, with chlorine), but concern arises from the very high efficiency with which bromine is reputed to destroy ozone, so that relatively small additional releases have a disproportionate effect on ozone levels. Ac-

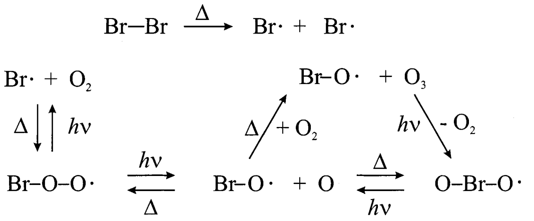


Figure 17. Scheme showing the reactions initiated by the interaction of Br atoms with dioxygen, the two isomers BrOO and OBrO being among the products (see ref 56).

cording to one estimate, bromine is 58 times more effective than chlorine at catalyzing the destruction of ozone.[33] On the other hand, Br atoms also combine with O_2 to form the BrOO radical,[56] an intermediate in the decomposition of O_3. By monitoring the effects of UV irradiation and annealing of a solid Ar matrix containing this product, the changes summarized in Figure 17 have been shown to take place, with dissociation of BrOO into BrO + O emerging as the primary photochemical step. In this respect BrOO differs from ClOO, and the observed buildup of O_3 on photolysis of BrOO must cast doubt on whether bromine is quite the scourge of ozone that has been portrayed in some quarters.

H. Xe Atoms

Noble gas atoms in their electronic ground state are unique in their failure to respond to other atoms or molecules with anything stronger than van der Waals interactions. Even with strongly acidic HX molecules, xenon forms very loosely bound 1:1 complexes measuring 3.78 or 4.25 Å between Xe and the center of mass of the HF or HCl molecule, respectively.[287] The $Xe\cdots HX$ stretching wavenumber and dissociation energy, D_0, are 43 and 181 cm^{-1} for X = F and 33 and ~206 cm^{-1} for X = Cl. The wavenumber of the $(10^00) \leftarrow (00^00)$ vibrational transition, corresponding to the H–X stretching fundamental, is thus 14–22 times that of the corresponding dissociation wavenumber. With other atoms, too, xenon forms diatomic systems XeX (X = F, Cl, Br, O, or S)[1,136,288] with, at best, the shallowest of potential wells. However, electronic excitation of these remarkable species gives access to one or more potential surfaces with appreciably deeper potential wells, reflecting a significant degree of charge transfer in the sense Xe^+X^-; some of the resulting exciplexes are noteworthy for the laser action they admit. The molecules have been detected by their electronic spectra in absorption or, more often, emission,[277,289] and by MCD[290] and EPR[291] measurements. XeCl is a good example. The $^2\Sigma^+$ ground state has a dissociation energy of only 242 cm^{-1}, whereas $\omega_e = 26.3$ cm^{-1} and r_e is estimated to be 3.18 Å: yet the B ($^2\Sigma^+$) excited state has $\omega_e = 195.2$ cm^{-1} and r_e is estimated to be 2.94 Å.[288] Recent studies have shown that *doubly* excited valence states of the van der Waals complexes M·Ng, where M is a group 2 metal atom and Ng a noble gas, can also be unusually strongly bound. For example, six vibrational bands associated with gaseous Ca·Xe can be attributed on the evidence of their partially resolved rotational structure to a Ca·Xe $[^3\Sigma^-] \leftarrow Ca(4s4p\pi\ ^3P_0)\cdot Xe[^3\Pi_0^-]$ transition (see Figure 18).[292] Hence, it appears that the $^3\Sigma^-$ upper state is characterized by a dissociation energy of ~1200 cm^{-1}, roughly 4 times that of the $^3\Pi_0^-$ lower state.

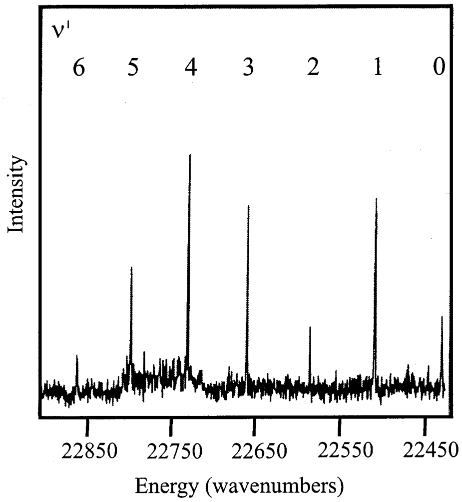


Figure 18. Spectrum showing the vibrational progression assigned to the Ca·Xe $[^3\Sigma^-] \leftarrow Ca\ (4s4p\pi^3P_0)\cdot Xe\ [^3\Pi_0^-]$ transition. The signal was collected in the $^{40}Ca^{129}Xe$ mass channel (see ref 292).

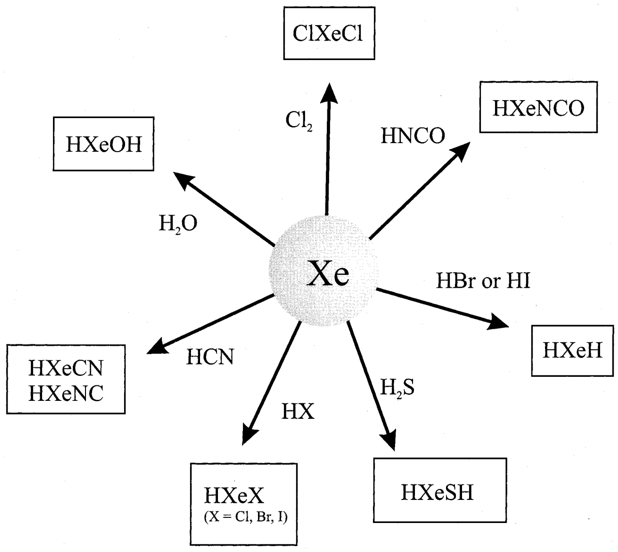


Figure 19. Overview of some of the reactions of Xe atoms that have been studied.

For the Xe atom to bind at all strongly to another atom calls for an unusually electrophilic reagent, for example, Xe^+ [293] or PtF_6.[294] In fact, molecules containing noble gas atoms were featured in some of the earliest matrix experiments to be carried out, when it was shown that UV photolysis of F_2 trapped in a solid Kr or Xe matrix led to the appearance of new IR absorptions attributable to the linear difluoride molecule KrF_2 or XeF_2.[295] The same principle has been exploited subsequently to prepare and characterize other divalent xenon compounds of the type X–Xe–Y (see Figure 19), a xenon matrix doped with the reagent X–Y being typically irradiated so as to rupture the X–Y bond and then annealed (X = Y = Cl;[296] X = H, Y = H, F, Cl, Br, I, OH, SH, CN, or NCO[235–242]). The HXeY products are all highly

Table 4. Representative Studies of the Interactions of Main Group Atoms

element	reagent	method of investigation	findings	ref
H	H	Ne, Ar, and Kr matrices EPR, ^{2}H	H···H spin-pair radicals investigated	303
H, D	H_2, D_2, HD	solid H_2 (or HD or D_2) and Ar matrix EPR	H···HD and H···D_2 pairs observed, the latter being formed by a tunneling reaction; rate constants of the tunneling reaction HD + D to give H and D_2 determined	304
H	CH_3	CH_4 matrix, γ-irradiation EPR	evidence of H···$CH_3^\bullet$ complex	305
H	alkanes, alkenes, alkynes, O_2, or CO	Ar or Xe matrix EPR	formation of radicals observed; relative rate constants established; H produced by photolysis of HI; thermal reaction leads to H atom abstraction from C_3H_8 and i-C_4H_{10} at 35−50 K and H addition to C_2H_4	1, 306
H	C_2H_6	Xe matrix EPR, ^{2}H	H abstraction reaction from C_2H_6 investigated and ratio of rate constants for ^{1}H and ^{2}H abstraction determined	307
H	CF_2	Ar and N_2 matrices IR	CF_2 generated from CF_2N_2, H from HI or H_2S; HCF_2 formed	308
H	NH_2	Ar and Kr matrices EPR, ^{2}H, ^{15}N	$H^\bullet NH_2$ radical pair investigated; spacing of 3.1 Å in Ar and 3.8 Å in Kr	309
H	O_2	Ar matrix IR; ^{1,2}H, ^{16,18}O	bent $HOO^\bullet$ radical formed	1
H	CO	CO, Ar, and other matrices IR, EPR; ^{1,2}H	$HCO^\bullet$ radical formed	1
H	NO	Ar or N_2 matrix IR; ^{1,2}H, ^{14,15}N	HNO formed	1
H	Br	Xe matrix IR	H and Br generated by HBr photolysis; recombination process to HBr and H_2 followed at 40 K; matrix morphology affects the diffusion coefficient of H atoms	310
			Group 1	
Li	C_2H_2, C_3H_4	Ar matrix IR; ^{6,7}Li, ^{12,13}C	Li(η^2-C_2H_2)Li formed; ∠CCH 140 ± 10°; π-bonded $C_2H_2\cdot Li$ and $C_3H_4\cdot Li$ complexes also identified	159
Li	C_2H_2, C_2H_4, benzene	Ar matrix EPR	π-complexes formed with either hydrocarbon → Li or hydrocarbon ← Li charge transfer; $C_6H_6\cdot Li$ complex has C_{2v} symmetry	160
Li, Na, K	C_2H_2	theoretical studies	metal atoms donate 0.6−0.8 electron from an excited p orbital to an antibonding C≡C π^* orbital; σ-bonded structure [M(H)C═CH] is not a bound state; π-bonded state is weakly bound; the Li−vinylidene structure is also an equilibrium state slightly less stable than the π-bonded state; high barrier to isomerization	311
Li, Na, K	C_2H_2	Ar matrix EPR	π-complexes of C_2H_2 formed with alkali metal atoms in the excited ^{2}P state; subsequent exposure to light corresponding to the $\pi \rightarrow \pi^*$ transition in the C_2H_2 moiety results in isomerization to the vinylidene form M:C═CH_2	95
alkali metal	C_2H_2, C_2H_4	gas phase	quenching of ^{2}P states of alkali-metal atoms by simple alkenes and alkynes results in E-V,R transfer	15
Li	C_2H_4	Ar matrix IR; ^{6,7}Li, C_2D_4, $C_2H_2D_2$, $^{13}C_2H_4$	with Na or Cs only weak perturbation of C_2H_4 occurs; with Li there is a large perturbation to form a complex (η^2-C_2H_4)Li with C_{2v} symmetry, in which f(C−C) is lowered by 30%; spectra also give evidence of products containing more than one C_2H_4 molecule and/or Li atom; binding energy of $Li\cdot C_2H_4$ only 2−3 kcal mol^{-1} (cf. $Ni\cdot C_2H_4$ ∼35 kcal mol^{-1})	252
Li, Na	C_6H_6	Ar matrix IR	no product formed with Na, but Li forms a complex (η^6-C_6H_6)Li with C_{2v} symmetry and involving significant electronic interaction between C_6H_6 and Li	312
Li	RCN (R = H, CH_3)	Ar matrix EPR	spontaneous formation of two complexes: (i) linear species Li·NCR, and (ii) (η^2-NCR)Li, the reaction being driven by the attainment of a three-electron bonding system	251
Li	CO	Ar, Kr, Xe, or N_2 matrix IR	two geometric isomers, LiCO and LiOC, are formed; each reacts with a second molecule of CO to give geometric isomers of LiC_2O_2 for which structures are suggested	226
Li	CO	theoretical studies	linear LiCO has a $^2\Pi$ ground state but is predicted to be unstable in the gas phase by 18.7 kcal mol^{-1}; it may be stable in a solid matrix	313
Li	SiO	Ar matrix IR; ^{6,7}Li, ^{28,29,30}Si	codeposition of Li atoms with SiO in an Ar matrix gives angular LiOSi	314

