

Photochemistry of Small Molecules in Low-Temperature Matrices

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I. Introduction

This review is concerned with photochemical processes and the photoproducts of small molecules in low-temperature matrices. The subject matter includes molecular photochemistry of a wide range of compounds but excludes organic and organometallic compounds other than C₁ compounds and selected C₂ and C₃ compounds. The review is organized according to photochemical processes with special sections on photochemical generation of ions and charge stabilization in matrices and on energy transfer and laser-induced fluorescence. Vibrational photochemistry is treated under headings of rotational isomerization, intermolecular photochemical reactions, and photobleaching of ions (sections IIIG, IVA, VC3). The review is concluded by some comparisons with methods for studying short-lived species in mobile phases.

The previous review contains an introduction to matrix isolation and summarizes matrix photochemistry involving atoms.¹ Also included is a discussion of the role of intermolecular complexes, diffusion, and the cage effect in atom-transfer reactions. There are several reviews which overlap with some of the material covered here: IR spectra of radicals and intermediates (1973),² matrix photochemistry (1976),⁴ radicals and ions (1978),⁵ molecular ions (1979, 1980, and 1983),⁶ and organic matrix isolation (1980).⁷ The present review aims to have complete literature coverage up to and including 1983, with a few 1984 references.

II. Photoelimination

Photoelimination is surely the photoprocess which has found most frequent application in the generation of unstable molecules in low-temperature matrices. Not only may atoms such as hydrogen and halogen be eliminated but also molecular groups such as XF (X = halogen), N₂, CO, and CF₄. Since the photoelimination of atoms from molecules has been considered extensively in the previous review, I will concentrate on elimination of molecular fragments. Topics such as the photodissociation of diatomic metals will not be considered again. In the examples of atomic elimination discussed below, I will lay stress on the fragments which are generated. Molecular photoelimination differs energetically from atomic dissociation in the sense that there may be considerable bond making in the transition state. Such bond making must be particularly important in the elimination of H₂ because of the strength of the H-H bond and the proximity of two

TABLE I. Molecular Photoelimination in Matrices^a

photoproducts		precursor	ref
ClF	F ₂ CO	F ₃ COCl	46
IF	CHF?	CHF ₂ I	55
IF	CHI?	CHI ₂	55
ClF, BrF	SF ₄	SF ₅ X	49
HX	XCCH	C ₂ H ₂ X ₂ (X = F, Cl)	56, 57
HX	C ₂ H ₂	C ₂ H ₃ X (X = F, Cl, Br)	57
HF	CiCCH	CH ₂ CFCl	57
HCl	FCCH	CH ₂ CFCl	57
HX	CH ₃ CCH	CH ₃ C(H)C(H)X (X = F, Cl)	57
O ₂	CF ₄	F ₃ COOF	68
O ₂	F ₃ COCF ₃	F ₃ COOOCF ₃	68
O ₂	H	HO ₂	17
O ₂	CH ₃	CH ₃ O ₂	17
N ₂	HN	HN ₃	72
N ₂	XN	XN ₃ (X = Cl, Br)	72, 73
N ₂	NCN, C	N ₃ CN	71, 75
N ₂	CH ₂ NH	CH ₃ N ₃	26, 69, 70
N ₂	HNE	EH ₃ N ₃ (E = Si, Ge)	29
N ₂	FNCO	FC(O)N ₃	76a
N ₂	CH ₃	(CH ₃) ₂ N ₂	17
N ₂	CF ₂	F ₂ CNN	77
N ₂	CH ₂ ?, C ₂ H ₄	CH ₂ N ₂	79
N ₂	CH	CHN ₂	80
N ₂	CH ₂	H ₂ CNN	81-83
N ₂	H ₂ CCO	N ₂ C(H)CHO	84
N ₂	HCCN	N ₂ C(H)CN	85a
N ₂	C ₂ F ₆	F ₃ CNNCF ₃	85b
N ₂	(HCN) ₂	s-tetrazine	86
CO	X	XCO (X = H, N, C, F)	see ref 1
CO	NH	HNCO	87, 74
CO	NF	FNCO	76a
CO	CISF	FC(O)SCl	76c
CO	CH ₂ OH	(CH ₂ O) ₂	89b
CO	CH ₂ O	(CHO) ₂	89a
CO	CH ₃	CH ₃ CO or CH ₂ CHO	15
CO	CH ₃ OH	HCO ₂ CH ₃	88
CO ₂	CH ₄	HCO ₂ CH ₃	88
CO, CO ₂	H ₂ O	HCO ₂ H	90
CO ₂	H	HOCO	90
CO ₂	R, R'	RC(O)OO(O)CR' (R', R = Me, Et, Ph)	18, 91
CS ₂	(CF ₃) ₂ S	(CF ₃ S) ₂ CS	76c
CF ₄	O ₂	F ₃ COOF	68
CF ₄	EF ₂	F ₃ CEF ₃ (F = S, Se)	92
CF ₄	X	F ₃ CXF (X = Cl, Br, I)	64
CH ₄	Cp ₂ W	Cp ₂ W(CH ₃)H	93
CH ₄	M	M(CH ₃)H (M = Fe, Mn)	20, 94
CH ₃	CuH	Cu(CH ₃)H	95
F ₂ CO	OF ₂	F ₃ COOF	68
F ₂ CO	F ₃ COOF	F ₃ COOOCF ₃	68
F ₂ CO	SF ₂	F ₃ CS(O)F	76b
HCO	H ₂ O	CH ₃ O ₂	17
HCN	CH ₂ NH	(CH ₂ N ₂) ₂	105
HBO	?	HBOB(H)OO	22
H ₂ CO	HCO ₂ H	H ₂ COC(H)OO	96
HNO	H ₂ O	CH ₃ ONO	97-100
HNO	H ₂ C=NCH ₃	(CH ₃) ₂ NNO	101

^a Excluding H₂ and F₂ elimination.

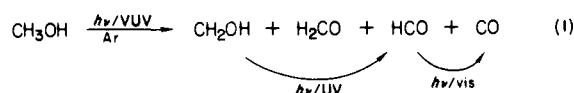
hydrogen atoms when bound to a common atom. Since the experimental distinction between elimination of atoms and homonuclear diatomics is a fine one (see ref 1, section IV), some of the photoprocesses will be considered in pairs. Molecular photoelimination processes (other than elimination of H₂ and F₂) are summarized in Table I.

A. Photoelimination of H and H₂

Photoelimination of H and H₂ has been a prolific source of molecular fragments. For instance, the major sources of dihalocarbenes have been (i) the photolysis

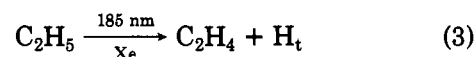
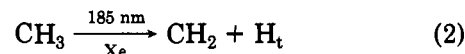
of dihalomethanes and (ii) the method of codepositing alkali atoms and halomethanes.⁸⁻¹² Table II summarizes some of the spectroscopic properties of matrix-isolated dihalocarbenes and halocarbenes. (This is an expanded version of a table published by Bondybey and English).¹¹ Despite several attempts no iodocarbenes have been detected.¹²

The vacuum-ultraviolet (VUV) photolysis of methanol illustrates the combination of atomic and molecular photodissociation of hydrogen.^{13,14} Four products are observed on VUV photolysis: CH₂OH, CH₂O, HCO, and CO. However, further UV (Hg arc) photolysis of CH₂OH causes growth in the HCO bands but not those of CH₂O, indicating that this process involves loss of H₂ not H. The formyl radical is decomposed by visible photolysis in a final stage of H atom photoelimination.



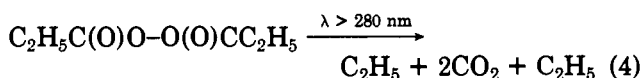
Such multiple loss of H/H₂ is a common feature of VUV photolysis. Indeed, recent experiments have been designed to obtain greater selectivity by using windowless discharge and abstraction reactions with fluorine atoms prior to deposition.^{5,14-16} This experiment also illustrates the effect of an open-shell electronic structure on the absorption spectrum and on the photochemistry. Methanol with its closed-shell structure is transparent in the UV and requires VUV radiation to eliminate H or H₂. However, CH₂OH and HCO with their open-shell structures have absorptions in the UV and visible spectrum. Accordingly, much longer wavelengths suffice to effect further elimination.