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Li	N_2	N_2 or Ar matrix IR	products can be formulated as $Li^+N_2^-$ with a ν(N−N) mode at 1800 cm^{-1} (cf. 2331 cm^{-1} in N_2)	250
Li	NH_3	gas phase millimeter/submillimeter-wave spectroscopy; ^2H	thermal reaction in the gas phase gives $LiNH_2$ with a lifetime <1 s; structure of the molecule (r_0) determined and shown to be planar	255
Li, Na, K, Cs	NH_3	Ar matrix IR	loosely bound $M{\cdot}NH_3$ complexes formed with minimal $M \leftarrow NH_3$ charge transfer (cf. $M \leftarrow C_2H_2$); M is a Lewis acid for Li or Na; acid → base change for M = K or Cs	225
Li	NH_3, H_2O	Ar matrix EPR	evidence for the formation of the complexes $Li{\cdot}NH_3$, $Li{\cdot}OH_2$, and $Li(OH_2)_2$, which are photolabile	93
Li, Na	NH_3	theoretical studies	binding energies of $Li{\cdot}NH_3$ and $Na{\cdot}NH_3$ 14.5−20 and 6.0 kcal mol^{-1}, respectively; bonding in $Li{\cdot}NH_3$ is primarily through overlap of the NH_3 lone pair orbital with the lithium p_z orbital	315
Li	$NO + O_2$	Ar matrix IR; $^{14,15}N$, $^{16,18}O$	products include the ion-pair Li^+OONO^-, where the biochemically important peroxynitrite anion may assume cis or trans forms	316a
Li	N_2O	gas phase R2PI	Li_2O is formed and characterized; ionization energy amounts to 6.3117 eV; a bond length of 1.606 Å is derived from analysis of the rotational structure of the $^1\Sigma^+ \rightarrow$ bent $^1B_1$ transition	316b
Li	H_2O	Kr matrix IR; $^{6,7}Li$, $^{1,2}H$	two kinds of 1:1 complex formed; charge transfer occurs in the direction $Li \leftarrow OH_2$ in one of these; photolysis gives LiOH	317
Li, Na, K, Rb, Cs	O_2	Ar matrix IR, Raman; $^{16,18}O$	primary product can be formulated as $M^+O_2^-$ with $\nu(O{-}O) = 1096.3{-}1114$ cm^{-1} (see Table 2); in addition, O_2MO_2 species with D_{2d} symmetry are observed	165
Li	HF, HCl	Ar matrix EPR	spontaneous formation of Li·HF and Li·HCl complexes with heats of complexation of 20 and 18 kcal mol^{-1}, respectively; unpaired electron is in the antibonding σ orbital of an elongated H-Cl moiety in Li·HCl, and the H-Cl is coordinated side-on to the Li atom bearing a substantial positive charge (+0.47 e); Li·HF has a linear Li−F−H structure with the unpaired electron in an s-p hybridized orbital of the Li atom directed away from the F atom; the complex is formed by the dative interaction of the F electrons with vacant Li orbitals giving a substantial negative charge (−0.18 e) on the Li	94
alkali metal	F_2	Ar matrix IR, Raman	products are $M^+F_2^-$, MF, and $[MF]_2$ (linear and/or cyclic)	167
alkali metal, Ba	Cl_2	Ar matrix Raman	spontaneous interaction occurs to form ion-pairs of the type $M^+Cl_2^-$ (M = Li, Na, K, Rb, Cs, or Ba)	168
alkali metal	ClF	Ar matrix IR, Raman, UV−vis	M^+ClF^-, MCl, MF, $M^+Cl_2F^-$, and $M^+ClF_2^-$ are the products; the following reaction pathways were established: $M + X_2 \rightarrow M^+X_2^- \rightarrow MX + X$; $MX + ClF \rightarrow M^+XClF^-$ (X = F or Cl)	318
alkali metal	Br_2	Ar matrix Raman, UV−vis	products are $M^+Br_2^-$, MBr, and $M^+Br_3^-$	169
alkali metal	I_2	Ar matrix resonance Raman	$M^+I_2^-$ is formed and characterized	112
Na	C_2H_2	Ar matrix EPR	photolysis at $\lambda > 500$ nm gives $Na^+[HCCH]^-$; increasing the C_2H_2 concentration results in an increasing yield of vinyl radicals instead	319
Na, K, Cs	$HC{\equiv}CH$, $CH_3C{\equiv}CH$, $CH_3C{\equiv}CCH_3$	Ar matrix IR; $^{1,2}H$	Cs forms a very weakly π-bonded complex, $(\eta^2\text{-}C_2H_2)Cs$, and $Cs^+C_2H_2^-$; alkali metal induces intermolecular H atom transfer resulting in the formation of the corresponding alkene	320
Na, K	CO	Ar matrix IR; $^{12,13}CO$, $^{13}C^{18}O$	upon deposition no products of the type M···CO are formed (cf. Li + CO); photolysis at 589 nm is necessary to give NaC_2O_2 and other products with more than one M atom; calculations show very little perturbation of CO in the Na·CO pair, whereas NaC_2O_2 has the structure O(Na)C═C═O; other products are CO_2 and $M^+CO_2^-$ (formed upon photolysis at 300−400 nm)	226b
Na, K	SiO	Ar matrix IR; $^{16,18}O$, $^{28,29}Si$	co-condensation of M atoms (M = Na or K) with SiO in an Ar matrix yields highly ionic MOSi	321
Na, K, Rb, Cs	N_2O	N_2 matrix IR; $N_2{}^{18}O$, $^{15}N_2O$	no product observed with Na, but the heavier metal atoms form angular MOM molecules (M = K, Rb, or Cs)	322

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Na, K	HCl	Ar matrix EPR	K atoms react spontaneously with HCl; electron jump process followed by stabilization of the otherwise unstable HCl^- anion by the K^+ cation; unpaired electron in the antibonding σ-orbital of the HCl moiety; the corresponding Na compound is formed only after prolonged irradiation by Xe-arc light	323
			Group 2	
Be	H_2	Ar matrix laser ablation IR; $^{1,2}H$	linear BeH_2 formed on deposition with ν_3 2159.1 cm^{-1} and ν_2 697.9 cm^{-1}; enthalpy change for $Be + H_2 \rightarrow HBeH$ estimated to be $\Delta H = -40$ kcal mol^{-1}	176
Be, Mg, Ca	CH_4	Ar matrix laser ablation IR; $^{1,2}H$, $^{12,13}C$	primary product is linear CH_3MH (M = Be, Mg, or Ca); other products with Be include BeH, CH_2BeH, HCBeH, CH_3Be, and CH_3BeCH_3	222
Be, Mg	C_2H_2	Ar matrix laser ablation IR; $^{1,2}H$, $^{12,13}C$	Be products are HBeCCH ($C_{\infty v}$ symmetry), HCCCCH, BeH_2, BeCCH, BeH, and CCH; no insertion product observed for Mg, only the decomposition products MgH, CCH, and MgCCH	217
Be, Mg	C_2H_2	theoretical studies	Be forms a σ-complex with HCCH, the metal coordinating to one C atom and the HCCH moiety adopting a trans conformation; the insertion product HMCCH (M = Be or Mg) has a linear singlet ground state for which vibrational wavenumbers have been calculated; geometries and vibrational wavenumbers of other possible structures studied	324
Be	HCN	Ar matrix laser ablation IR; $^{1,2}H$, $^{12,13}C$	products are HBeNC, HBeCN, BeNC, and BeCN	205
Be	CO_2	Ar matrix IR; $^{12,13}C$, $^{16,18}O$	products are CO, Ar•BeO, BeOBe, and two new molecules, OCBeO and COBeO	325
Be, Mg	NO	Ar matrix laser ablation IR; $^{14,15}N$, $^{16,18}O$	BeNO, BeOBeNO, and MgNO identified and characterized	326
Be	H_2O	Ar matrix laser ablation IR; $^{1,2}H$, $^{16,18}O$	products are HBeOH (C_s symmetry), BeO, HOBeOH, and BeOH	327
Be, Mg, Ca	H_2O	theoretical studies	binding energies (in kcal mol^{-1}) for the complexes $M{\cdot}OH_2$ are 0.62 (M = Be), 2.33 (M = Mg), and 7.18 (M = Ca); the Mg complex has C_{2v} symmetry and the Be complex C_s symmetry	328
Be	O_2	Ar, Kr, or Xe matrix laser ablation IR; $^{16,18}O$	noble gas complexes of BeO and Ng−BeO (Ng = Ar, Kr, or Xe) formed; the reaction $Be + O_2 \rightarrow OBeO$ is exothermic by 64 kcal mol^{-1}; OBeO is a linear molecule; other products are BeO, Be_2O, Be_2O_2, $OBeO_2$, and BeO_3; OBeO reacts with Be to form BeOBeO or rhombic $Be(\mu\text{-}O)_2Be$	329
Be, Mg, Ca	O_2	N_2 matrix laser ablation IR; $^{16,18}O$	MO_2 (cyclic or linear OMO), O_2MO_2, and MO products are formed; cyclic MO_2 is preferred in N_2 matrices as a result of rapid quenching of the ^3P excited state to the $^1A_1$ ground state	184
Be, Mg, Ca, Sr	O_2	theoretical studies	optimal structure of the molecule MO_2 changes from linear $^3\Sigma_g^-$ for M = Be or Mg to cyclic $^1A_1$ for M = Ca or Sr	185
alkaline earth metal	O_3	Ar or N_2 matrix IR, UV−vis, resonance Raman; $^{16,18}O$	spectra give evidence for $M^+O_3^-$, MO, and MO_2 species; additional weak signals assigned to $[MO]_2$	111, 330
Mg	H_2	Ar matrix laser ablation IR; $^{1,2}H$, $^{24,26}Mg$	MgH_2 formed; on annealing formation of aggregates such as $HMg(\mu\text{-}H)_2MgH$ observed	186
Mg, Zn, Cd, Hg	H_2	gas phase LIF	for Mg, Zn, Cd, and Hg (all ^3P), the exit channel is entirely chemical in nature; for Hg two reactions are possible: Hg (^3P) + $H_2 \rightarrow HgH + H$ and Hg (^3P) + $H_2 \rightarrow Hg + H + H$; for Cd and Zn, only MH formation occurs	331
Mg, Zn, Cd, Hg	H_2, SiH_4, alkanes	gas phase various studies	a comprehensive overview of the interactions of valence M(nsnp ^3P) and M(nsnp $^1P_1$) excited states with H−H, Si−H, and C−H bonds, where M = Mg, Zn, Cd, or Hg	179
Mg	H_2	gas phase LIF	temperature dependence of the rate constant for quenching of Mg(3s3p ^3P_j) by H_2 and D_2 established; the data provide information about the barrier to reaction; there are two exit channels, one physical and one chemical	332
Mg	H_2	gas phase pump-probe experiment with laser-induced fluorescence	nascent rotational energy distributions in the MgH product derived from the reaction of Mg(4^1S_0) with H_2 suggest a harpoon-type reaction pathway	333
Mg	H_2	theoretical studies	the reaction Mg(3s3p ^3P) + $H_2 \rightarrow MgH + H$ can proceed with essentially no activation barrier above the endothermicity of the reaction via side-on attack of the H−H bond, whereas end-on attack gives rise to a barrier of ∼14 kcal mol^{-1}; MgH_2 is predicted to have a $^1\Sigma_g^+$ ground state with $D_{\infty h}$ symmetry; potential surfaces calculated for the reactions $Mg + H_2 \rightarrow MgH_2$ and $Mg + H_2 \rightarrow MgH + H$	334