Further illustrations of the susceptibility of open-shell molecules to photochemical reaction will be found throughout the review, but there are a number of recent examples which illustrate this principle by H/H₂ elimination. UV photolysis of HO₂ induces dissociation to H + O₂.¹⁷ X radiation has been used to generate radicals from hydrocarbons trapped in Xe matrices. Subsequent photolysis (λ = 185 nm) of CH₃ results in an increase in trapped hydrogen atoms, H_t, detected by ESR. The byproduct CH₂ is not detected. Similarly, ethyl radicals are photolyzed to generate ethylene:¹⁷



In methane matrices, CH₂ may be generated similarly, but its presence is betrayed by reaction to form C₂H₅ and C₂H₃ on annealing.¹⁷

The ethyl radical has also been studied by IR spectroscopy following UV irradiation of dipropionyl peroxide, a method which circumvents the cage effect by placing two molecules of CO₂ between the radical products.¹⁸



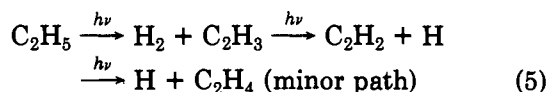
Photolysis of C₂H₅ (λ < 280 nm) generates a small amount of C₂H₄ and larger amounts of C₂H₂ together

TABLE II. Molecular Constants of Halocarbenes in Ar Matrices^a

species	T_0	ν_1''	ν_2''	ν_3''	ν_1'	ν_2'	ν_3'	τ^b	ref
HCF	17330		1405	1182		988			8, 9
HCCl			1201	811					10
FCF	36878	1218	688	1110		494		0.027	see 11
FCCl	24983	1148	442	740	1265	392	712	0.33	see 11
FCBr	23300	1157	656	327					12
CICCl	17093	726	333	745	626	309		3.6	see 11
CICBr	16044	744	260	612		246	526	5.6	see 11
BrCBr	14962	595	196	640.5	468	186	588	14.5	see 11

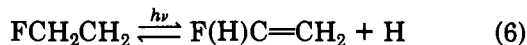
^aIn cm^{-1} . ^bLifetime of excited state at energy T_0 above ground state in ns.

with products of reaction with CO_2 . It is proposed that C_2H_2 is formed via production of the vinyl radical which in turn loses H too rapidly to be observed.¹⁸



Clearly this study is more informative than the ESR method which does not follow the diamagnetic products.

A further example of H_2 elimination from radicals comes from CH_2F which yields CF on photolysis.¹⁵ Reaction of F atoms with C_2H_4 is a source of $\text{C}_2\text{H}_4\text{F}$ which proves to be photostable in the matrix. However, using ^2H -labeled ethylene, it is found that FCD_2CH_2 and FCD_2CD_2 are photosensitive, whereas FCH_2CD_2 is not.¹⁹ It is proposed that $\text{C}_2\text{H}_4\text{F}$ decomposes by loss of H atoms, but that the back reaction is fast for the isomers containing a CHF group:



This in-cage recombination may take place via a tunneling mechanism,¹⁹ but this would imply a very rapid reaction if no decomposition of FC_2H_4 is to be observed.

A group of photosensitive open-shell molecules of a different type are the dihydrides of manganese and iron.²⁰ These molecules, formed by photolysis of the metal atoms in H_2 doped matrices reductively eliminate H_2 on long-wavelength photolysis (see ref 1, section IIB2 and eq 15).

A final case of multiple loss of H or H_2 is formed by H_3BNH_3 and its photoproducts: HNBH, HNB, and BN.²¹ Unfortunately, there is no information as to whether atomic or molecular hydrogen is lost. BN is detected by its UV spectrum on VUV photolysis in neon matrices, but HNBH and HNB are detected by IR spectroscopy following VUV photolysis in argon. Photolysis of H_3NBD_3 and D_3NBH_3 reveals an unexpected exchange process which results in statistical mixtures of HNB and DNBH. The molecule HNBH has a high B-N stretching force constant (1314 N m^{-1}) comparable to its isoelectronic analogue, acetylene (1580 N m^{-1}), suggesting considerable multiple bonding. HNBH also has a remarkably high N-H stretching frequency (3700 cm^{-1}) as does HNB. The IR fundamentals for HNB may be found in Table III together with those for other HXY molecules observed in matrices.^{8-10,21-39} Almost all of these molecules have been synthesized photochemically.

Many of these molecules have been studied by other spectroscopic methods, too. For instance, in addition to IR, UV, and ESR studies,^{23,40,41} the photofragment

TABLE III. Vibrational Fundamentals of Neutral HXY in Argon Matrices^a

	ν (HX)	δ (HXY)	ν (XY)	ref
H^{11}BO	(2849) ^b	754	1817	22
HCC	3612		1848	23
HCN	3303	720	2093	24
HCO	2483	1087	1863	25
HCF		1405	1182	8, 9
HCCl		1201	811	10
HN^{11}B	3675		2035	21
HNC	3620	477	2029	26
HNO	2716	1505	1563	27
HNF		1432	1000	28
HNSi	3583	523	1198	29
HNGe	3521	394	969	29
HONa		337	431	30
HORb		309	354	30
HOCs		310	336	30
HOAl	3790		810	31
HOGa	3692	424	613	31
HOIn		422	523	31
HOO	3414	1389	1101	32
HOF	3537	1359	886	33 ^c
HOCl	3578	1239	728	34
HOBBr	3589	1164	626	34
HOI	3597	1103	575	35
HSiF	1913	859	834	36
HGeCl	1862			37
HGeBr	1858	701	283	38
HPO	2095		1188	39

^aIn cm^{-1} . ^bCalculated from $\nu(\text{BD})$ of DBO. ^c N_2 matrix.

from acetylene, C_2H , has recently been studied by VUV spectroscopy in matrices⁴² (see Figure 1, section IIC).

B. Photoelimination of F, F_2 , and XF (X = Cl, Br, I, H)

1. **Photoelimination of F and F_2 .** One of the classic papers on fluorine atom photoelimination is surely that of Arkell et al.⁴³ who investigated the generation of OF from OF_2 . Arkell observed that shorter photolysis wavelengths are required than in the gas phase and that the yield decreased with increasing wavelength, reaching zero at 366 nm. That these are qualitative yields appropriate to IR detection and mercury-arc photolysis is demonstrated by the detection of OF using Raman spectroscopy following laser photolysis at 458 or 488 nm.⁴⁴ Evidently the high laser intensity allows the use of photochemical processes with lower quantum yields.

The photochemistry of UF_6 provides unique insight into quantum yields of fluorine elimination. Paine et al.⁴⁵ followed the production of UF_5 at 561 and 584 cm^{-1} after UV photolysis of UF_6 in Ar and Xe with light of bandwidth 10 nm. They observed a constant quantum yield, ϕ , over the $\tilde{\text{B}} \leftarrow \tilde{\text{X}}$ absorption (250–300 nm) which dropped sharply at the long-wavelength edge. Over the $\tilde{\text{A}} \leftarrow \tilde{\text{X}}$ absorption (340–410 nm) the quantum yield was

$<10^{-4}\phi$. In CO matrices which scavenge fluorine atoms (see ref 1, section IVD), the product conversion increased to 100%. Clearly Arkell's observation of increasing yield with photon energy, interpreted as a requirement for excess translational energy to overcome the cage effect (see ref 1, section VC4), does not apply to UF_6 in its \tilde{B} excited state.

Two examples in which photoelimination of F_2 is strongly suspected are (i) the matrix photolysis of F_3COF yielding F_2CO but not F_3CO ,⁴⁶ and (ii) the photolysis of F_3NO yielding FNO but not F_2NO .⁴⁷ Corroborating evidence in the first case comes from photolysis of F_3COCl which gives ClF (see below). There are two difficulties associated with arguing for molecular F_2 elimination on the basis of the absence of radical products: first, the radicals may be much more photosensitive than the precursors and may therefore exist in very low concentration in the photostationary state; second, any F_2 should be subject to secondary photolysis itself which would, in turn, give the radical products. Photolysis of F_2 can only be avoided at wavelengths longer than 450 nm where it no longer absorbs.⁴⁸ This photosensitivity also complicates testing for F atoms with CO.

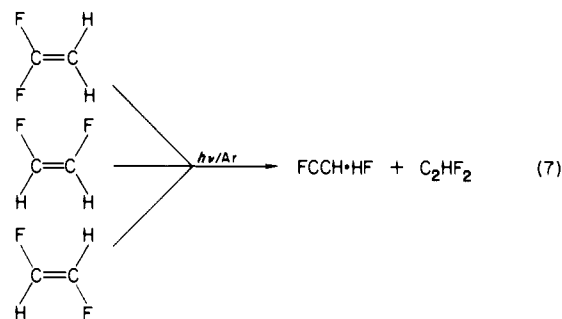
Photolysis of SF_6 with a windowless lamp during deposition results in SF_4 , SF_5 , and probably SF_5^- (see section VB). Evidence for production of SF_4 in a primary step was obtained from the detection of ClF and BrF on photolysis of SF_5X .⁴⁹ Here the case for molecular elimination is weakened slightly by using simultaneous deposition and photolysis. On the other hand the recombination of ClF and SF_4 on annealing suggests that the two molecules are present as a cage pair. This reaction is one of the few examples of oxidative addition in a matrix. SF_6 has also been photolyzed with a hydrogen discharge lamp⁵⁰ but the assignments differ from those of Smardzewski and Fox.⁴⁹ The feature at 808/810 cm^{-1} assigned by Barefield and Guillory⁵⁰ to SF_2 is probably the same as the 812 cm^{-1} band assigned to SF_5 in ref 49. SF_2 has since been found to absorb in matrices at 804 and 832 cm^{-1} .⁵¹ The second feature of SF_5 (551 cm^{-1}) was assigned to SF_4 in ref 50; direct matrix isolation of SF_4 demonstrates this to be incorrect.⁴⁹ This example illustrates one of the commonest weaknesses among matrix-isolation papers. It is not sufficient to assign bands by comparison with gas-phase spectra even if there is agreement within 1%. It is essential that no bands be assigned to stable compounds without verification by direct matrix isolation of those compounds.

The recent claim that it is possible to dissociate SF_6 in matrices with isotopic selectivity using a high power CO_2 laser⁵² (IR multiphoton dissociation) has been shown convincingly to be a spectroscopic artefact of damage to the matrix by the laser.^{53,54}

2. Photoelimination of XF ($X = Cl, Br, I, H$). It is easier to obtain convincing evidence for molecular elimination of the interhalogens XF than of F_2 itself, since they may be recognized by their IR or UV/vis spectra. Since in situ loss of heavier halogen atoms is fairly uncommon, the presence of XF strongly suggests molecular elimination rather than atom recombination. Examples are the production of ClF and F_2CO from F_3COCl ,⁴⁶ of IF on photolysis of CHF_2I or CHF_2I_2 ,⁵⁵ and of XF on photolysis of SF_5X ($X = Cl, Br$).⁴⁹ BrF and

ClF were detected by their IR absorptions while IF was detected by its laser-induced emission (see section VI). (Unfortunately the photochemical behavior of F_3COF is not directly comparable to that of F_3COCl , since the latter shows extra pathways resulting in F_3COF and F_3COOCF_3 .)

Hydrogen halides would seem prime candidates for photoelimination in view of their high bond energies and photostability (HI excepted). In order to find a convincing example we have to turn to fluoroethylenes. The three isomeric difluoroethylenes all yield the HF -fluoroacetylene complex on selective VUV photolysis⁵⁶ (see also ref 57). In CO matrices the absorptions due to FCO and HCO are very weak suggesting only minor occurrence of radical pathways, whereas in Ar an additional product, C_2HF_2 , is identified:



The effect of CO matrices is explained in terms of suppression of the intersystem crossing necessary for atom photodissociation. More detailed IR studies of the VUV or argon resonance photolysis of vinyl fluoride show that the major product is the T-shaped π complex $C_2H_2\cdot HF$.⁵⁷ This is a more effective way of making the complex than the cocondensation method. Indeed, free acetylene and fluoroacetylene show much weaker absorptions than the complexes. Photolysis of vinyl chloride and bromide gives the corresponding HX complexes; when the precursor is CH_2CFCl both $C_2H_2\cdot HF\cdot HCl$ and $C_2HCl\cdot HF$ complexes are generated. The methylacetylene- HF complex has been observed similarly.⁵⁷

If it is possible to eliminate HF from fluoroethylenes, why is the major photochemical process in halo-methanes invariably hydrogen loss (see, e.g., ref 58)? It seems plausible that HF is a relatively minor product in, for instance, the photolysis of CH_3F ⁵⁹ because of in-cage recombination with methylene rather than because the pathway is not viable. Clearly the activation energy for reaction of HF with fluoroacetylene considerably exceeds that for HF with CH_2 .

C. Photoelimination of Halogen Atoms (Cl, Br, I) and HX ($X = Cl, Br, I$)

As has already been indicated in ref 1 (section III) loss of the heavier halogen atoms in matrices is relatively unusual. Some molecules such as ICl ⁶⁰ and CrO_2Cl_2 ⁴ which are very photosensitive in the gas phase are rendered photostable in matrices by the cage effect. In other examples the cage effect is circumvented by molecular elimination of XF (section IIB). There are exceptions: the cleanest source of the HCC radical for ESR spectroscopy is $HCCl$.⁴⁰ This radical is shown to have 72% spin density on C_α and only 3% on H (Figure

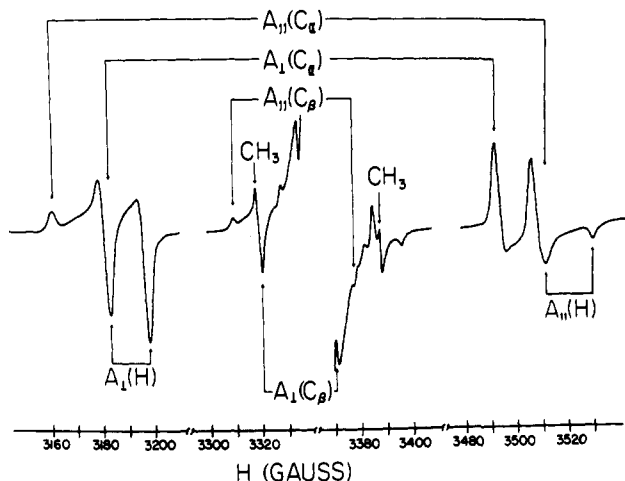
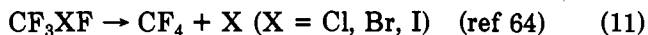
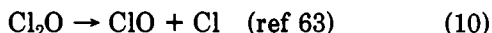
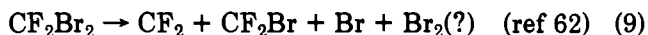
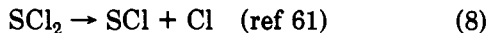


Figure 1. ESR spectrum $^{12,13}\text{C}_2\text{H}$ at 4 K arising from the natural abundance of ^{13}C in the photolysis products of HC_2I . The intense $^{12}\text{C}_2\text{H}$ lines have been omitted from the central portion of the spectrum ($\nu = 9398$ MHz). Reproduced with permission from ref 40. Copyright 1974, American Institute of Physics.

1). Other examples of in situ photolysis with IR detection are:

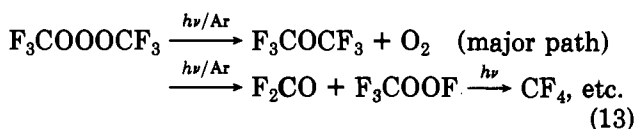
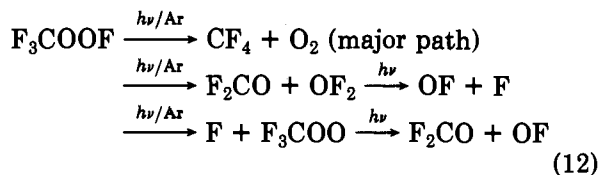


By using a windowless argon discharge during deposition, Miller and Andrews have generated BX_2 from BX_3 ($\text{X} = \text{Cl, Br}$) and deduced bond angles of about 125° from the $^{11}\text{B}/^{10}\text{B}$ and halogen isotopic structure in the IR absorptions.⁶⁵ Similar photolysis of MCl_4 ($\text{M} = \text{Si, Ge, Sn}$) gave MCl_3 and MCl_2 ,⁶⁶ species which had been observed previously by VUV photolysis of MHCl_3 . However, the absorptions of GeCl_3 have been reassigned. Both the boron and the group 14²⁷⁸ studies also gave ions which will be discussed in section VB.

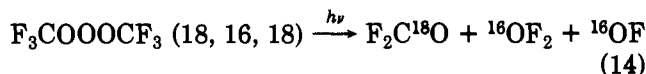
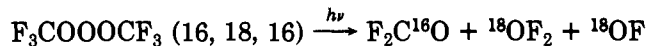
Argon resonance photolysis of vinyl chloride and vinyl bromide gives the T-shaped complexes: $\text{C}_2\text{H}_2\cdot\text{HX}$ ($\text{X} = \text{Cl, Br}$).⁶⁷ The complexes $\text{C}_2\text{HF}\cdot\text{HCl}$, $\text{C}_2\text{HCl}\cdot\text{HCl}$, and $\text{C}_2\text{H}(\text{CH}_3)\cdot\text{HCl}$ have been formed analogously.⁶⁷

D. Photoelimination of O and O₂

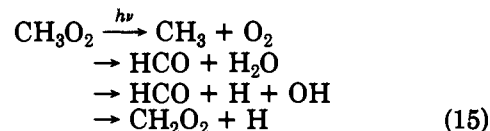
The conventional sources of oxygen atoms in matrices are discussed in ref 1. A more unusual example is the conversion of FNO_2 to FNO on prolonged photolysis⁶⁷ which presumably involves simultaneous dissociation of atomic oxygen. Examples of the production of molecular oxygen come from the major dissociation pathways of F_3COOF and $\text{F}_3\text{COOOCF}_3$,⁶⁸ and the photolysis of RO_2 ($\text{R} = \text{H, CH}_3$):



The byproducts of O_2 dissociation in the last two examples are CF_4 and F_3COCF_3 with no evidence for CF_3 . In some elegant isotopic work with ^{18}O , Smardzewski et al. photolyzed the (16, 18, 16) and (18, 16, 18) isotopomers of $\text{F}_3\text{COOOCF}_3$ and showed that the C–O bonds remain intact in the F_2CO photoproduct:⁶⁸

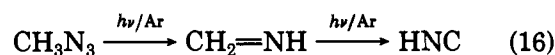


The peroxy radical $\text{CH}_3\text{O}_2\cdot$ has been detected by ESR following radiolysis of O_2 -doped methane and annealing to 46 K, and by photolyzing $(\text{CH}_3)_2\text{N}_2$ in O_2/CH_4 .¹⁷ Both CH_3O_2 and HO_2 are found to dissociate O_2 on 254-nm photolysis, but another photoprocess generates $\text{HCO} + \text{H}$ as further products from CH_3O_2 . The following photochemical reactions of CH_3O_2 have been postulated:



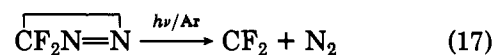
E. Photoelimination of N₂

Photochemical loss of dinitrogen from azido and diazo compounds is observed frequently in matrices. One of the well-known cases is that of azidomethane.^{26,69}