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Mg	H_2, CH_4	Kr, Xe or CH_4 matrix UV−vis, IR; $^{1,2}H$	photolysis at the 3p $^1P \leftarrow$ 3s ^1S resonance transitions of Mg atoms results in insertion to give the linear molecule HMgH or CH_3MgH; there is no evidence of the fragmentation products, e.g., MgH, formed in the gas phase	222, 259
Mg	CH_4	CH_4 matrix IR, UV−vis, time-resolved luminescence	repulsive interaction between Mg and CH_4 matrix; CH_3MgH formed on photolysis, in addition to atomic triplet magnesium emission	259b, 335
Mg	RH (CH_4, C_2H_6, C_3H_6, c-C_3H_6, C_3H_8, i-C_4H_{10}, or n-C_4H_{10})	gas phase pump-probe technique	analysis of the quantum-state distribution of rotational energy of MgH molecules produced by abstraction reactions of electronically excited Mg(3s3p $^1P_1$) atoms: Mg ($^1P_1$) + RH → MgH (v, N) + R; in fact, this distribution has minimal dependence on the strength of the C−H bond or the size or structure of RH	336
Mg	CH_3X (X = H, F, Cl, Br, I)	Ar matrix laser ablation IR; $^{24,26}Mg$, $^{12,13}C$, $^{1,2}H$	the primary reaction product of excited Mg atoms is CH_3MgX, secondary products being MgX, MgX_2, MgH, MgH_2, CH_4, C_2H_6, CH_2X, CH_3MgCH_3, $MgCH_2$, CH_2MgX, and CH_2XMgX; the bonding in $MgCH_2$ is analyzed with the aid of quantum mechanical calculations	260, 337
Mg, Ca	CH_3X (X = F, Cl, Br, I)	Ar matrix UV−vis	UV−vis absorptions of Mg_x species have been traced; clusters of Mg claimed to react to give $CH_3(Mg)_xX$, whereas Mg atoms are inert; Ca species are more reactive than Mg ones	338
Mg, Ca, Sr, Zn	CH_3X (X = Cl, Br, I)	Ar matrix IR	Zn does not react, but Mg, Ca, and Sr (M) all react to give products of the type CH_3MX with C_{3v} symmetry	339
Mg	CO_2, C_2H_4	CO_2 and Ar matrices IR, UV−vis	weakly bound complexes of the type $Mg{\cdot}CO_2$, $Mg(C_2H_4)_n$ (n = 1 or 2), and $C_2H_4{\cdot}Mg{\cdot}CO_2$ have been characterized; in $Mg{\cdot}CO_2$ Mg is bound to both O atoms forming a 4-membered ring	256
Mg	CO_2	theoretical studies	the mechanism of the overall reaction leading to MgO and CO via cyclic $MgCO_2$ is studied	340
Mg, Ca, Sr, Ba	HCN	Ar matrix IR; $^{12,13}C$	linear MNC is the only product detected, with no sign of either MCN or insertion products; hence, it appears the M atom attacks the N atom and not the C−H bond	215
Mg	NH_3	gas phase TOF-MS, photoelectron spectroscopy	$Mg(NH_3)_n$ clusters formed by reaction of Mg with $(NH_3)_n$ clusters, Mg + $(NH_3)_n$ → $Mg(NH_3)_{n-1}$ + NH_3 ($n \leq 37$), were investigated to model the solvation of Mg in NH_3 and their ionization energies determined	114
Mg	NH_3, H_2O, neopentane, haloalkane	codeposition at 77 K and analysis of products formed on warming	a solvent-free Grignard reagent RMgX is reported as being produced on warming	341
Mg, Ca, Sr, Ba	H_2O	Ar or Kr matrix IR, UV−vis; $^{1,2}H$, $^{16,18}O$	insertion of group 2 metal atoms into H_2O is caused by photoexcitation of the metal atom in the $M{\cdot}OH_2$ adduct formed on co-condensation (M = Mg, Ca, Sr, or Ba); photolysis results in oxidative insertion to form HMOH molecules; prolonged UV photolysis causes cleavage of the M−H bond in HSrOH or HBaOH and formation of MOH	257
Mg	O_2, N_2O	Ar matrix laser ablation IR; $^{24,26}Mg$, $^{16,18}O$	the following products have been identified: linear OMgO and MgOMgO, cyclic MgO_2, MgO_3, and MgO; thermally evaporated Mg atoms do not react under similar conditions; N_2 enhances the reactivity of the metal atoms with respect to O_2	258
Mg	O	Ar matrix IR; $^{16,18}O$	evidence for the formation of Mg_3O_3 with a planar 6-membered ring	342
Mg	F_2	gas phase millimeter/submillimeter direct absorption studies; $^{24,25,26}Mg$	MgF radicals, produced by reaction of Mg vapor with F_2-seeded He gas, were characterized by their pure rotational spectrum	343
Mg	Cl_2	gas phase millimeter/submillimeter direct absorption studies; $^{24,25,26}Mg$, $^{35,37}Cl$	reaction of laser-ablated Mg vapor with Cl_2 or dc discharge of a mixture of Mg vapor, Ar, and CCl_4 produces the radical MgCl, which has been characterized by its rotational spectrum	344
Mg	Br_2	gas phase microwave spectrum; ^{24}Mg, $^{79,81}Br$	laser-ablated Mg vapor reacts with Br_2 (in an Ar carrier gas) to give MgBr, the rotational spectrum of which has been analyzed	345
Mg	Ar	theoretical studies	potential energy curves for the different van der Waals states of $Mg{\cdot}Ar$ have been established	346
Mg	Ar	gas phase R2PI	a strongly bound doubly excited valence state of $Mg{\cdot}Ar$ is found, exhibiting a very short bond length of 2.41 Å and a dissociation energy D_0 of 2850 ± 100 cm^{-1} (cf. 1240 cm^{-1} for $Mg{\cdot}Ar^+$ in its ground state)	347

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Mg	Kr	gas phase R2PI	a strongly bound doubly excited van der Waals state of Mg·Kr is found; the potential curves for several states of Mg·Kr have been established	348
Mg	He, Ne	theoretical studies	potential energy curves for the different van der Waals states of $Mg^{n+}{\cdot}He$ and $Mg^{n+}{\cdot}Ne$ ($n = 0-2$) have been estimated; as with analogous doubly excited states of Mg·Ar and Mg·Kr, the $Mg(3p\pi 3p\pi){\cdot}He[^3\Sigma^-]$ and $Mg(3p\pi 3p\pi){\cdot}Ne[^3\Sigma^-]$ states are found to be unusually strongly bound	349
Ca, Zn	H_2	Ar, Xe, or Kr matrix IR; $^{1,2}H$	CaH_2 and ZnH_2 are formed on photolysis; the results suggest a slightly bent CaH_2 and a linear ZnH_2 molecule with $f(Ca-H) = 89$ N m^{-1} and $f(Zn-H) = 217$ N m^{-1}	350
Ca, Sr, Ba	H_2	theoretical studies	geometries and energies of MH_2 and MH^+ species are discussed (M = group 2 or group 12 element); strong d orbital contributions are found for the heavier alkaline earth metals, with the exception of Ra, in which relativistic effects are more dominant	351
Ca	C_2H_2	gas phase LIF	linear CaCCH is identified and characterized as the reaction product; from an analysis of the rotational bands of the A $^2\Pi$ - X $^2\Sigma^+$ transition dimensions are established	352
Ca, Sr	C_2H_2, H_2O, NH_3, CH_3CN	gas phase laser vaporization supersonic jet LIF	reactions of the Ca atoms give CaCCH (from C_2H_2), $CaNH_2$ (from NH_3), CaOH (from H_2O), and CaNC (from CH_3CN); Sr atoms likewise react with C_2H_2 to give SrCCH which, like CaCCH, is linear	353
Ca	$CF_3CF{=}CFCF_3$, C_6F_6	analysis of products following co-deposition and warming	Ca atoms defluorinate $CF_3CF{=}CFCF_3$ to give $CF_3C{\equiv}CCF_3$	354
Ca, Sr, Ba	O_2	Ar matrix laser ablation IR; $^{16,18}O$	linear OMO and rhombic $[MO]_2$ are the main products; MO is also detected; cyclic MO_2 peroxides are minor products	166
Ca, Sr, Ba	O_2	Ar or N_2 matrix IR; $^{16,18}O$	products are MO_2, MO, and cyclic $[MO]_2$	355
Ca	O_2	Kr or Xe matrix IR, UV−vis; $^{16,18}O$	CaO and O_3 are formed when Ca and O_2, passed through a discharge, are isolated in a solid Kr or Xe matrix	356
Ca, Mg	O_2	gas phase LIF	analysis of the distribution of CaO vibrational quantum states in the reaction $Ca\,(^3P) + O_2 \rightarrow CaO\,(v) + O$ indicates that the $v = 0$ level is mostly populated; prediction of a $Ca^+O_2^-$ charge transfer intermediate; rate coefficients measured	357
Ca	O_2	gas phase LIF	ground-state Ca atoms combine with O_2 to form a triplet ($^3B_2$) bent dioxide CaO_2, apparently with a very low frequency bending mode; rate coefficients determined	358
Ca, Cd	O_2	gas phase chemiluminescence	chemiluminescence of CaO excited states from the interaction of a molecular beam of Cd (^3P) and Ca ($^1D_2$) metastables with O_2 is due to the Ca ($^1D_2$) state; reaction of Ca (^3P_J) with O_2 produces ground-state CaO, probably for reasons of energy conservation; the dynamics of the reactions are dominated by the intermediate formation of the stable $Ca^+\,O_2^-$ charge-transfer complex	359
Ca, Mg, Ba, Sr	O_3	N_2 matrix IR; $^{16,18}O$	MO is formed as a product of the reaction $M + O_3 \rightarrow MO + O_2$	360
Ca	H_2S	gas phase LIF optical Stark spectra	laser-ablated Ca reacts with H_2S/Ar to give CaSH, for which spectroscopic parameters have been determined	361
Ca	Xe	gas phase laser evaporation LIF, R2PI	detection of the $Ca{\cdot}Xe\,[^3\Sigma^-] \leftarrow Ca(4s4p\pi\,^3P_0){\cdot}Xe\,[^3\Pi_0{}^-]$ transition of Ca·Xe with a dissociation energy of ~1200 cm^{-1}	292
Ca	Ar	gas phase laser evaporation LIF, R2PI	detection of the $Ca(4s4d\sigma\,^3D_3){\cdot}Ar[^3\Sigma^+] \leftarrow Ca(4s4p\pi\,^3P_0){\cdot}Ar(^3\Pi_0{}^-)$ transition of Ca·Ar	362
Group 12				
Zn, Cd	H_2	Ar matrix discharge method IR; $^{1,2}H$	photoinduced reactions give ZnH_2 and CdH_2; evidence also of ZnH, CdH, ZnZnH, HZnZnH, HZnOH, and HCdOH, as well as adducts of some of these molecules with H_2 or H_2O	178
Zn	H_2	gas phase LIF	suggestion that reaction between $Zn(^3P_1)$ and H_2 proceeds to ZnH via the decomposition of a bent excited H−Zn−H insertion intermediate	363
Zn	CH_4	CH_4 matrix IR	photolysis at $\lambda > 330$ nm results in insertion to give CH_3ZnH; the study also includes a number of other metal atom reactions with CH_4 (Mn, Co, Cu, Ag, Au, Ca, Ti, Cr, and Ni)	364
Zn, Cd, Hg	CH_4, C_2H_6	Ar matrix IR; $^{1,2}H$, $^{12,13}C$	the photoexcited metal atom (M) inserts into a C−H bond of CH_4 to give CH_3MH; with C_2H_6 photoexcited Hg atoms form C_2H_5HgH but not CH_3HgCH_3	182

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Zn, Cd, Hg	alkenes and alkynes	gas phase flash photolysis kinetic absorption spectroscopy pump-probe studies	for ^{3}P levels of Hg, Cd, and Zn triplet−triplet energy transfer is exothermic for all alkenes and alkynes as well as for aromatic species, e.g., isomerization of ethene-d_2 and *cis*--butene in the quenching of Hg($^3P_1$) and Cd(^3P_j); metal hydride exit channel appears to open when singlet−triplet pathway is closed, e.g., Mg($^1P_1$) + C_3H_6 gives MgH; with Cd ($^1P_1$) there is competitive attack at both C−H bond and π-bond sites	365
Zn	CH_2N_2	Ar matrix IR; ^{1,2}H, ^{12,13}C	formation on deposition of the adduct Zn·CH_2N_2, which decomposes on photolysis at $\lambda \geq 400$ nm to give Zn=CH_2 and, on UV photolysis, to give HZnCH	209
Zn	CH_4, SiH_4	theoretical study	potential energy curves for the reactions of Zn(^{1}S, ^{3}P, and ^{1}P) with SiH_4 to give H_3SiZnH, and then ZnH and $ZnSiH_3$ are established	187
Zn, Cd	SiH_4	gas phase LIF	Cd or Zn in their excited $^3P_1$ states react with SiH_4 to give CdH and ZnH; quantum state distributions of CdH and ZnH studied	366
Zn	H_2O	Ar matrix IR; ^{1,2}H, ^{16,18}O	Zn·OH_2 and ZnOH characterized; other metals (Cr, Mn, Fe, Co, Ni, and Cu) also studied; more recent studies indicate the formation of HZnOH on photolysis	367
Zn, Cd	O_2	Ar or N_2 matrix laser ablation IR; ^{16,18}O, ^{64,66,68}Zn, ^{112,114}Cd	products include ZnO, linear OZnO, CdO, and linear OCdO; no cyclic Zn(O_2) observed, although calculations suggest a possible $^3A_2$ cyclic species	203
Zn	Ar	gas phase LIF, R2PI photoionization threshold measurements	bond energies and potential curves of Zn·Ar and Zn^+·Ar analyzed	368
Zn	Ne	gas phase LIF	Zn·Ne van der Waals states analyzed, bond lengths determined, and potential curves studied	369
Cd, Hg	CH_4	gas phase fluorescence excitation and action spectroscopy	van der Waals complex M·CH_4 formed and characterized	221
Cd, Hg	SiH_4	theoretical studies	study of the reaction of M(^{1}S, ^{3}P and ^{1}P) with SiH_4 to give H_3SiMH as an intermediate to MH, $MSiH_3$, H, and SiH_3 formation	370
Hg	H_2	Ar, Kr, H_2 or N_2 matrix IR; ^{1,2}H	$^3P_1$ state of Hg reactive (Hg excited with KrF laser) giving HgH_2 with f(HgH) = 223 N m^{-1} in Ar matrix; an electronic-to-vibrational (E−V) transfer takes place in an Hg-doped N_2 matrix when Hg is excited to the $^3P_1$ state so that vibrationally excited molecules are generated, but HgH_2 is still formed	371
Hg	H_2, He, Ne, Ar, Kr, Xe, CH_4, H_2O, N_2, NH_3	theoretical studies	HgH but no HgH_2 observed in gas phase studies; bonding in complexes of ground-state Hg($^1S_0$) and excited Hg($^3P_1$) with rare gas atoms and small molecules analyzed	372
Hg	H_2, CH_4, SiH_4, C_3H_8, C_2H_4	theoretical studies	reactions of Hg($^3P_1$) studied and reaction barriers estimated	373
Hg	CH_4	CH_4 or N_2 matrix IR; ^{1,2}H	insertion shows a strong kinetic isotope effect between CH_4 and CD_4; reaction much more efficient with CH_4, implying that there is a small barrier to insertion; Hg is excited at 249 nm to $^3P_1$ state; CH_3HgH linear molecule with f(Hg−H) = 224 N m^{-1} and f(Me−Hg) = 234 N m^{-1}	374
Hg	CH_4	CH_4 or Ar matrix absorption and emission spectra	analysis of the influence of CH_4 on the absorption and emission spectra of Hg atoms	375
Hg	SiH_4	Ar, Kr or N_2 matrix IR; ^{1,2}H theoretical studies	insertion reaction to give H_3SiHgH is, as anticitpated, easier with the Si−H bond than with the C−H bond; Hg photoactivated $^3P_1 \leftarrow {}^1S_0$: 249/246.5 nm for N_2, 246 nm for Ar, and 249.5 nm for Kr; other products are Si_2H_6 (in Kr), SiH, and SiH_2; no potential barrier to Hg* insertion	183
Hg	NH_3, H_2O	gas phase emission spectra	for several molecules with unshared pairs of electrons, such as NH_3 and H_2O, exciplex emission observed to be an important exit channel in the quenching of Hg($^3P_0$) and Cd(^3P_j)	15
Hg	NH_3	gas phase LIF, action spectroscopy; ^{1,2}H	Hg·NH_3 complex studied in its ground and excited electronic states	376
Hg	NH_3, H_2O	Ar or Kr matrix absorption, excitation and emission spectra; ^{1,2}H	Hg·NH_3, Hg·OH_2, Hg·$(NH_3)_n$, and Hg·$(OH_2)_n$ clusters analyzed; interaction relatively weak in the ground electronic state of Hg, much stronger in the excited 6s6p (^{3}P) state; estimated binding energies: Hg·OH_2, 1700 cm^{-1}; Hg·NH_3, 7300 cm^{-1}	89
Hg	N_2	N_2 matrix fluorescence, absorption and emission spectra gas phase LIF	interaction of Hg with N_2, including relaxation of Hg($^3P_1$), analyzed; properties of the weakly bound Hg·N_2 complex in its electronic ground and excited states explored	377

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Hg	H_2O, NH_3	gas phase phase-sensitive modulation spectroscopy	reaction $Hg(^3P_0) + H_2O \rightarrow HgH + OH$ studied; $(Hg{\cdot}OH_2)^*$ and $(Hg{\cdot}NH_3)^*$ exciplexes observed	378
Hg	HCl	Ar, Kr, or N_2 matrix IR; $^{1,2}H$, $^{35,37}Cl$	Hg excited into $^3P_1$ state by KrF laser emission at 249 nm; evidence of $Hg{\cdot}HCl$ adduct in N_2 matrix; HHgCl formed on photolysis; in Ar and Kr matrices the ions $ClHCl^-$ and Ar_2H^+/Kr_2H^+ are formed	379
			Group 13	
B	H_2	Ar matrix laser ablation IR; $^{1,2}H$, $^{10,11}B$	detection of BH, the complex $(H_2)BH$, and B_2H_6 as major products; minor products include BH_3, $BH_3(H_2)$, HBBH, and BH_4^-	380
B, B^+, B^-, Al, C	CH_4	theoretical studies	low activation barriers toward insertion predicted for all atoms with valence p electrons (cf. later studies)	381
B	CH_4	theoretical studies	insertion reaction is exothermic by $\sim$50 kcal mol^{-1}; CH_3BH has C_1 symmetry (unlike CH_3AlH with C_s symmetry); decomposition and tautomerization of CH_3BH to CH_3B, CH_2BH, and CH_2BH_2 discussed	382
B	CH_4, H_2O	theoretical studies	B insertion into CH_4 and H_2O has activation energies of 16.2 and 0.0 kcal mol^{-1}, respectively; lower energies are calculated for the corresponding reactions of B_2	383
B, Al, Ga, In	CH_4	Ar matrix laser ablation UV−vis, IR	UV spectra of atoms monitored vs time; conclusion: B is consumed rapidly by CH_4, Al more slowly, and Ga and In are not consumed at all; B and Al react upon deposition	384
B	CH_4	Ar matrix laser ablation IR; $^{1,2}H$, $^{10,11}B$, $^{12,13}C$	HBCBH is formed and characterized by its IR spectrum allied with quantum mechanical calculations; bands at 2561 and 2979 cm^{-1} tentatively assigned to ν(B−H) and ν(C−H) modes, respectively, of CH_3BH; other major products include H_2CBH_2, H_2CBH, HCBH, and HBCBH	385
B	CH_4, H_2O, CH_3Br	Ar matrix IR, UV−vis; $^{1,2}H$, $^{12,13}C$	CH_3BH, CH_3BBr, and HBOH are the insertion products; the reactions of boron clusters are also discussed	386
B	C_2H_4, C_2H_6	Ar matrix laser ablation IR; $^{1,2}H$, $^{10,11}B$, $^{12,13}C$	characterization of several species with the formula BC_2H_n ($n = 1-5$), including borirene, $(CH)_2BH$, ethynylborane, H_2BCCH, and borallene, $HBCCH_2$; reaction with C_2H_4 proceeds through both exothermic C═C addition and C−H insertion	387
B	C_2H_2	Ar matrix laser ablation IR; $^{1,2}H$, $^{10,11}B$, $^{12,13}C$	evidence of cyclic borirene, BC_2H_2, with C_{2v} symmetry and estimated to be 74 kcal mol^{-1} more stable than $B + C_2H_2$; experiments indicate the formation of bent HBCCH insertion and cyclic BC_2H_2 addition products, linear HBCC, linear HCCB, and cyclic HBC_2 (C_{2v}); there are also signs of a $HBCCH{\cdot}C_2H_2$ complex	388
B, Al	C_2H_2	theoretical studies	investigation of the BC_2H_2 and AlC_2H_2 isomers; C−H insertion of B and Al atoms has a significant activation barrier and is thus not expected to occur thermally	389
B, Al, Li, Na, Be, Mg	C_2H_2	theoretical studies	studies of the acetylene → vinylidene rearrangement in MC_2H_2 systems	390
B	C_2H_4	theoretical studies	the borirane radical, BC_2H_4, is calculated to have a $^2A_1$ structure with a binding energy of 43.0 kcal mol^{-1} with respect to $B + C_2H_4$; the corresponding energy for the $^2B_2$ π complex is 13.2 kcal mol^{-1}; this contrasts with Al−C_2H_4, where the $^2B_2$ π complex is the more stable species	391
B	C_2H_4	gas phase CMB technique with mass spectrometric detection	borirene, cyclic $(CH)_2BH$, detected as a product of the reaction of $B(^2P)$ with C_2H_4	116
B	C_2H_6	theoretical studies	six isomers of BC_2H_5 studied, with vinylborane (H_2BCHCH_2, C_s symmetry) having the lowest energy	392
B	CH_3NH_2, $(CH_3)_2NH$	Ar matrix laser ablation IR; $^{10,11}B$	no insertion into the C−H bonds observed; no CH_3BNH_2 or CH_3NHBH observed with CH_3NH_2, but these species are believed to be responsible for the products observed, viz., CH_3BNH, CH_3NBH, and CH_2BNH_2	393
B	CH_3OH	Ar matrix laser ablation IR; $^{1,2}H$, $^{10,11}B$	CH_3BO is the primary product; minor products are CH_2BOH, CH_2BO, and HBO; no CH_3BOH is observed, but CH_3BOH and CH_3OBH are responsible for all products detected; insertion into a C−O bond is exoergic by 107 kcal mol^{-1}, that into an O−H bond by 87 kcal mol^{-1}, and that into a C−H bond by only 49 kcal mol^{-1}	394
B	CH_3X (X = F, Cl, Br)	Ar matrix laser ablation IR; $^{1,2}H$, $^{10,11}B$, $^{12,13}C$	CH_3BX, CH_2BX, CHBX characterized (X = F, Cl, or Br); CH_2BX and CHBX formed via insertion into the C−X bond followed by loss of one or two H atoms	395
B	HCN	Ar matrix laser ablation IR; $^{1,2}H$, $^{10,11}B$, $^{12,13}C$	major products are BNC and BCN, minor products HBNC, HBCN, and cyclic HB(CN); HBNC and HBCN are close in energy and only $\sim$10 kcal mol^{-1} lower than the cyclic molecule HB(CN), but this converts to either HBNC or HBCN upon broad-band photolysis; HBCN has a bent structure (<H−B−C $\sim$135°)	396

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
B	CO_2	Ar matrix laser ablation IR; $^{10,11}B$, $^{12,13}C$, $^{16,18}O$	insertion product OBCO with a bent structure has been identified and characterized	397
B	NH_3	theoretical studies	$B + NH_3 \rightarrow B{\cdot}NH_3$ (C_s symmetry) $\rightarrow HBNH_2$ (C_s symmetry); binding energy of $B{\cdot}NH_3 = 13.1$ kcal mol^{-1}; energy change for $B{\cdot}NH_3 \rightarrow HBNH_2 = -91.3$ kcal mol^{-1}, and the reaction barrier only $+10.9$ kcal mol^{-1}	398
B	NH_3	Ar matrix laser ablation IR; $^{1,2}H$, $^{10,11}B$, $^{14,15}N$	products are $HBNH_2$, HBNH, BNH, and BH; in addition, cyclic B_2N and linear BNBN are detected; reaction sequence believed to be $NH_3 + B \rightarrow [HBNH_2] \rightarrow$ $(BH + NH_2)$ or $(H{-}B{\equiv}N{-}H)$	399
B	NH_3, O_2, H_2O	Ne matrix laser ablation EPR; $^{1,2}H$, $^{10,11}B$, $^{14,15}N$, $^{16,17}O$	passage of NH_3, O_2, or H_2O over the boron target; the BNH radical and BO characterized as products; BNH has a linear geometry and an electronic structure similar to that of the isoelectronic BO	400
B	N, N_2	N_2 matrix laser ablation IR; $^{10,11}B$, $^{14,15}N$	several new B_xN_y species produced and identified; the major product is NNBN, with NBN and BNN as minor products	204
B	O_2, N_2O	gas phase chemiluminescence and emission spectra	reactions give BO exclusively in a highly exothermic reaction	401
B	O_2	Ar, Kr, Xe, or O_2 matrix laser ablation IR; $^{10,11}B$, $^{16,18}O$	formation of BO, BO_2, linear B_2O_2, B_2O_3, and BO_2^- detected; estimated energy changes: $B + O_2 \rightarrow BO_2$, -206 kcal mol^{-1}; $BO_2 \rightarrow BO + O$, $+134$ kcal mol^{-1}; if the energy released by the formation of BO_2 is not quenched by a third body, the reaction is likely to proceed to the formation of BO, which is accordingly the major reaction product in the gas phase	188
B	H_2O	Ar matrix laser ablation IR; $^{1,2}H$, $^{10,11}B$, $^{16,18}O$	HBO and BO are the major products, presumably with HBOH as the unsighted precursor; increasing concentrations of B atoms in the matrix result in formation of BOB with a nearly linear structure	402
B	H_2O	theoretical studies	the reaction sequence $B + H_2O \rightarrow B{\cdot}OH_2 \rightarrow HBOH \rightarrow BO + H_2$ is studied	403
B	SO_2	Ar matrix laser ablation IR; $^{10,11}B$, $^{16,18}O$, $^{32,34}S$	the insertion product OBSO identified and characterized by a strong IR absorption near 2000 cm^{-1}	404
B	X_2 (X = F, Cl, Br or I)	Ar matrix laser ablation IR; $^{10,11}B$, $^{35,37}Cl$	BX, BX_2, and BX_3 molecules formed but BX_2 decays on annealing; estimated bond angles: BF_2, 114°; BCl_2, 115−127°; BBr_2, ≥112°; BI_2, ≥105°	405
Al	H_2	Kr matrix UV−vis, IR, EPR; $^{1,2}H$	inefficient reaction leading to AlH_2 and AlH + H; production of AlH is dependent on AlH_2 formation, indicating that AlH arises from excited-state fragmentation of AlH_2 immediately following its formation	406
Al	H_2	theoretical study	AlH_2 should have a visible absorption around 680 nm; estimated strength of Al−H bond, D_0(H−AlH), 45 kcal mol^{-1}	407
Al	H_2, CH_4	theoretical studies	theoretical studies of the pathways for the reactions of Al atoms with H_2 and CH_4	408
Al, Ga, In	H_2	Ar matrix IR; $^{1,2}H$, $^{69,71}Ga$	MH_2 formed upon photolysis at $\lambda = 290$ or 335 nm; decomposition with light having $\lambda = 547$ nm to MH; AlH reacts with H_2 to give AlH_3; MH_3 also formed by reaction of the metal atoms with H atoms; analysis of the force constants	135, 409
Al	CH_4	theoretical studies	species CH_3AlH, CH_3Al, and AlH investigated	410
Al	CH_4	theoretical study	estimated activation barrier to insertion 49.4 kcal mol^{-1}	411
Al, mainly Ga	CH_4, H_2	Ne matrix EPR; $^{1,2}H$, $^{69,71}Ga$	GaH_2 and CH_3GaH generated on photolysis at $\lambda = 289$ or 334 nm and their electronic structures explored	97
Al, Ga	CH_4	CH_4 matrix IR; $^{1,2}H$	Al claimed to react with CH_4 upon deposition, Ga to react only on UV photolysis	412
Al	CH_4	CH_4 or Kr matrix UV−vis, IR, EPR; $^{1,2}H$	photoactivation of Al atoms at $\lambda = 348/368$ or 305 nm causes insertion into methane; further photolysis of CH_3AlH at $\lambda = 270$ nm results mainly in fragmentation to form secondary products, whereas photolysis at $\lambda > 450$ nm results in regeneration of Al atoms; the CH_3AlH molecule exhibits a bent geometry with the unpaired electron residing mainly in an Al-centered orbital	98
Al	propene, 1- and 2-butene, 1,3-butadiene, propyne, 2-butyne	co-condensation at 77 K followed by warming to room temperature and hydrolysis of the products with D_2O	Al atoms add to unsaturated hydrocarbons with insertion to produce compounds with Al−C bonds	413
Al	C_2H_4	theoretical studies	complexes of Al with C_2H_4 studied; $(\eta^2\text{-}C_2H_4)Al$ is strongly bound with $D_0 > 11$ kcal mol^{-1}	414