Both the primary rearrangement product, methanimine, and the secondary product, HNC (see Table II) have since been observed in interstellar space. Subsequently, Jacox and Milligan gave a very thorough force-field analysis of the CH_2NH spectrum.⁷⁰ Unlike their carbon analogues, photolysis of EH_3N_3 ($\text{E} = \text{Si, Ge}$) results in HNE without detection of the imines H_2ENH ²⁹ (Table II). Other early examples of dinitrogen loss from azides are the photolysis of cyanogen azide which loses two molecules of N_2 sequentially⁷¹ (see section IIIA and ref 1, section III) and of XN_3 ($\text{X} = \text{H, Cl, Br}$) to yield XN .^{28,72–74} More recently the complexity of the photolysis of NCN_3 has been highlighted by a study using IR detection together with an optical multichannel analyzer to follow emission during warmup (Figure 2).⁷⁵ The acyl azide FC(O)N_3 yields the previously unknown FNCO on matrix photolysis (see section IIF).⁷⁶

An early success with a diazo compound was the photolysis of difluorodiazirine giving difluorocarbene (see Table I) which was detected by its IR spectrum and its striking UV spectrum.⁷⁷



In contrast to CF_2 the search for CH_2 by photoelimination of N_2 has been fraught with difficulty. Diazomethane, one of the standard gas-phase sources of CH_2 , yields no photoproducts on pyrex-filtered photolysis in matrices. Proof that the cage effect thwarts observation of CH_2 comes by using labeled nitrogen. In the photostationary state obtained on photolysis of

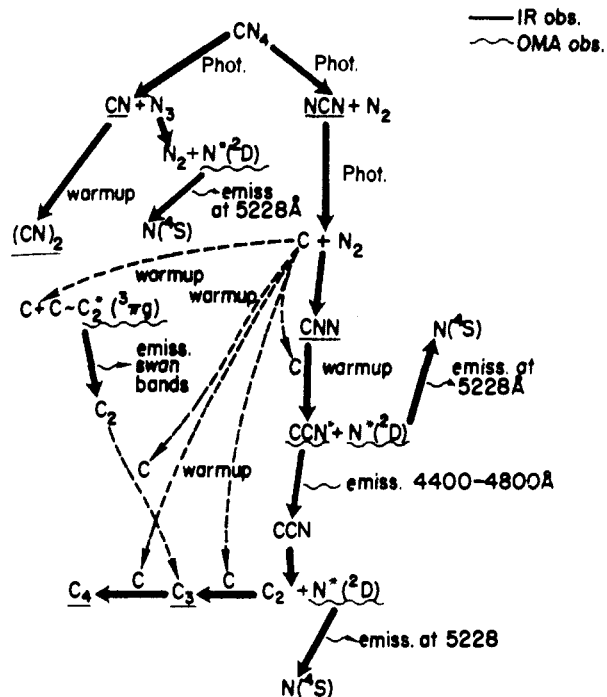
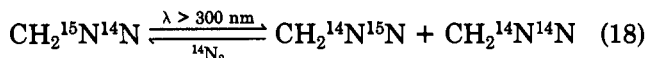


Figure 2. Reaction mechanism proposed for photolysis and subsequent annealing of N_3CN in argon matrices. Reproduced with permission from ref 75. Copyright 1982, American Chemical Society.

$CH_2^{15}N^{14}N$ in a $^{14}N_2$ matrix an equilibrium between three isotopomers is reached:⁷⁸



The photolysis of diazomethane at moderately high concentrations (1/300) with an unfiltered arc has been reexamined by Lee and Pimentel.⁷⁹ They assign the photoproducts as CH_2NH , C_2H_4 , C_2H_2 , and CH_4 on the basis of IR spectra. In addition they revive Milligan and Pimentel's (see ref 79) very early suggestion that the bands at 1116 cm^{-1} (Ar matrix) and 819 cm^{-1} (from CD_2N_2) should be assigned to the bending modes of CH_2 and CD_2 , respectively. The wealth of photoproducts strongly suggests loss of H atoms as well as N_2 from diazomethane as was postulated by Ogilvie,⁸⁰ but photolysis of dimers may also be significant at these concentrations (see section III). Lee and Pimentel also returned to the chemiluminescence observed during warmup and reinforced the evidence for an assignment of the 598.7-nm band to emission from excited C_2H_4 formed by reaction of CH_2 (3B_2) with itself or with CH_2N_2 .⁷⁹ Another band at 522 nm may be associated with emission from atomic nitrogen ($^2D \rightarrow ^4S$).

The cyclic isomer of diazomethane, diazirine, failed to give sufficient methylene for IR detection, the only photolysis product being diazomethane itself.⁷⁸ Fortunately, CH_2 is observed on Pyrex-filtered photolysis of diazirine in matrices if ESR detection is employed. It was these experiments which proved that CH_2 has a nonlinear triplet ground state (angle $136 \pm 2^\circ$). The most thorough account of the work of the Bernheim/Skell group is to be found in ref 81, while that of the Wasserman group is summarized in ref 82.

It is straightforward to spot the nonlinearity of CH_2 from its ESR spectrum since the 2-fold symmetry results in three distinct g values, and the s character of one of the unpaired electrons reveals itself in the iso-

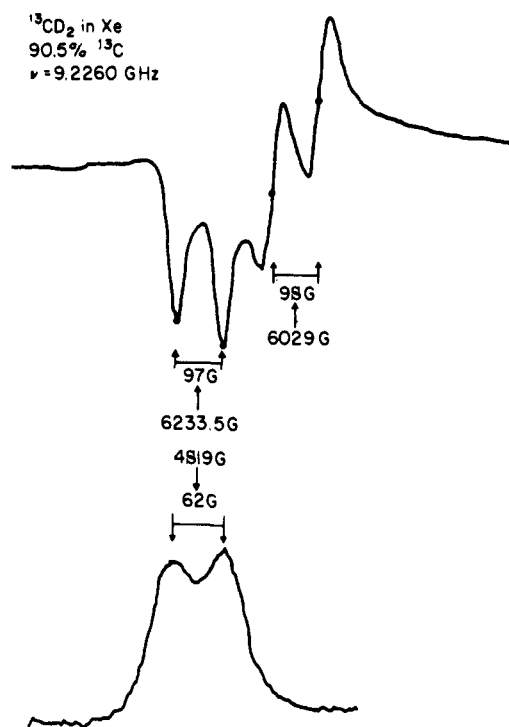


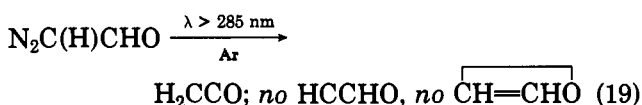
Figure 3. First-derivative ESR spectrum of $^{13}CD_2$ (90.5% ^{13}C) at 9.226 GHz in Xe at 4.2 K. The Y_2 and X_2 lines are at the top and the Z_1 line is at the bottom. Note that the ZFS is small enough that three ESR transitions are observed at X band. Reproduced with permission from ref 81. Copyright 1976, American Institute of Physics.

tropic ^{13}C hyperfine coupling ($A(^{13}C) = 242 \text{ MHz}$, Figure 3). Assuming unit occupancy of the C $2p_y$ orbital by one unpaired electron (as is required by symmetry), the other unpaired electron is deduced to have 83% spin density in C $2p_z$ and $\sim 11\%$ in C $2s$. No proton hyperfine structure is observed, in accord with a very low proton spin density; any remaining splitting must be within the bandwidth.

Complications in understanding the ESR spectrum of methylene arise from the effects both of deuteration and of matrix material on the zero-field parameters (ZFS). Deuteration alters the ZFS because CH_2 is free to rotate in the matrix about the H-H axis; as a consequence, the ZFS reaches a maximum for CHD. Even when corrected for motional averaging the parameter D varies from 0.76 in Ne to 0.93 cm^{-1} in Xe because of a heavy atom perturbation of the molecule.⁸³

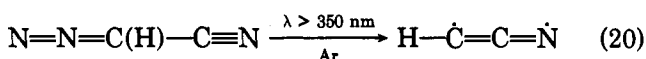
An interesting feature of the Bernheim experiments was their codeposition of diazirine with 0.1 mol % *cis*- and *trans*-2-butene, which was followed by photolysis at 4 K, warming, and gas analysis. The reaction products, of which they recovered almost 100%, include C_5 products which show remarkable stereospecificity.

Another diazo compound which has been subjected to matrix photolysis is diazoacetaldehyde, giving ketene as the only product. Neither the carbene nor oxirene was detected.^{84a}



(The more successful experiments on thiirene are not described here.)^{84b} Dendramis and Leroi have characterized the diradical HCCN by IR spectroscopy fol-

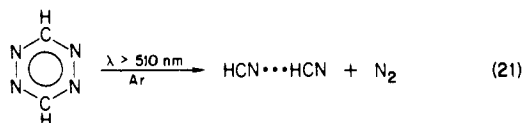
lowing photolysis of diazoacetonitrile and its isotopically labeled analogues:^{85a}



This molecule, which is isoelectronic with the other matrix-isolated species NCN and CCO, has a C-C stretching force constant intermediate between single and double bond values, and a C=N force constant somewhat lower than that of cyanoacetylene.