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Al	C_2H_4	Ar matrix IR; ^{1,2}H, ^{12,13}C	a symmetrical π-complex, (η^2-C_2H_4)Al, is formed exhibiting C_{2v} symmetry and a C−Al−C angle of ~40°	164
Al	C_2H_4	cyclohexane or adamantane matrix EPR	cyclodimerization of C_2H_4 occurs with the formation of aluminacyclopentane, C_4H_8Al	163
Al	C_2H_2, C_2H_4	Ar or Ne matrix EPR; ^{1,2}H	C_2H_4 gives π-coordinated (η^2-C_2H_4)Al with a dative bond in the direction Al → C_2H_4 on deposition; photolysis leads to $Al(C_2H_4)_2$ complexes; C_2H_2 gives a σ-bonded adduct with a vinyl structure on deposition; photolysis brings about cis−trans isomerization	162
Al, Ga, In	C_2H_2	Ar matrix IR; ^{1,2}H, ^{12,13}C	π-complexes with C_{2v} symmetry formed; at higher concentrations 1/2 and 2/1 metal−ethyne complexes also formed; in the case of Al photolysis induces insertion to form $HAlC_2H$ and AlC_2H; Al exerts a smaller influence on the bonding of the C_2H_2 subunit than do Ga and In; bonding in the complexes is discussed	161a
Al	C_2H_2, C	Ar matrix laser ablation IR; ^{12,13}C	π-complex and cyclic AlC_2H_2 observed; other products are HCCAl and HAlCCH; reaction sequence appears to be $Al + C_2H_2 \rightarrow (HAlCCH)^* \rightarrow HAlCCH \rightarrow H + AlCCH$; Al and C atoms give AlC, Al_2C, and AlCCAl	161b
Al	C_2H_2	theoretical studies	AlC_2H_2 isomers investigated; the aluminum−vinylidene structure, $AlCCH_2$, is ~12 kcal more stable than the vinyl structure, Al(H)CCH, but the barrier for isomerization is ~8 kcal, too high to allow isomerization in solid Ar matrices	415
Al	1,3-butadiene	adamantane matrix EPR; ^{1,2}H	two paramagnetic compounds, σ-bonded aluminacyclopentene, C_4H_6Al, and an aluminum-substituted allyl, $AlCH_2CHCHCH_2$, are detected	416
Mg, Al, Ga, In	CH_3X	Ar or CH_3Br matrix IR	formation of CH_3MBr species (M = Mg, Al, Ga, or In) on deposition indicated; Tl, Ge, Sn, and Pb atoms do not react on deposition	417
Al, Ga, In	NCCN, CH_3CN	gas phase pulsed jet cavity FT microwave studies ^{12,13}C, ^{14,15}N, ^{27}Al, ^{69,71}Ga, ^{113,115}In	both MCN and MNC are products of the reaction between laser-ablated M vapor and NCCN or CH_3CN in an Ar carrier gas (M = Al, Ga, or In); the structures and spectroscopic properties of the molecules have been determined	418
Al, Ga, In, Tl	HCN	Ar matrix laser ablation IR; ^{12,13}C, ^{14,15}N	MCN and MNC are formed; as with the group 2 elements, but not with B, no hydrogen-containing product is observed; suggested reaction scheme is $M^* + HCN \rightarrow [HMCN]^* \rightarrow MCN/MNC + H$	216
Al	dimethyl ether, diethyl ether, tetrahydrofuran	gas phase time-resolved resonance fluorescence excitation	studies of the equilibria between free Al atoms and bound Al−ether complexes allow binding energies in the order of 10 kcal mol^{-1} to be determined	419
Al	R−O−R′, symmetric, cyclic and acyclic ethers	adamantane matrix EPR; ^{1,2}H	mononuclear organoaluminum compounds formed by insertion of Al into C−C, C−H, and C−O bonds; mono- and diligand complexes Al[ether] and Al[ether]$_2$ tentatively identified	420
Al	CO	Kr matrix IR; ^{16,18}O	first sighting of a dicarbonyl of aluminum, $Al_x(CO)_2$	421
Al	CO	Ar or hydrocarbon matrix EPR; ^{12,13}C	first suggestion of a bent Al−C−O arrangement in the $Al(CO)_2$ molecule, C−Al−C angle estimated to be 110°	99
Al	CO	Ar matrix IR; ^{12,13}C	AlCO observed for the first time and shown clearly to be bound; ab initio geometry calculated for $Al(CO_2)_2$: <Al−C−O, 166° and <C−Al−C, 74°	154
Al	SiH_4	Ar matrix UV−vis, IR, EPR; ^{1,2}H	$Al{\cdot}SiH_4$ complex formed upon deposition; photolysis at $\lambda = 410$ nm leads to an insertion reaction to give H_3SiAlH; the $Al{\cdot}SiH_4$ complex can be re-formed upon photolysis at $\lambda = 580$ nm; for the complex the mode of coordination is η^2-SiH_4; broad-band photolysis of H_3SiAlH leads to decomposition, with H_3SiAl being the detectable product	171
Al	NH_3	adamantane matrix EPR	$HAlNH_2$, formed on deposition, reported to have one bridging H atom; additional products are $Al(NH_3)_4$, $Al(NH_3)_2$, and HAlOH	422
Al	NH_3	Ar matrix laser ablation IR; ^{1,2}H, ^{14,15}N	$HAlNH_2$ identified; additional products are $AlNH_2$ and possibly HAlNH, $Al(NH_2)_2$ and $Al(NH)_2$	423
Al, Ga, In	NH_3	Ar matrix IR, UV−vis, EPR; ^{1,2}H, ^{14,15}N, ^{69,71}Ga	$M{\cdot}NH_3$ complexes (M = Al, Ga, or In) formed on deposition and characterized by IR, UV−vis, and EPR spectra; photolysis at $\lambda = 440$ nm gives $HMNH_2$; following broad-band photolysis ($\lambda = 200-800$ nm) MNH_2 and H_2MNH_2 are formed	148, 149
Al	NH_3	theoretical studies	HAlNH, $AlNH_2$, $Al{\cdot}NH_3$, $HAlNH_2$, H_2AlNH_2, $HAlNH_3$, and $H_3Al{\cdot}NH_3$ and the transition states for interconversion of the isomers studied by ab initio methods	424

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Al	NH_3, H_2O, HF, HCl, H_2S, PH_3	theoretical studies	each molecule forms an adduct with an Al atom, which is the precursor to insertion of the metal atom into the X−H bond; the energies of the adducts and insertion products are calculated, as are the energy barriers to insertion	425
Al	NH_3, H_2O, HCl, Cl_2	theoretical methods	investigation of the potential energy surfaces and transition states for insertion reactions of Al atoms	426
Al	N_2, N	Ar or N_2 matrix laser ablation IR; $^{14,15}N$	the product NAlN with an IR band at 656.9 cm^{-1} (σ_u) builds up on annealing but decays on photolysis; calculated to be a linear molecule with a $^4\Pi_u$ ground state: $N + AlN \rightarrow NAlN\ (^4\Pi_u)$ −44 kcal mol^{-1}; NAlN is higher in energy than Al + N_2 by 120 kcal mol^{-1}; $Al{\cdot}N_2$ complex bound by 4 kcal mol^{-1} relative to Al + N_2; other products are AlN_3, Al_2N, and Al_3N	49
Al, Ga, In, Tl	NO or NO + O_2	Ar matrix laser ablation IR; $^{14,15}N$, $^{16,18}O$	GaNO, InNO, and TlNO are formed on deposition of NO with Ga, In, and Tl, respectively; GaNO and InNO have linear $^3\Sigma^-$ ground states, but TlNO has a bent $^3A''$ structure; Al or In reacts with NO + O_2 to give M^+OONO^- ion-pairs	316a, 427
Al, Ga, In	PH_3	Ar matrix IR, UV−vis; $^{1,2}H$	$M{\cdot}PH_3$ adducts formed initially are photolabile and convert to $HMPH_2$ and H_2MPH on photolysis	153
Al, Ga, In, Tl	H_2O	Ar matrix IR	HAlOH, formed on deposition, decays on photolysis at λ >330 nm; Ga, In, and Tl form adducts on deposition but insert into an O−H bond on brief photolysis at λ > 330 nm; HMOH products have C_s symmetry and decompose to MOH and H on further photolysis at λ > 330 nm; $Tl{\cdot}OH_2$ is relatively stable to photolysis; only traces of TlOH or $TlOH{\cdot}OH_2$ observed on prolonged photolysis	266a
Al, Ga, In	H_2O	Kr matrix UV−vis	the electronic structures of the $M{\cdot}OH_2$ adducts, HMOH, MOH, and MO species are studied	266b
Al	H_2O	Ar or Ne matrix laser vaporization EPR; $^{1,2}H$, $^{16,17}O$	the nonlinear geometry and electronic structure of HAlOH are established, the data being consistent with a molecule having a trans-configuration; the electronic structures of AlH_2 and $Al(OH)_2$, both formed on photolysis at λ = 254 nm, are investigated	96, 428
Al, Ga, In, Tl	O_2	Ar matrix IR; $^{16,18}O$	cyclic MO_2 molecules with C_{2v} symmetry formed on deposition; in addition, M_2O_2 molecules are detected; the MO_2 species are compared with those of group 1 elements	265
Al	O_2	Ar matrix laser ablation IR; $^{16,18}O$	the major product is cyclic AlO_2; in addition, OAlOAlO, AlOAlO, OAlO (all linear), and OAlOO are found	200
Al	HCl, Cl_2	Ar matrix EPR; $^{35,37}Cl$	HAlCl and $AlCl_2$ formed on deposition, both having bent structures with the unpaired electron localized in a nonbonding, sp-hybridized orbital of Al pointing away from the ligand atoms; MNDO studies indicate that Al and HCl undergo either the insertion reaction $HCl + Al \rightarrow HAlCl$ or the displacement reaction $HCl + Al \rightarrow H + AlCl$, depending on the direction of approach	102
Al	F_2, Cl_2, Br_2, I_2	Ar matrix laser ablation IR; $^{35,37}Cl$, $^{79,81}Br$	main products are AlX_2 species (x = F, Cl, Br or I), $^2A_1$ radicals which decay on annealing; bond angles are estimated to be: AlF_2, 118°, $AlCl_2$, 115°, and $AlBr_2$, ca. 106°; other products are AlX_3, Al_2X_6, Al_2X_4 and AlX	429
Al	Cl_2	Ar matrix IR	$AlCl_2$, AlCl, $AlCl_3$, and Al_2Cl_6 formed; $AlCl_2$ also formed by other methods, e.g., $2AlCl_3 + Al \rightleftarrows 3AlCl_2$	430
Ga	H_2, CH_4	Ar, Kr or CH_4 matrix IR; $^{1,2}H$	excited Ga reacts with H_2 to form GaH and GaH_2, whereas Ga_2 reacts on deposition to form $Ga(\mu\text{-}H)_2Ga$, which can be converted photoreversibly to HGaGaH; CH_3GaH formed on photolysis at 270−380 nm	267
Ga	H_2, CH_4	Ne matrix EPR; $^{1,2}H$, $^{69,71}Ga$	electronic structures of GaH_2 and CH_3GaH, both formed on photolysis at λ = 289 or 334 nm, have been studied; a comparison is made with the B and Al analogues	97
Ga	CH_4	Ar matrix IR, UV−vis; $^{1,2}H$, $^{12,13}C$	no reaction with ground state Ga atoms; CH_3GaH formed on photolysis at λ = 354 nm; decomposition to Ga and CH_4 appears to occur on photolysis at λ > 495 nm	268
Ga, In	CH_4	Ar matrix IR, UV−vis; $^{1,2}H$, $^{12,13}C$	CH_3MH molecules (M = Ga or In) formed on photolysis at λ = 200−400 nm; decomposition occurs on photolysis at λ = 200−800 nm to form CH_3M + H	152
Ga	C_2H_4	Ar matrix EPR; ^{69}Ga	electronic structure of $(\eta^2\text{-}C_2H_4)Ga$ investigated	431
Ga, In	CO	Ar or Kr matrix IR; $^{12,13}C$	GaCO, InCO, $Ga(CO)_2$, and $In(CO)_2$ formed on deposition; $In^+\ C_2O_2^-$ formed on photolysis at λ = 200−800 nm	155
Ga	CO	Ar, cyclohexane or adamantane matrix EPR, IR; ^{69}Ga, $^{12,13}C$	formation of $Ga(CO)_2$ investigated; weak signals tentatively assigned to GaCO	100