Photolysis of F_3CNNCF_3 in Ar at 254 nm is ineffective probably because of recombination of CF_3 with CF_3N_2 within the matrix cage. However, photolysis at 122 nm effects production of C_2F_6 and loss of N_2 .^{85b}

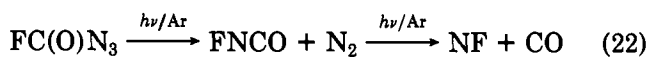
In a further example of N_2 photoelimination, Pacansky showed that *s*-tetrazine is an excellent source of the dimer $(\text{HCN})_2$.^{86a}



Studies of the intermolecular motions of this dimer by far-IR spectroscopy are consistent with a linear dimer and not an antiparallel structure.^{86b}

F. Photoelimination of CO, CO₂, and CS₂

It comes as a surprise to one familiar with organometallic photochemistry to find that photoelimination of CO and CO₂ are infrequent events among small matrix-isolated molecules. Indeed, ketene, like diazomethane, undergoes in-cage recombination on matrix photolysis so it cannot be used as a source of methylene.⁷⁸ The photodissociation of the triatomics XCO (X = H, C, N, F) is more appropriately described as atom photodissociation (see ref 1, section IVD1). The photodissociation of HNCO to NH and CO was probably the first example of genuine CO dissociation in a matrix.^{74,87} Recently the fluorine analogue, FNCO, itself a product of N_2 photodissociation, has been shown to react similarly.^{76a}



Another reaction of this type gives FSCl and CO:^{76b}



Methyl formate exists as the *cis* rotamer at room temperature. UV photolysis (248 nm) initially isomerizes it to the *trans* isomer which decomposes photochemically in three alternative pathways to $\text{CH}_3\text{OH} \cdots \text{CO}$ as a cage pair, to $\text{CO}_2 \cdots \text{CH}_4$ as a cage pair, or to acetic acid.⁸⁸

The increased photosensitivity of radicals relative to closed-shell molecules was mentioned earlier. Thus, both acetyl and its isomer, CH_2CHO are dissociated by UV irradiation to CO and CH_3 .¹⁵ It is suggested that CH_2CHO may isomerize to CH_3CO before dissociation.

Visible photolysis of glyoxal is sufficient to cause photoelimination of CO in the gas phase. However, excitation into the S_2 manifold at considerably higher energy is necessary in the matrix.^{89a} There is also some site dependence of photochemical yield reminiscent of a reversible reaction. As a prelude to the discussion of photochemistry of dimers (section IIIH), the photodis-

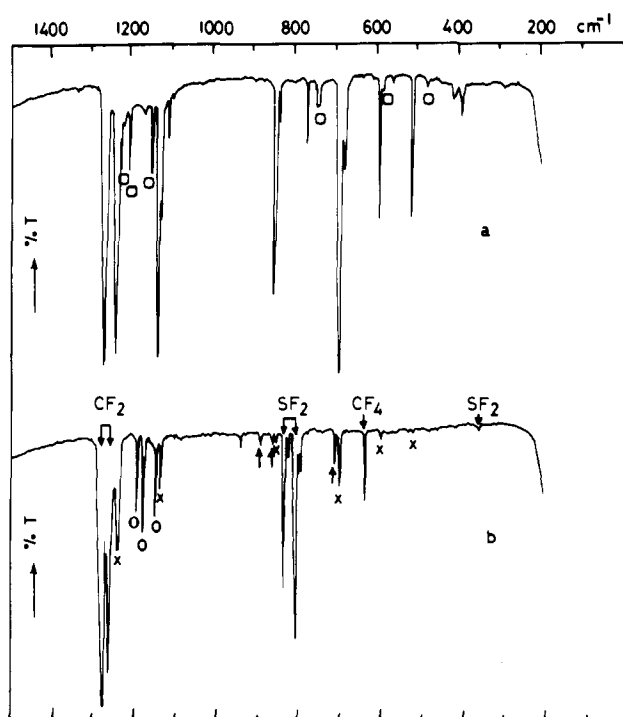
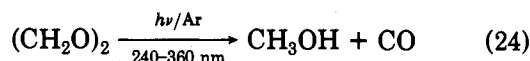


Figure 4. IR spectrum of F_3CSF_3 in Ar (1:500) (a) before and (b) after 5-min photolysis with 150-W high-pressure mercury arc. (□) $\text{F}_3\text{CS}(\text{O})\text{F}$ impurity, (×) F_3CSF_3 , (○) F_3CSF , (†) SF_4 . Reproduced with permission from ref 92. Copyright 1981, Johann Ambrosius Barth Verlag.

sociation of formaldehyde dimer should be mentioned here:^{89b}



Formic acid also undergoes matrix photodissociation to give CO, CO₂, and H₂O.⁹⁰

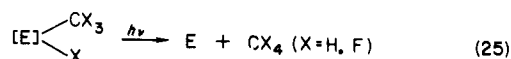
Photodissociation of two molecules of CO₂ from diacyl peroxides has been used by Pacansky et al. to generate methyl, ethyl, and other alkyl and aryl radicals in sufficient quantity for IR observation^{18,91} (eq 4).

Photolysis of $(\text{CF}_3\text{S})_2\text{CS}$ ($\lambda \lesssim 300 \text{ nm}$) generates $(\text{CF}_3)_2\text{S}$ and CS_2 probably via cleavage of $\text{CF}_3\text{-S}$ and $\text{CF}_3\text{S-C}$ bonds and subsequent recombination of CF_3 with CF_3S .^{76c}

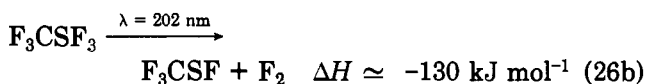
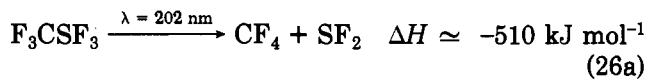
G. Other Photoelimination and Fragmentation Reactions: Elimination of CF₄, CH₄, F₂CO, HCN, HBO, HNO

The majority of photoelimination reactions fall into one of the categories of the preceding sections, but occasionally other fragments are formed. If it is recombination reactions which restrict the incidence of photodissociation into larger fragments, they should be avoidable if the fragments have exceptional kinetic and thermodynamic stability.

Examples would be the photoelimination of *tetra*-fluoromethane or methane:



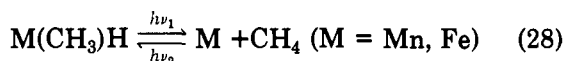
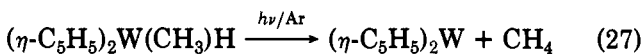
We have seen one example of CF_4 production in the photolysis of F_3COOF ⁶⁸ (eq 12). Another example observed recently shows a strong preference for the more exothermic elimination of CF_4 over elimination of F_2 ; the first pathway (26a) shown below is much more important than the second (26b) (Figure 4).⁹²



The sulfur difluoride, and also the SeF_2 produced in the analogous reaction of F_3CSeF_3 , are perturbed by the CF_4 which remains in the same matrix cage.

Photolysis of F_3CXF ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) radicals, generated by condensing atomic fluorine from a discharge with CF_3X , also yields CF_4 .⁶⁴ The photolysis threshold varies with the halogen: F_3CIF diminished using $\lambda > 490 \text{ nm}$, F_3CBrF required $\lambda > 345 \text{ nm}$, F_3CCIF required the unfiltered mercury arc. It is not possible to distinguish whether the CF_4 is generated in the primary step, or whether the primary step is bond fission followed by reaction of CF_3 with XF . Such distinctions are equally difficult in the other reactions in which CF_4 is generated.

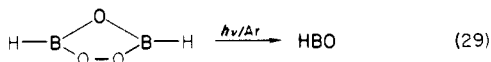
Apart from the reaction of HCO_2CH_3 (see above),⁸⁸ photoelimination of methane is confined to organo-transition-metal chemistry (see also ref 1, section IIB).^{20,93,94}



Both elimination of CH_4 and CF_4 must require a cis disposition of the groups involved in photochemical bond formation (see eq 25). The photodissociation of $\text{Cu}(\text{CH}_3)\text{H}$ to $\text{CuH} + \text{CH}_3$ or $\text{CuCH}_3 + \text{H}$ may be associated with a change to a linear geometry.⁹⁵

The minor pathways of photodissociation of F_3COOF and $\text{F}_3\text{COOOCF}_3$ involve generation of difluorophosgene, F_2CO (see section IID).⁵⁰ This molecule has also been observed following photolysis of $\text{F}_3\text{CS}(\text{O})\text{F}$.^{76b} Like CF_4 , the generation of so stable a species as F_2CO must inhibit recombination.

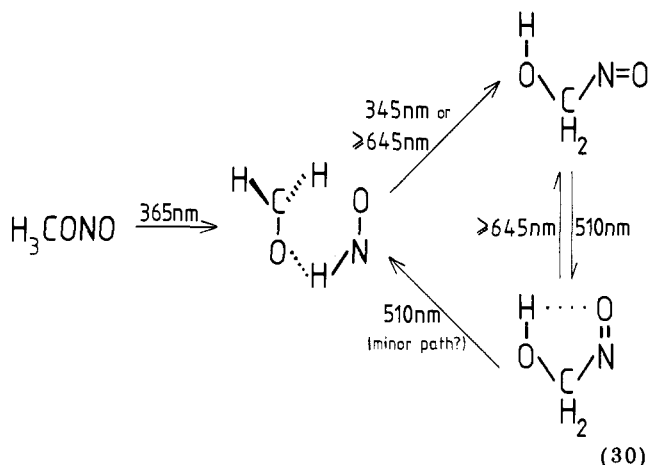
In the reaction of $(\text{CH}_2\text{N}_2)_2$ one of the products of fragmentation was HCN (section IIG). Another triatomic photofragment is HBO (isoelectronic with HCN), generated by photolysis of $\text{H}_2\text{B}_2\text{O}_3$.²²



No other products have been reported. The assignment to HBO is secured by the observation of 10 isotopic frequencies including exceptional values for $\nu(^{11}\text{B}-^2\text{H})$ (Table III). The closely related secondary ozonide of ethylene photolyses in an Ar matrix to an excited state of $\text{HC}(\text{O})\text{OCH}_2\text{OH}$. This may fragment to $\text{HCOOH} + \text{CH}_2\text{O}$ or decay to its ground state.⁹⁶ The formyl radical, HCO , has been reported as a photoproduct of CH_3O_2 (see eq 15).¹⁷

There has been renewed interest in the photolysis of methyl nitrite and nitromethane to formaldehyde and HNO ,^{97,98} first demonstrated by Brown and Pimentel many years ago.⁹⁹ It is suggested that the primary products of both *cis*- and *trans*- CH_3ONO are CH_3O and NO . These fragments either recombine or react to form $\text{CH}_2\text{O} + \text{HNO}$ (CH_3O is not detected). Some HNO may also be formed directly.⁹⁷ High-energy VUV photolysis generates some uncomplexed HNO and CH_2O .⁹⁷ In

contrast, Müller et al. formed a high yield of products as the complex $\text{CH}_2\text{O}\cdots\text{HNO}$ by using monochromatic 365-nm photolysis. The most dramatic effect of complexation is on $\nu(\text{NH})$: uncomplexed HNO 2717 cm^{-1} , complexed 2804 cm^{-1} .⁹⁸ The increase in the NH stretching force constant is supported by ab initio calculations which suggest the geometry shown in eq 30.



In a striking application of selective photolysis Müller and Huber went on to excite either CH_2O (at 345 nm) or HNO (at 645 nm) and found that they were both converted to a new product, identified as HOCH_2NO .¹⁰⁰ Furthermore, excitation of this product allowed interconversion of two distinct rotamers (see section IIG). The nitrosomethanol spectrum includes an absorption at 1107 cm^{-1} , at last providing an explanation of the band misassigned to HNO 25 years earlier.⁹⁹ Nitrosomethanol has been studied further by Jacox.^{100b}

Photolysis of Me_2NNO yields an analogous complex to that formed from methyl nitrite: $\text{H}_2\text{C}=\text{NMe}\cdots\text{HNO}$. The complex again shows high-frequency shifts for $\nu(\text{NH})$. Additionally, intermolecular modes of the complex are observed below 350 cm^{-1} (cf. $(\text{CHCN})_2$).¹⁰¹

H. Formation of Dimers and Cage Pairs: Photoreactions of Dimers

When a solute is photolyzed in a matrix the photofragments may remain within the same matrix cage or may diffuse apart. If they remain close to one another they will perturb each other's vibrational or ESR spectra; if they diffuse apart one of the photofragments may react thermally with a like fragment from another site. Such reaction is enhanced by increasing the solute concentration or by annealing following photolysis. If the solute concentration is high, precursor molecules will be isolated as cage pairs. It is well-known that such pairs exhibit perturbed vibrational spectra; however, it has been recognized only recently that such pairs, although weakly bound, may exhibit quite different photochemistry from their monomeric counterparts. In this section I will illustrate each of these phenomena.

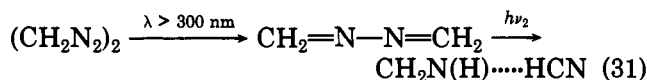
Examples of production of mutually perturbing cage pairs by photoelimination include $\text{FCCH}\cdot\text{HF}$ and $\text{HCCH}\cdot\text{HX}$ (sections IIB, IIC) from haloalkenes,^{56,57} $(\text{HCN})_2$ from *s*-tetrazine,⁸⁵ $\text{CH}_3\text{OH}\cdot\text{CO}$ from $\text{HCO}_2\text{C}\cdot\text{H}_3$,⁸⁸ $\text{CH}_2\text{O}\cdot\text{CO}$ from $(\text{CHO})_2$,^{89a} and the HNO complexes described in section IIG. In atom-transfer reactions the same phenomenon is observed (e.g., $\text{HO}\cdot\text{F}\cdot\text{HF}$ from $\text{F}_2/\text{H}_2\text{O}$).³³ Notice that the shifts can be

very substantial: e.g., $\nu(\text{HF})$ is shifted 208 cm^{-1} on complexation to HCCCH .⁵⁷

The generation of dimers by reaction of photofragments in moderately concentrated matrices is illustrated by the group of $(\text{ClO})_2$ isomers formed on photolysis of Cl_2O in matrices.^{63,102} One of the isomers is also generated by the $\text{Cl}_2\text{O}/\text{O}_3$ atom-transfer reaction.⁶³ In other examples the dimers are well-known as stable molecules, e.g., the production of $(\text{CN})_2$ from N_3CN (Figure 2), of C_2H_2 and C_2H_4 from CH_2N_2 ,⁷⁹ of *trans*- N_2F_2 and N_2F_4 from NF_3 ,¹⁰³ or of H_2S_2 from H_2S .¹⁰⁴ Some of these investigations would be enhanced by proper comparison of the photoproducts with directly deposited samples of the dimeric molecules. I should also mention the production of diatomics by atom recombination which may be observed in UV/vis absorption or emission studies (ref 1, section IVB).

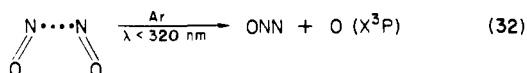
Among examples of photochemistry unique to dimers I have already referred to the photolysis of $(\text{CH}_2\text{O})_2$ to CH_3OH and CO (eq 22).⁸⁹ In this experiment, not only is it the dimer bands which decrease on photolysis but also some of the product bands appear as mutually perturbing pairs. (Notice that the spectrum of $(\text{CH}_2\text{O})_2$ is only slightly shifted from CH_2O monomer. This is not a strongly bound oligomer like paraformaldehyde.)

Another remarkable case is the generation of CH_2NH and HCN on photolysis of diazomethane dimers¹⁰⁵ (see section IIE and ref 79). Here the HCN is hydrogen bonded to the methanimine resulting in such a large perturbation of its spectrum as to make identification problematical. The methanimine is thought to arise via secondary photolysis of 2,3-diazabuta-1,3-diene, CH_2NNCH_2 .⁸⁰



Although diazabutadiene is not observed conclusively in these experiments photolysis of directly deposited samples does generate CH_2NH .⁸⁰ (Unfortunately these experiments have not been reported in full.)

A recent discovery is the photochemistry of the *cis* dimer of nitric oxide which acts as a source of N_2O and oxygen atoms¹⁰⁶ (see ref 1, sections III, V).



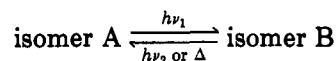
Finally we may cite the reaction of $(\text{SO}_2)_2$ in oxygen matrices (see eq 28, section VB of ref 1).¹⁰⁷

In all these examples the role of complex formation in determining photochemistry is of paramount importance. The reactions of dimers discussed here represent an extreme type of intermolecular reaction. Further examples involving two different reactants are discussed under the heading of *intermolecular reactions* in section IV. The role of complex formation is also discussed extensively in ref 1 (section VC2, VC3) in the context of atom-transfer reactions.

III. Photoisomerization and Photochemical Hydrogen Migration

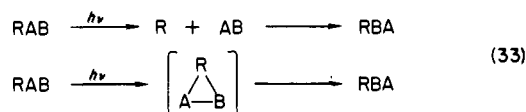
One of the strengths of matrix isolation lies in the ability to convert a stable molecule to an unstable isomer, which is unable to react back because of the low temperature. Because so little energy is available at

matrix temperatures, it is sometimes possible to select rotamers in addition to bond isomers. Occasionally, by judicious choice of photolysis wavelength or annealing temperature, a complete cycle of isomerization is observed:



However, my reading of the literature suggests that all too few isomerization studies are backed up by careful measurement of UV/vis spectra and choice of monochromatic photolysis source. One of the key conditions for observing isomerization is photostability, so it is disappointing to read of examples where the experimenter seems to choose between an unfiltered mercury arc and a pyrex-filtered arc. Indeed, use of the classic filter solutions¹⁰⁸ is now rare and use of a high-intensity monochromator almost sensational.

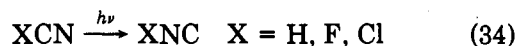
There are two major mechanisms for isomerization of small molecules which are encountered repeatedly, the dissociation-recombination (DR) mechanism and the intramolecular mechanism via a cyclic intermediate or transition state (C):



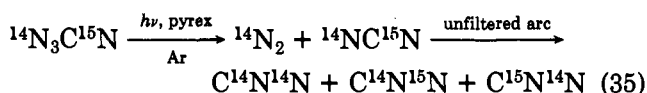
I have classified the isomerization reactions by compound type with the exception of rotational isomerization which is treated separately. Photochemical hydrogen migrations which include some isomerizations are treated in section IIIH. Isomerization reactions and photochemical hydrogen migration reactions are summarized in Tables IV and V, respectively.