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Ga, In, Tl	N_2, N	Ar matrix laser ablation IR; $^{14,15}N$, $^{69,71}Ga$	NMN linear molecules with a $^4\Pi_u$ ground state formed, e.g., Ga + N → GaN (-49.7 kcal mol^{-1}), GaN + N → NGaN (-36.3 kcal mol^{-1}); other products identified are MN, M_3N, and MN_3	50
Ga, In	O_2	Ar matrix laser ablation IR; $^{16,18}O$, $^{69,71}Ga$	linear OGaO and OInO, linear GaOGaO and InOInO, and bent GaO_2 and InO_2 [later identified as $M(O_2)^-$ anions, see ref 202] are the main products	201
Ga, In	O_2	N_2 or Ar matrix IR; $^{16,18}O$	MO_2 superoxide is the main product formed on codeposition; in addition, O_2MMO_2 (D_{2d} symmetry), $M(\mu\text{-}O)_2M$ (rhombic), and $[In_2O]_2$ are found	265
Ga, In, Tl	O_2	theoretical studies	cyclic (η^2-O_2)M species are predicted with $^2A_2$ ground states; dissociation energies and vibrational properties have been calculated	432
Ga, In	HCl, H_2	Ar matrix IR; $^{1,2}H$, $^{35,37}Cl$	photolysis with broad-band UV−vis light brings about reaction to give $HMCl_2$ (M = Ga or In) and H_2GaCl (but not H_2InCl)	433
In	CO	Ar matrix EPR, IR; $^{12,13}C$, ^{115}In	formation of $In(CO)_2$ investigated	101
Tl	O_2	N_2 or Ar matrix IR; $^{16,18}O$	superoxide TlO_2 is the primary product; secondary products include the O_2TlTlO_2 dimer with D_{2d} symmetry, rhombic $Tl(\mu\text{-}O)_2Tl$ with D_{2h} symmetry, and $[Tl_2O]_2$	434
Tl	O_2	Ar matrix laser ablation IR; $^{16,18}O$	products are linear OTlO, TlOTlO, cyclic (η^2-O_2)Tl, $Tl(\mu\text{-}O)_2Tl$, Tl_4O_2, $[TlO_2]_2$, TlO_3, TlOTl, and cyclic $Tl(O_2)^-$; cyclic (η^2-O_2)Tl is formed on annealing without significant activation energy, but insertion to form linear OTlO requires activation energy, which is provided by the laser ablation process; as with gallium, the 7s (^2S) ← 6p (^2P) excitation is not effective for insertion, but the higher energy 6d (^2D) ← 6p (^2P) excitation does promote insertion	202
			Group 14	
C	H_2, hydrocarbons, and organic N-, O-, S-, and halogen-containing compounds	various conditions	review of the preparation and reactions of C atoms	11
C	H_2, C, CH_4, C_2H_4, C_2H_2, O_2	gas phase discharge flow system radio-gas-chromatographic analysis	rate of recombination of C atoms determined, as well as the relative rates of other C atom reactions	435
C, Si	CH_4, SiH_4	theoretical studies	activation energy for insertion of C(^3P) into a C−H bond of CH_4 estimated to be 30.6−38.1 kcal mol^{-1}; behaviors of Si(^3P)/SiH_4, C(^1D)/CH_4 and Si(^1D)/SiH_4 systems also investigated	436
C	CH_4, CH_3Br, H_2O	Ar matrix IR, UV−vis	ground state C(^3P) does not react with CH_4, but C(^1S) and C(^1D) insert into a C−H bond to give CH_3CH, which rearranges to C_2H_4; C atoms react with CH_3Br to give the carbene CH_3CBr; C atoms, probably as C(^1D), react with H_2O to give CO	437
C	aldehydes, ketones, aromatic compounds	co-condensation of reagents	C atoms from a carbon arc reactor are co-condensed with the organic reagent at 77 K in a typical experiment; analysis of the products reveals deoxygenation of >CO groups and/or insertion into C−H bonds to form carbenes	438
Si	H_2	Ar matrix IR; $^{1,2}H$	SiH_2 formed as the primary product on deposition; in addition, SiH_4 and Si_2H_6 are observed	270
Si	H_2	gas phase visible absorption	rotational structure analyzed to determine dimensions of SiH_2 in its upper ($^1B_1$) and lower ($^1A_1$) electronic states	439
Si	H_2	theoretical studies	unlike CH_2, the $^1A_1$ state and not the $^3B_1$ state is established as being the ground state of SiH_2	440
Si	C_2H_4, C_2H_2	Ar matrix IR; $^{1,2}H$, $^{12,13}C$	products C_2H_2Si and C_2H_4Si are observed; in both cases the silicon atoms add to the π system rather than insert into the C−H bonds, leading to cyclic silylenes as the primary reaction products; on photolysis, additional isomers are generated	207
Si	C_2H_4, C_2H_2	theoretical studies	potential surfaces examined by ab initio methods; lowest triplet equilibrium structure for SiC_2H_4 is a silacyclopropylidene structure ($^3A_2$), for which there is no barrier to formation; similar studies reported for Si(^3P) with C_2H_2; relative energies of the different isomers calculated	441
Si	CH_2O	Ar matrix IR; $^{1,2}H$, $^{12,13}C$	on photolysis at $\lambda > 385$ nm, the following reactions occur: $Si + CH_2O \rightarrow H_2CSiO \rightarrow H_2Si{\cdot}CO$; H_2CSiO has a pyramidal and not a planar, ketene-like structure	208

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Si	CH_3OCH_3, CH_3OH	Ar matrix IR	complexes $Si{\cdot}O(CH_3)_2$ and $Si{\cdot}O(H)CH_3$ formed initially; photolysis then gives CH_3OSiCH_3, $(CH_3)_2SiO$, and $\overline{OCH_2Si}(H)CH_3$ in the first case, whereas $Si{\cdot}O(H)CH_3$ yields CH_3OSiH, $CH_3(H)SiO$, $\overline{OCH_2Si}H_2$, and CH_3SiOH	442
Si	HCN	Ar matrix IR; $^{1,2}H$	$HCN{=}Si$ is formed on deposition, indicating that the lone pair of the nitrogen atom is more basic than the π system; on photolysis, $H{-}Si{-}C{\equiv}N$ ($\angle H{-}Si{-}C = 92°$), the lowest energy CHNSi species, is formed; this can be converted reversibly to $H{-}Si{-}N{=}C$ on further photolysis	206
Si	CO, N_2	Ne, Ar, N_2, or CO matrix IR, UV−vis, EPR; $^{12,13}C$, $^{14,15}N$, $^{16,18}O$	SiCO, $Si(CO)_2$, and SiN_2 formed and characterized	157
Si	N_2	Ar or N_2 matrix IR; $^{14,15}N$	SiNN is formed on codeposition; photoisomerization leads to the π-adduct $Si{\cdot}NN$; at higher N_2 concentrations, $Si(N_2)_2$ is formed; other products include $[SiNN]_2$, $Si(\mu\text{-}N)_2Si$, SiNNSi, and SiNSiN	443
Si, Ge	NH_3	Ar matrix IR; $^{14,15}N$	Si and Ge atoms (M) react with NH_3 to form the complex $M{\cdot}NH_3$ on annealing the Ar matrix in which they are codeposited; UV and then UV−vis photolysis form $HMNH_2$ and MNH, respectively	444
Si	H_2O	Ar matrix IR; $^{1,2}H$, $^{16,18}O$	the following reaction sequence occurs: $Si(^3P) + H_2O \rightarrow Si{\cdot}OH_2\,(^3A_2) \rightarrow HSiOH^*\,(^3A'') \rightarrow HSiOH\,(^1A')$; rearrangement of the adduct to HSiOH occurs spontaneously over several hours; estimated heats of reaction: formation of $Si{\cdot}OH_2$, -5 kcal mol^{-1}; formation of HSiOH, -58 kcal mol^{-1}; there is a significant isotope effect with Si inserting into only the O−H bond of HOD; geometry, bonding, and photochemistry of HSiOH explored	269
Si, Ge	O_2	Ar matrix laser ablation IR; $^{16,18}O$	Si reacts to give SiO_2, SiO, Si_2O_2, and O_3; Ge reacts to give GeO_2, GeO, Ge_2O_2, Ge_3O_3, and O_3	190
Si	HF	Ar matrix IR; $^{1,2}H$	reaction occurs to give HSiF on deposition; a kinetic effect is observed, the reaction being slower for Si + DF; the angle $\angle$HSiF is estimated to be ∼100°, whereas $f(Si{-}H) = 211.2$ N m^{-1} and $f(Si{-}F) = 469.2$ N m^{-1}	271
Ge	H_2, H	Ne or Ar matrix IR; $^{1,2}H$	laser-ablated Ge atoms react on co-condensation with H_2 to produce GeH_n, where $n = 1, 2, 3$, or 4; Ge_2H_2, Ge_2H_4, and GeH_3^- are the products of further reactions	445
Ge	O_2	N_2 or Kr matrix IR; $^{16,18}O$, Ge isotopes	O_3 and GeO are the main products in Kr matrices; GeO_2 (linear, $D_{\infty h}$) is the main product in an N_2 matrix; the mechanisms leading to the products are discussed	446
Ge	O_2	CH_4 matrix Raman; $^{16,18}O$	characterization of GeO_2 in which the bonding is quite different from that in CO and CO_2	447
Ge, Sn	CO	Kr or CO matrix IR; $^{16,18}O$	spectroscopic evidence implying the formation of germanium and tin carbonyls	158
Sn, Pb	H_2, H	Ne or Ar matrix IR; $^{1,2}H$	laser-ablated Sn or Pb atoms react on co-condensation with H_2 to produce SnH_n ($n = 1{-}4$) or PbH_n ($n = 1{-}3$), respectively; evidence is also presented for the formation of Sn_2H_2 and the anions MH_3^-	448
Sn	O_2	Kr or N_2 matrix IR; $^{16,18}O$	products detected on deposition are SnO_2 ($D_{\infty h}$), Sn_2O_2 (D_{2h}), and small amounts of O_3, SnO, and Sn_3O_3; $^{16}O_2/^{18}O_2$ experiments indicate that SnO_2 is formed by direct insertion, with the O−O bond being retained in the transition state	449
Pb	O_2	Ar or N_2 matrix laser ablation IR; $^{16,18}O$	products identified are PbO, OPbO, $Pb(O_2)$, $OPb(O_2)$, PbOPb, Pb_2O_2, $PbPb(O_2)$, and Pb_4O_4; OPbO is linear and $Pb(O_2)$ peroxide-like, both products being formed in Ar and N_2 matrices, although the yield of OPbO is higher in an Ar matrix; excited Pb atoms react as follows: $Pb^* + O_2 \rightarrow OPbO$, whereas ground state Pb atoms react thus: $Pb + O_2 \rightarrow Pb(O_2)$	193
Pb	O_2	Ar matrix IR; $^{16,18}O$	low concentrations of Pb give cyclic $Pb(O_2)$ but no PbO; high concentrations of Pb give PbO; Pb_2O_2 also detected	450
			Group 15	
N	N_2	N_2 matrix IR; $^{14,15}N$	bombardment of a N_2 matrix with fast atoms and/or ions or with fast nitrogen atoms from a neutralized atom beam source results in the formation of the $N_3^{\bullet}$ radical	451
N	B, BN	N_2 matrix laser ablation IR; $^{10,11}B$, $^{14,15}N$	radiation from the focused laser plume dissociates the N_2 into N atoms, which then enter into the following reactions: $B + N \rightarrow BN$; $BN + N \rightarrow NBN$; $N + N_2 \rightarrow N_3$	204
N	M, MN (M = Al, Ga, In or Tl)	Ar or N_2 matrix laser ablation IR; $^{14,15}N$, $^{69,71}Ga$	N_2 dissociated into N atoms, which then react as follows: $M + N \rightarrow MN$; $MN + N \rightarrow NMN$; $N + N_2 \rightarrow N_3$	49, 50

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
N	M (M = transition metal or lanthanide)	Ar or N_2 matrix laser ablation IR; $^{14,15}N$, some metal isotopes	N atoms react to form diatomic MN in all cases and NMN in some cases; N_2 complexes also frequently observed, and some systems show evidence of oligomers, e.g., $[MN]_2$	452
N	P or P_2	Ar matrix IR; $^{14,15}N$	passage of an Ar stream containing N_2 and P_4 through a microwave discharge and condensation at 10 K reveal evidence for the formation of PN and PNP	453
N	S or S_n	Ar matrix IR; $^{14,15}N$, $^{32,34}S$	action of a discharge on an Ar/S vapor/N_2 mixture gives on deposition NS, NS_2, NSS, and N_2S	454
N	Se or Se_n	Ar matrix IR; $^{14,15}N$, $^{76,80}Se$	action of a discharge on an Ar/Se vapor/N_2 mixture gives on deposition NSe, NSe_2, and NSe_2^+	455
N	alkene	inert matrix EPR	intermediates formed in the gas-phase reaction of N atoms (produced in an rf discharge) with alkenes include $H_2C{=}N^\bullet$ and $R(H)C{=}N^\bullet$ radicals	456
P	P_2, P_3	Ar matrix UV−vis	P_4 vapor subjected to an Ar discharge and vacuum-UV irradiation during condensation with an excess of Ar shows evidence suggestive of the reactions $P + P_2 \rightarrow P_3$ and $P + P_3 \rightarrow P_4$	457
P	O_2	Ar matrix laser ablation IR; $^{16,18}O$	PO_3^-, PO_2, PO_2^-, P_2O, OPOPO, P_4, and higher oxides are the products	194
P	S, S_n	Ar matrix IR; $^{32,34}S$	condensation of the products of the action of an Ar discharge on a P_4/S_8 mixture gives evidence for the formation of the species PS, P_2S, and PS_2	458
Group 16				
O	CO, CO_2, CH_4, C_2H_6, C_3H_8, iso-C_4H_{10}	Ar matrix IR	$O(^1D)$ atoms, produced by photolysis of N_2O, react to give CO_2, CO_3, and alcohols; attack on the C−H bonds of iso-C_4H_{10} is indiscriminate	459
O	CF_3Br	Ar matrix IR	CF_3OBr characterized as a product of the reaction of CF_3Br with $O(^1D)$ generated from photolysis of O_3; mechanism proposed for the reaction involves initial generation of CF_3BrO^*	460
O	CF_3Br	theoretical studies	triplet and singlet potential energy surfaces studied by the DFT method; in the gas phase OBr is the main product	461
O	HCN	gas phase LIF	CO and NH are the dominant products; minor products are OH and CN; rotational and vibrational distributions of the products are analyzed; an oxazirine intermediate is formed by insertion of $O(^1D)$ into the C−N bond in the dominant reactive pathway	462
O	CH_3CN, CF_3CN	gas phase flash photolysis-resonance fluorescence; $^{1,2}H$	reaction of $O(^3P)$ displaces CH_3 or CF_3 in the major reaction channel; kinetic parameters determined	463
O	CH_3CN	Ar matrix IR; $^{1,2}H$, $^{14,15}N$, $^{16,18}O$	O atoms formed from O_3 photolysis give $HOCH_2CN$ and CH_3CNO, together with complexes of $HOCH_2CN$	464
O	$CHCl_3$	Ar matrix IR; $^{1,2}H$, $^{16,18}O$	reaction of $O(^1D)$ atoms generated from O_3 gives as main products $OCCl_2$ and OCHCl; with $O(^3P)$ atoms only $OCCl_2$ is formed; CO···HCl complexes are also observed as a result of secondary photolysis reactions	465
O	CH_3OCH_3	Ar matrix IR; $^{1,2}H$, $^{16,18}O$	O atoms generated by photolysis of O_3 or N_2O react with CH_3OCH_3 to give two conformers of CH_3OCH_2OH	466
O	CH_4, CH_3OH	Ar matrix IR; $^{1,2}H$, $^{16,18}O$	$O(^1D)$ generated from O_3 reacts to give as the main products CH_3OH with CH_4 and CH_2O with CH_3OH	467
O	RH (saturated and unsaturated hydrocarbons)	gas phase LIF	hydrogen abstraction reactions studied; rotational and vibrational state distribution of OH analyzed; potential surfaces calculated	468
O	H_3CCCl_3	Ar matrix IR; $^{1,2}H$, $^{16,18}O$	$O(^1D)$ produced from O_3 gives various products that have been characterized, CCl_3CH_2OH being the main product; the reaction mechanisms are discussed	469
O	SiO	Ar matrix IR; $^{16,18}O$, $^{28,29}Si$	O atoms react with SiO to give SiO_2; the reaction SiO + $Cl_2 \rightarrow OSiCl_2$ is also studied	470
O	P_4, PH_3, PCl_3, PBr_3	gas phase chemiluminescence, LIF	characterization of the product PO_2	471
O	P_4	Ar matrix IR; $^{16,18}O$	O atoms produced by discharge of O_2 or by photolysis of O_3 give P_4O (C_{3v}) with a terminal PO bond, its isomer with a bridging bond and C_{2v} symmetry, linear P_2O, and (for higher discharge powers) PO and bent PO_2	472
O	PF_3, AsF_3	Ar or Kr matrix IR; $^{16,18}O$	O atoms formed by UV photolysis of O_3 react with EF_3 molecules to give OEF_3 (E = P or As)	473
O	PH_3	Ar matrix IR; $^{1,2}H$, $^{16,18}O$	O_3 forms a complex with PH_3, $O_3{\cdot}PH_3$; photolysis of $O_3{\cdot}PH_3$ gives H_3PO, H_2POH, and $(HO)_2HPO$ as the primary products; O atoms, produced by discharge of O_2, react with PH_3 to give PO, HPO, PO_2, PO_3 (with D_{3h} symmetry), HOPO, P_2O_5, H_2PO, and HPOH (from photoisomerization of H_2PO)	55
O	ClF	Ar matrix IR; $^{16,18}O$, $^{35,37}Cl$	O atoms formed by UV photolysis of O_3 react with ClF to form FClO; secondary reactions afford $FClO_2$	474

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
O	ICl	Ar, Kr or N_2 matrix IR; $^{16,18}O$, $^{35,37}Cl$	photolysis of a matrix containing O_3 and ICl results in O atom transfer to form first OICl and then O_2ICl; on deposition, a complex O_3·ICl is formed and this is highly photolabile, yielding OICl on irradiation at $\lambda > 470$ nm	475
O	HCl, HBr, HI	Ar or N_2 matrix IR; $^{1,2}H$, $^{16,18}O$	O atoms formed by UV photolysis of O_3 insert into the H−X bond to form HOX (X = Cl, Br, or I)	476
S	SiS	Ar or CH_4 matrix IR, Raman; $^{28,29,30}Si$, $^{32,34}S$	S atoms generated by photodissociation of OCS react with SiS to form linear SSiS, the bonding in which is compared with that of similar molecules	477
S	N, N_2	Ar matrix IR; $^{14,15}N$, $^{32,34}S$	action of a discharge on an Ar/S/N_2 mixture gives on deposition NS, NS_2, NSS, and N_2S	454
S	NO, $[NO]_2$	Ar matrix IR; $^{14,15}N$, $^{16,18}O$, $^{32,34}S$	S atoms generated by photodissociation of OCS add to NO and $[NO]_2$ to form SNO and two isomers of SN_2O_2; S atoms and other species produced in a discharge give, in addition to SNO, SNO^+, SSNO, and SNNO	276
S	PH_3	Ar matrix IR; $^{1,2}H$, $^{32,34}S$	S atoms produced by the action of a discharge on S_8 react with PH_3 to give $HSPH_2$, HPSS, $HSPS_2$, and, presumably, HSPH	478
S	PF_3, PCl_3, CH_4, C_2H_4, C_2H_2	Ar or CH_4 matrix IR; $^{1,2}H$	S atoms, generated by photolysis of OCS at $\lambda = \sim 230$ nm, add to PX_3 (X = F or Cl) to form SPX_3; $S(^1D)$ inserts into a C−H bond of CH_4 to form CH_3SH, with H_2CS as a secondary product; addition to C_2H_4 yields thiirane, $\overline{SCH_2C}H_2$, whereas C_2H_2 gives H_2CCS, HC≡CSH and CS_2 as the main products, and thiirene, $\overline{SCH{=}C}H$, as a minor product	274
S	O_2, S	Ar, Kr or Xe matrix chemiluminescence	excited SO_2 molecules formed when S atoms diffuse in matrices containing O_2; recombination of S atoms gives an intense S_2 emission	273
S	S_2	Ar matrix IR; $^{32,34}S$	S atoms combine with S_2 to form the bent S_3 molecule (“thiozone”)	479
S	V, Nb, Ta	Ar matrix IR; $^{32,34}S$	discharged S vapor reacts with laser-ablated M atoms (M = V, Nb, or Ta) during co-condensation in an Ar matrix to give MS and angular SMS	480
Se	N, N_2	Ar matrix IR; $^{14,15}N$, $^{76,80}Se$	action of a discharge on an Ar/Se/N_2 mixture gives on deposition NSe, NSe_2, and NSe_2^+	455
Se	O_2	Ar matrix IR; $^{16,18}O$	Se atoms produced by the action of a discharge on Se vapor react with O_2, and analysis of the products trapped under various conditions of deposition leads to the characterization of SeO, SeO_2, SeO_3, the complex $(Se_2)(O_2)$, SeSeO, SeOO, Se_2O_2, and OSeOO	481
Se	Se_2	N_2 matrix resonance Raman; $^{76,80,82}Se$	double furnace is used to produce a gas mixture of Se and Se_2, which is then co-condensed with an excess of N_2; annealing then results in the formation of Se_3	482
Te	CO	CO or Ar matrix IR; $^{12,13}C$, $^{16,18}O$	Te atoms produced by photodissociation of H_2Te add to CO to form OCTe	272
Te	Te_2	N_2 matrix resonance Raman; $^{126,130}Te$	annealing an N_2 matrix containing Te atoms and Te_2 results in the formation of Te_3	110
			Group 17	
F	HCN	Ar matrix IR, EPR; $^{1,2}H$	F atoms add to HCN to form H(F)C=N, which isomerizes to FC=NH on photolysis at $\lambda = \sim 355$ nm; F atoms can diffuse over long distances in solid Ar at $T > 20$ K and react with other molecules of interest	210
F	CH_3ONO	Ar matrix IR; $^{1,2}H$	F atoms produced in a microwave discharge react with CH_3ONO to give FNO, H_2CO, HF, and NO as the chief products	483
F	CH_3OH	Ar matrix IR; $^{1,2}H$	H abstraction and other reactions take place; CH_2OH is the main product; H_2CO and HCO also observed	484
F	CH_3F	Ar matrix IR; $^{1,2}H$	CH_2F and HCF are among the products; at higher F atom concentrations, CH_2F_2 is detected	485
F	NH_3	Ar matrix EPR; $^{1,2}H$, $^{14,15}N$	the complex H_2N·HF is formed; this is planar with C_{2v} symmetry and has a binding energy estimated to be 12.3 kcal mol^{-1}	486
F	NO_2	N_2 matrix IR; $^{14,15}N$, $^{16,18}O$	thermal reaction of F atoms with NO_2 gives ONOF, which photo-rearranges to FNO_2 ($\lambda < 400$ nm)	212
F	O_2	O_2, N_2 or Ar matrix IR; $^{16,18}O$	F atoms react with O_2 to form O_2F as well as OF_2 and O_2F_2; the O−O bond in O_2F has double-bond character	487
Cl, Br, I	various arenes	CCl_4 or C_6H_6 solutions containing X_2 molecules UV−vis	photolysis of the Br_2·arene and I_2·arene complexes leads to π-bonded Br·arene and I·arene complexes; Cl·arene complexes are formed on photolytic generation of Cl from Cl_2 in CCl_4	488
Cl	NO_2	Ar matrix IR; $^{14,15}N$, $^{16,18}O$, $^{35,37}Cl$	Cl atoms react thermally with NO_2 to give ClONO, $ClNO_2$, and a third isomer OClNO formed by insertion of a Cl atom into an N−O bond of NO_2	214
Cl	O_2	Ar or O_2 matrix IR; $^{16,18}O$, $^{35,37}Cl$	photolysis of Cl_2 in an O_2 matrix gives the ClOO radical; ClOO is also formed by the matrix reaction ClO + O following photolysis of OClO	489
Cl, Br	Br_2, BrCl, ICl, IBr	gas phase atomic resonance fluorescence	rate coefficients reported for reactions of $Cl(^2P_{3/2})$ and $Br(^2P_{3/2})$ atoms; evidence of trihalogen intermediates	283