A. Cyano and Cyanato Compounds

An early demonstration of the possibility of photoisomerization came with the photolysis of hydrogen cyanide and the cyanogen halides.²⁶



Since the CN radical is also observed, a DR mechanism seems a reasonable assumption. Such a mechanism was conclusively demonstrated in the photolysis of NCN .¹⁰⁹



CNN , which can also be generated via photolysis of other carbon-atom sources in nitrogen (e.g., C_3O_2 or CH_4) has been reinvestigated recently.^{75,110,111}

The isomerization of the Renner-Teller molecules CCN and CNC is less well established. IR and UV/vis absorption studies of the photolysis of CH_3CN with a hydrogen-discharge lamp indicate production of CNC with inconclusive evidence for CCN . (Notice that CH_3NC is also observed).¹¹²



Laser-induced fluorescence studies using slightly different photolysis conditions select out the CCN radical.¹¹³ The gradual photobleaching of the fluorescence

TABLE IV: Summary of Photochemical Isomerization Reactions in Matrices^a

isomerization reaction	ref
HCN → HNC	26
XCN → XNC (X = F, Cl, Br)	26
NCN → CNN	109, 75
CH ₃ CN → CH ₃ NC	112
CCN → CNC	112, 113
CH ₃ CN → H ₂ CCNH	114
LiCN → LiNC	115
HNCO → HOCN	87, 116, 117
HCNO → HOCN	117
H ₂ CNN → H ₂ CNN	78
H ₂ CNN → HCNNH	80
FON → FNO	118
Li ⁺ ON ⁻ → Li ⁺ ON ⁻ isomer	120
O ₂ NNO → ONONO	121, 122
CH ₃ NO ₂ → <i>cis</i> -CH ₃ ONO + <i>trans</i> -CH ₃ ONO + HOCH ₂ NO	99, 100
CH ₃ ONO → HOCH ₂ NO	100
FONO → FNO ₂	123
CIONO → OCl-NO → ClONO ₂	124
BrNO ₂ → BrONO	125
<i>cis</i> -HNSO → <i>trans</i> -HNSO + <i>cis</i> -HOSN + <i>cis</i> -HSNO + <i>trans</i> -HSNO	127
OCIO → ClOO	128
ClOCl → ClClO	63
BrBrO → BrOBr	129
FSSF = SSF ₂	130, 131
FSeSeF → SeSeF ₂	132
ClSSCl → SCl ₂	133, 134
BrSSBr → SBr ₂	134
LiCO ₂ (C ₂) → LiCO ₂ (C _{2v})	135
M ₂ CO ₂ (C _{2v}) → M ₂ CO ₂ (C ₂) (M = Na, K, Cs)	135
<i>cis</i> -HONO = <i>trans</i> -HONO	136, 137, 140
FCH ₂ CH ₂ OH → rotamer	141, 150, 151
ClCH ₂ CH ₂ OH → rotamer	142, 147
XCH ₂ CH ₂ OH → rotamer (X = Br, I)	144
H ₂ NCH ₂ CH ₂ OH → rotamer	143
O ₂ NCH ₂ CH ₂ OH → rotamer	145a
HOCH ₂ CH ₂ OH → rotamer	146, 147
CH ₃ CH ₂ CH ₂ OH → rotamer	145b
FCH ₂ CH ₂ NH ₂ → rotamer	145b
H ₂ C=CHCH ₂ OH → rotamer	148, 149
H ₂ C=CHCH ₂ NH ₂ → rotamer	149
H ₂ C=CFCH ₂ F = rotamer	152
<i>trans</i> -CH ₃ ONO → <i>cis</i> -CH ₃ ONO	104, 105
<i>cis</i> -HOCH ₂ NO = <i>trans</i> -HOCH ₂ NO	106
SC(SCF ₃) ₂ → rotamer	76b
FC(O)SCI → rotamer	76a
<i>cis</i> -HCO ₂ CH ₃ → <i>trans</i> -HCO ₂ CH ₃	88
<i>trans</i> -HCO ₂ CH ₃ → CH ₃ CO ₂ H	88

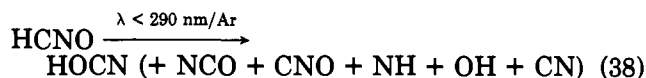
^a Excluding hydrogen migration, see Table V.**TABLE V. Photochemical Hydrogen Migration in Matrices**

precursor	product	section in text	ref
CH ₃ N ₃	CH ₂ NH, HNC	IIE	26, 70, 71
SiH ₃ N ₃	HNSi	IIE	29
GeH ₃ N ₃	HNGe	IIE	29
N ₂ C(H)CHO	H ₂ CCO	IIE	84
CH ₂ N ₂	HCNNH	IIE, IIIB	80
(CH ₃) ₂ Si	CH ₃ (H)SiCH ₂	IIIH	153, 154
CH ₃ SiX	(H)SiCH ₂	IIIH	154

suggests that isomerization is occurring. When CH₃CN is condensed with argon which has passed through a windowless discharge (see section VA2) another isomer, H₂CCNH, is observed.¹¹⁴ This is probably formed by recombination of CH₂CN with hydrogen atoms.

Reaction of Li vapor with CH₃CN in a matrix results in production of LiNC. However, evidence that the isomer LiCN may be generated by using CH₃NC has been obtained recently. UV photolysis of LiCN causes isomerization to LiNC.¹¹⁵

In addition to the cyanide-isocyanide isomerization, the conversion of isocyanate and fulminate to cyanate has been observed in matrix experiments on the corresponding acids.^{87,116,117}



Conversion of fulminic acid to isocyanic acid takes place without passing through HNCO as an intermediate. The isomer HONC remains unobserved.¹¹⁷

B. Diazo Compounds

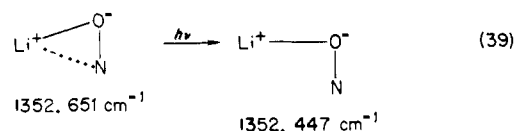
Pyrex-filtered photolysis of diazirine in a ¹⁵N₂/¹⁴N₂ matrix has been used to demonstrate isomerization to diazomethane via dissociation of N₂.⁷⁸ Among the products of short-wavelength photolysis of diazomethane is the isomer, HCCNH, isodiazomethane (see section IIE).⁸⁰

C. Nitrogen-Oxygen and Sulfur-Nitrogen-Oxygen Compounds

Both the nitrito (ONO) to nitro (NO₂) isomerization, familiar in room-temperature chemistry, and the -NO to -ON isomerization have been the subject of many matrix-isolation studies. These experiments have also revealed the possibility of other isomers including the product of insertion into a nitro group. The *cis*-*trans* isomerism of HONO, CH₃ONO, and HOCH₂NO is discussed in section IIIF.

Codeposition of F₂ and NO with excess Ar or N₂ yields two F(NO) products with very similar IR frequencies.¹¹⁸ While annealing increases FON, UV photolysis converts FON to the stable isomer FNO, supporting the assignment of these bands to independent isomers rather than site effects. Since diffusion gives more FON only, the isomerization must follow the intramolecular C route. Reaction of F atoms with CH₃ONO also gives FON,¹¹⁹ but these studies cast doubt on the assignment of ν(NO) in ref 118. There is no evidence for isomerization of other nitrosyl halides or of HNO.

The condensation product of Li vapor and NO in matrices has been examined several times, most recently by Tevault and Andrews.¹²⁰ The initial product is shown to be bonded primarily through oxygen by large isotopic shifts of the interionic mode on Li and O substitution but small shifts on N substitution. It isomerizes on photolysis to another oxygen-bonded species with a common ν(NO) mode but a different interionic mode.



A change in structure from a triangular to a more open form is argued to underlie the reaction, although I see no reason for any barrier to returning to the more stable of the two structures. Heavier alkali M⁺(NO⁻) complexes are not photosensitive.

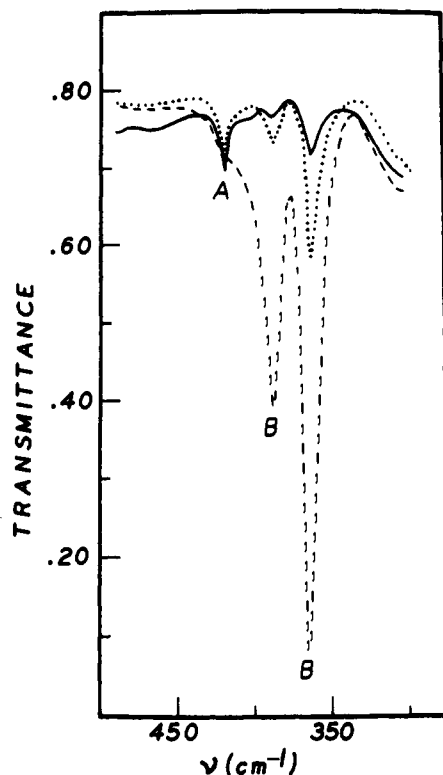
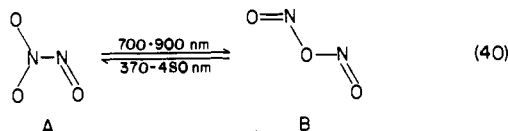


Figure 5. IR spectrum of $N_2/NO/NO_2$ (1120:6.1:1) before photolysis (—); after 180 min, near IR irradiation (---); after 100 min, UV irradiation (···). A = O_2NNO , B = $ONONO$. Reproduced with permission from ref 121. Copyright 1971, American Institute of Physics.