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Cl, Br, I	ClO_2	Ar matrix IR, UV−vis; $^{16,18}O$, $^{35,37}Cl$	evidence that X atoms (X = Cl, Br, or I) react with OClO to form both XOClO and $XClO_2$; near-UV radiation causes $ClClO_2$ and $BrClO_2$ to isomerize back to ClOClO and BrOClO, respectively	211
Br	C_6H_6	Ar matrix IR, UV−vis; $^{1,2}H$	the complex $Br{\cdot}C_6H_6$ characterized; the spectra indicate that the symmetry is lower than C_{6v}	280
Br	NO_2	Ar matrix IR; $^{14,15}N$, $^{16,18}O$	$BrNO_2$ is produced initially but isomerizes to BrONO on photolysis at $\lambda > 300$ nm	213
Br	NO_2	gas phase IR	isomer *cis*-BrONO is the main product; at room temperature rapid decomposition occurs to regenerate Br and NO_2, but at lower temperatures isomerization to $BrNO_2$ sets in; rate constants established	285
Br	O_2, O	Ar matrix IR, UV−vis; $^{16,18}O$, $^{79,81}Br$	products $O_2Br{\cdot}$, ${\cdot}BrO_2$, and ${\cdot}BrO$ characterized; photoisomerization of $O_2Br^{\bullet}$ to $^{\bullet}BrO_2$ is reversible	490
Br	O_2	Ar matrix flash pyrolysis of $Br_2/O_2/Ar$ gas mixtures IR, UV−vis; $^{16,18}O$, $^{79,81}Br$	reactions summarized in Figure 17 shown to take place	56
Br, I	H_2O, HCl	Ar matrix IR; $^{1,2}H$	halogen atom complexes of the types $X{\cdot}H_2O$ and $X{\cdot}HCl$ (X = Br or I) characterized	281
Br	Br_2	Ar, Kr or Xe matrix Raman	evidence for the formation of the Br_3 radical	282
I	O_2	Ar or O_2 matrix IR, UV−vis	the radical IOO is formed on deposition; photolysis at $\lambda = 254$ nm results in dissociation to IO + O followed by recombination to give O=I=O	156
			Group 18	
noble gas solids	H, F, O, S, HX (X = Cl or I), H_2O, H_2S, Cl_2	reviews	reviews of the photodynamics of molecules trapped in noble gas solids	136, 491
noble gas atoms	H_2, HF, HCN, CO_2	theoretical studies	structures and energies of complexes of noble gas atoms with various small molecules are investigated	492
He, Ne, Ar, Kr	HF	theoretical studies	compounds of the type HNgF (Ng = He, Ne, Ar, or Kr) each have a linear $^1\Sigma^+$ electronic ground state; the activation barrier for the decomposition HNgF → HF + Ng is calculated to be 8.6, 28.0, and 34.7 kcal mol^{-1} for Ng = He, Ar, and Kr, respectively; these charge-transfer species may be strongly stabilized in a polar matrix environment, the charge transfer occurring from F to the NgH moiety (0.4−0.75e)	493
He, Ne	H_2^+	theoretical studies	collisional properties and reaction probabilities calculated for the reaction $Ng + H_2^+ \rightleftharpoons NgH^+ + H$ (Ng = He or Ne)	494
Ne	HCN	theoretical studies	potential energy surfaces of the Ne/HCN system investigated by ab initio methods	495
Ne, Ar, Kr, Xe	$M(CO)_5$ (M = Cr, Mo, or W)	noble gas matrix, inert solvent IR, UV−vis; $^{12,13}C$ time-resolved studies	$(Ng)M(CO)_5$ complexes with C_{4v} symmetry formed (Ng = Ar, Kr, or Xe) and characterized by their IR spectra in the ν(CO) region and visible absorption bands	145, 496
Ne, Ar, Kr, Xe	OH	Ne, Ar, Kr, or Xe matrix digital emission and excitation spectroscopy	OH generated by vacuum-UV photolysis of H_2O forms $Ng{\cdot}OH$ complexes (Ng = Ne, Ar, Kr, or Xe)	497
Ar, Kr, Xe	$M(CO)_5$ (M = Cr, Mo, or W)	gas phase flash photolysis fast time-resolved IR spectroscopy	photolysis of $M(CO)_6$ at $\lambda = 355$ nm gives $M(CO)_5$, which reacts with the noble gas to form $(Ng)M(CO)_5$ complexes; rate constants have been determined for Ng = Xe and M = Cr, Mo, or W; bond dissociation energies estimated for some of the complexes	298
Ar	HF	Ar matrix IR; $^{1,2}H$, $^{36,40}Ar$	irradiation of an Ar matrix doped with HF at $\lambda = 127{-}160$ nm photodissociates the HF, leading to the formation of HArF; this product photobleaches under UV irradiation	243a
Ar	HF	theoretical studies	survey of the properties of HArF as calculated up to the CCSD(T)/aug-cc-pV5Z level; the molecule is stable by 0.15 eV compared with the dissociated atoms	243b
Ar, Kr, Xe	HF	gas phase IR, radiofrequency and microwave spectroscopy, Stark spectra; $^{1,2}H$	van der Waals complexes $Ng{\cdot}HF$ (Ng = Ar, Kr, or Xe) characterized; rotational and hyperfine constants and dipole moments determined	287, 498
Ar	NO	gas phase fluorescence excitation spectra	van der Waals complex $Ar{\cdot}NO$ undergoes direct photodissociation at $\lambda = 224$ nm	499

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Ar, Kr, Xe	S	gas phase and Ar, Kr, or Xe matrix photoluminescence	emission spectra of ArS, KrS, and XeS observed in the near-IR; emission lifetimes are in the order of several μs; a broad emission centered at 346 nm in crystals of Xe is assigned to the Xe−S charge transfer exciplex	277
Ar, Kr, Xe	F	gas phase molecular beam study, magnetic and mass spectrometric analysis	cross sections determined for scattering of ground state F atoms; potential energy curves investigated for the systems Ar−F, Kr−F, and Xe−F	500
Ar, Kr, Xe	CUO	Ne IR; ^{12,13}C, ^{16,18}O	CUO formed from the reaction of laser-ablated U atoms with CO interacts specifically with Ar, Kr, or Xe atoms; binding energy of the CUO···Ar complex estimated to be 3.2 kcal mol^{-1}	501
Kr, Xe	F_2	Kr or Xe matrix IR	FKrF or FXeF generated by photolysis of F_2 in a Kr or Xe matrix, respectively	295
Kr, Xe	F_2, ClF, Cl_2	Ar, Kr or Xe matrix IR, Raman; ^{35,37}Cl	photolysis of noble gas−XY mixtures (X, Y = F, Cl) gives KrF_2, XeF_2, $XeCl_2$, and XeClF identified by their IR and Raman spectra	502
Kr	OH	gas phase free jet expansion LIF	OH produced by photolysis of CH_3(H)CN−OH yields Kr•OH, which has been characterized by vibrational analysis; the lower limit of the binding energy of the complex is ∼1131 cm^{-1}	503
Kr, Xe	HCl, HBr, HI	Kr, Xe, or Ne matrix IR; ^{1,2}H	UV irradiation of the HX molecule (X = Cl, Br, or I) in a Kr or Xe matrix results in photodissociation of HX and the identification of the noble gas compounds HKrCl, HXeH, HXeCl, HXeBr, and HXeI; with an Ne matrix, however, there is appreciably less stabilization; the halide molecules can be regarded as neutral charge-transfer molecules HNg^+X^- (X = halogen), and their role in the photodissociation of HX in a solid noble gas is discussed	237a,c,d−h
Kr, Xe	HCN	Kr or Xe matrix IR; ^{1,2}H	molecules HKrCN, HXeCN, and HXeNC have been characterized following photolysis of HCN in a Kr or Xe matrix; HXeNC photodissociates rapidly under 350 nm radiation, whereas HXeCN is stable; the isomerization HXeNC → HXeCN is induced by pumping the fundamental vibrations of HXeNC at 3300 and 1200 cm^{-1}; geometries, energetics, and activation barriers calculated for HNgCN and HNgNC molecules (Ng = Kr or Xe)	241
Kr, Xe	HX, H_2O	review	review of the synthesis and characterization of HNgX compounds, where Ng = Kr or Xe and X = an electronegative atom or group; bonding is discussed	238
Kr, Xe	(η^5-C_5R_5)M$(CO)_2$ (M = Mn or Re; R = H, Me, or Et)	*n*-heptane or supercritical noble gas solution flash photolysis, fast time-resolved IR spectroscopy	formation and decay of the complex (η^5-C_5R_5)M$(CO)_2$(Ng) (Ng = Kr or Xe) monitored; kinetics and activation parameters measured for the reaction of the complex with CO	299
Kr, Xe	(η^5-C_5Me_5)RhCO	liquid noble gas solution flash photolysis, fast time-resolved IR spectroscopy	photolysis of (η^5-C_5Me_5)Rh$(CO)_2$ gives (η^5-C_5Me_5)RhCO, which adds Kr or Xe to give (η^5-C_5Me_5)RhCO(Ng); reaction kinetic parameters have been determined	300
Xe	(η^5-C_5H_5)M$(CO)_3$ (M = Nb or Ta)	supercritical Xe solution flash photolysis, fast time-resolved IR spectroscopy	photolysis of (η^5-C_5H_5)M$(CO)_4$ yields (η^5-C_5H_5)M$(CO)_3$, which adds Xe to give (η^5-C_5H_5)M$(CO)_3$(Xe); kinetics of the formation and decay of the complexes have been studied	301
Xe	H_2S	Xe matrix IR; ^{1,2}H	photodissociation of H_2S by irradiation at $\lambda = 193$ or 235 nm yields H, SH, and S atoms; annealing to 50−60 K and then recooling to 7.5 K affords HXeSH for which significant ion-pair character is predicted; with respect to the dissociation HXeSH → H + Xe + SH, D_e is estimated to be ∼0.4 eV	240
Xe	HBr, HI	Xe matrix IR; ^{1,2}H	photolysis of HX (X = Br or I) in solid Xe gives inter alia $XeHXe^+$; annealing of the solid then produces, in addition, HXeX, HXeH	235
Xe	H_2	Ar matrix emission and excitation spectra; ^{1,2}H	XeH and Xe_2H detected and characterized after photolysis of an Ar matrix doped with H_2	504
Xe	HI	Xe matrix IR; ^{1,2}H	study of the formation and IR-induced decomposition of HXeI; the molecule has a low dissociation energy, $D_0 = 2950$ cm^{-1}; formation from the atoms is opposed by a barrier estimated to be ∼700 cm^{-1}	237b
Xe	HX (X = Cl, Br, or I)	Xe matrix IR; ^{1,2}H	UV photolysis results in the efficient generation of $[Xe-H-Xe]^+$ ions, which are believed to be vibrationally bound	137

Table 4 (Continued)

element	reagent	method of investigation	findings	ref
Xe	O	Xe matrix emission spectra luminescence	study of Xe excimer species with oxygen, XeO* and Xe_2O*	505
Xe	hydrocarbons	hydrocarbon matrix IR	irradiation of the Xe-doped matrix at 15 K with fast electrons gives a product identified by its IR spectrum as XeH_2; the spectrum indicates that the compound decays when the matrix is annealed and reacts with *trans*-2-butene	236
Xe	H_2O	Xe matrix IR; $^{1,2}H$	photodissociation of H_2O to H + OH is effected by irradiation at 193 nm with an ArF laser; annealing to 35 K then gives H_2O and O_3; further annealing to 48 K gives XeH_2 and HXeOH; calculations predict substantial ion-pair character for HXeOH, which is ~4.69 eV higher in energy than Xe + H_2O but ~0.6 eV lower than H + Xe + OH	239
Xe	HNCO	Xe matrix IR; $^{1,2}H$	photolysis at 193 nm followed by annealing of the matrix affords HXeNCO; this is photolabile, decomposing under irradiation at $\lambda = \sim 405$ nm	242
Xe	Cl_2	Xe matrix IR, Raman; $^{35,37}Cl$, Xe isotopes	$XeCl_2$ formed and trapped either following passage of an Xe/Cl_2 mixture through a discharge or on photolysis of a Cl_2-doped Xe matrix	296

metastable with respect to Xe + HY, but bound with respect to Xe + H + Y, with energies on the order of 30−40 kJ mol^{-1} (2500−3400 cm^{-1}). As noted earlier (section III), binding of comparable strength is achieved in organometallic complexes of the type Xe·M(CO)$_5$ (M = Cr, Mo, or W).[145] An even stronger bond is predicted in the hypothetical complex $[Au-Xe]^+$ with a dissociation energy of 126 kJ mol^{-1}.[297] Organometallic xenon complexes other than Xe·M(CO)$_5$, which have been characterized as transients in the gas phase[298] and in solution,[145] include Xe·(η^5-C_5R_5)M-(CO)$_2$ (M = Mn or Re; R = H, Me, or Et),[299] Xe·(η^5-C_5Me_5)RhCO,[300] and Xe·(η^5-C_5H_5)M(CO)$_3$ (M = Nb or Ta).[301] Longest lived of these is Xe·(η^5-C_5H_5)Re(CO)$_2$, which exchanges Xe for CO in supercritical xenon with a second-order rate constant of 2.0×10^3 dm^3 mol^{-1} s^{-1} at 298 K. The reactivity of the complexes, which is similar to that of analogous alkane complexes, then increases in the order $Re \leq W \approx Ta < Nb < Mo \approx Cr \approx Mn$.[301]

VI. Summarized Research in the Field

Table 4 is designed to summarize representative studies of the reactions that main group atoms undergo, with matrix isolation as the primary method of attack. The atoms are listed first in order of periodic group and then of atomic number within the group. Although the coverage is extensive, highlighting particularly studies undertaken in the past two decades, it does not pretend to be comprehensive. Nevertheless, we dare to hope that the table reflects faithfully the areas of activity, some of the strategies of investigation, and the findings typically delivered by these investigations.

VII. Acknowledgments

We acknowledge with thanks (i) the Deutsche Forschungsgemeinschaft for financial support and the award of a Habilitation grant (to H.-J.H.), (ii) the EPSRC for the award of an Advanced Fellowship (to T.M.G.), as well as financial support of the research at Oxford (for A.J.D.), and (iii) Dr. Andrew Shaw for helpful advice.

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