Cocondensation of NO/NO_2 mixtures in a matrix leads to production of N_2O_3 . Varetto and Pimentel¹²¹ showed that the stable asymmetric isomer could be converted reversibly to the previously unknown symmetric isomer (Figure 5):



The photon energies correspond to electronic absorptions of the two molecules. The symmetric structure of isomer B was demonstrated by examining the photochemical cycle using isotopic labeling: $O^{15}N^{14}NO_2$ gave only one form of B which reverted to UV irradiation to $O^{15}N^{14}NO_2$ and $O^{14}N^{15}NO_2$. This experiment was repeated using $O^{14}N^{15}NO_2$ and ^{18}O labels. Recently, this reaction has been reexamined by using Raman spectroscopy, NO matrices,¹²² and employing a defocused laser as the photolysis source. The two isomers of N_2O_3 have also been detected following unfiltered photolysis of *cis*-(NO)₂ in Ar.⁹⁶

Photolysis of nitromethane ($\lambda > 265$ nm) in Ar generated both *cis* and *trans* isomers of methyl nitrite,⁹⁷ (not just the *trans* isomer as first thought),⁹⁹ via C-N bond photodissociation. Another isomer, $HOCH_2NO$ is generated on prolonged photolysis of either CH_3ONO or CH_3NO_2 probably via $CH_2O \cdots HNO$ (see section IIG).¹⁰⁰

The compounds FNO_2 and $ClNO_2$ are well-known in the gas phase, but neither isomeric forms nor bromine and iodine analogues are known. Codeposition of F_2 and NO_2 in a nitrogen matrix followed by UV photolysis ($230 < \lambda < 400$ nm) gives FNO_2 , but an additional

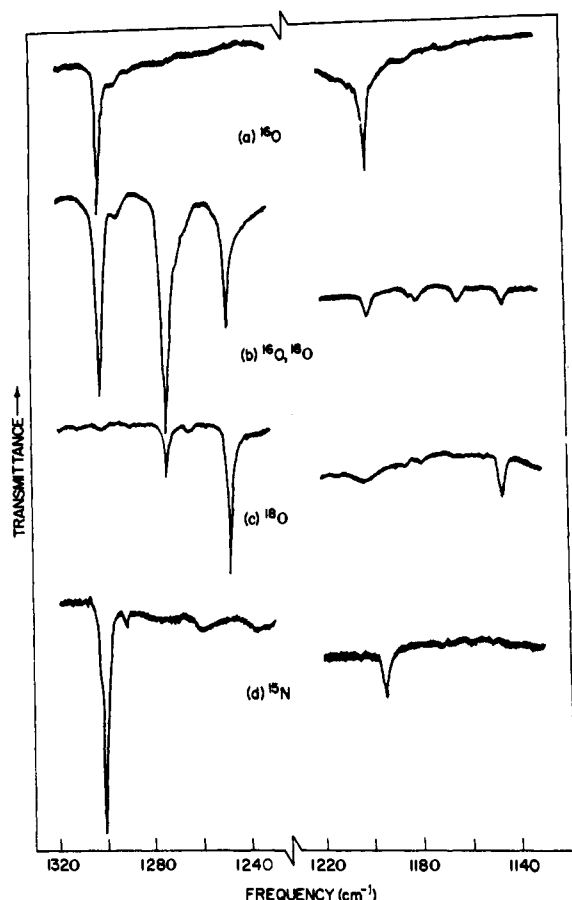
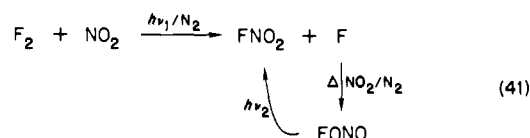


Figure 6. ^{18}O and ^{15}N isotopic splittings of FNO_2 and $ONOF$ in the $\nu_{sym}(NO_2)$ region for $N_2/F_2/NO_2$ (1000:2:1). (a) $10 \mu M N^{16}O_2$; (b) $19 \mu M N^{16}O_2/^{16}ON^{18}O/N^{18}O_2$ (1:2:1); (c) $20 \mu M N^{18}O_2$ (93% ^{18}O); (d) $22 \mu M ^{15}NO_2$ (99% ^{15}N). Reproduced with permission from ref 123. Copyright 1974, American Institute of Physics.

species is detected on annealing to 19 K.¹²³ Selective photolysis ($300 < \lambda < 400$ nm) converts this species to FNO_2 .



The new molecule is assigned as $FONO$ on the basis of a mixed $N^{16}O_2$, $^{16}ON^{18}O$, $N^{18}O_2$ experiment which shows a triplet $\nu(NO)$ pattern for FNO_2 and a quartet for $FONO$ (Figure 6). This indicates equivalent oxygen atoms for the former and inequivalent ones for the latter. The IR absorptions of $FONO$ including ^{15}N and ^{18}O data, differ substantially from those of FNO_2 (unlike the FNO/FON pair).

In order to synthesize $ClNO_2$, Tevault and Smardzewski condensed atomic chlorine from a discharge with NO_2/Ar mixtures, using a bent deposition tube and a light trap to avoid photolysis of the sample by the discharge.¹²⁴ As in the fluorine experiments a second isomer was observed, assigned as $ClONO$, which formed in the initial condensation and was converted to $ClNO_2$ by long-wavelength photolysis ($\lambda > 300$ nm). Subsequent annealing to 22 K generated further $ClONO$ presumably by diffusion of Cl atoms. The ^{15}N and ^{18}O shifts of $\nu(NO)$ were those expected of a diatomic NO oscillator, evidence in favor of the $ClONO$ formulation. Slightly weaker evidence was obtained for a third iso-

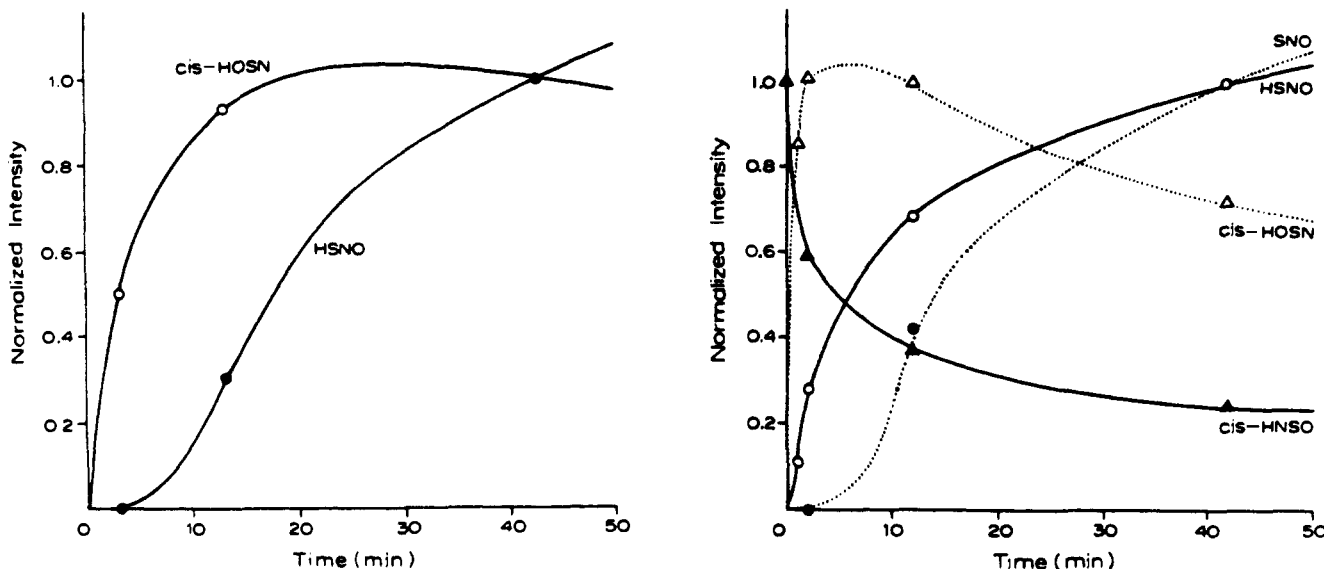
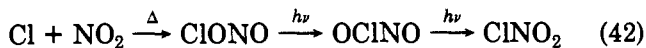


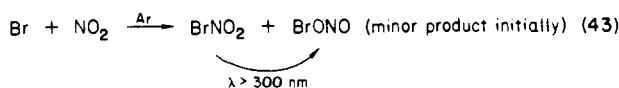
Figure 7. Plots of absorption intensity vs. photolysis time for the photolysis of *cis*-HNSO in Ar. Left: photolysis with $\lambda > 300$ nm. Right: photolysis with $\lambda > 200$ nm. Reproduced with permission from ref 127. Copyright 1975, National Research Council of Canada.

mer which increased slightly and then decreased slowly on photolysis with $\lambda > 300$ nm. This isomer can be generated more effectively by incorporating O_2 in the discharge to produce ClO and condensing with Ar/ NO mixtures (N.B. not Ar/ NO_2). This species is argued to be OCINO, an intermediate in the ClONO/ClNO₂ isomerization:



A serious criticism which can be levelled against this otherwise striking set of experiments is that the authors did not matrix isolate pure FNO₂ and ClNO₂ to compare with the products of their atom reactions.

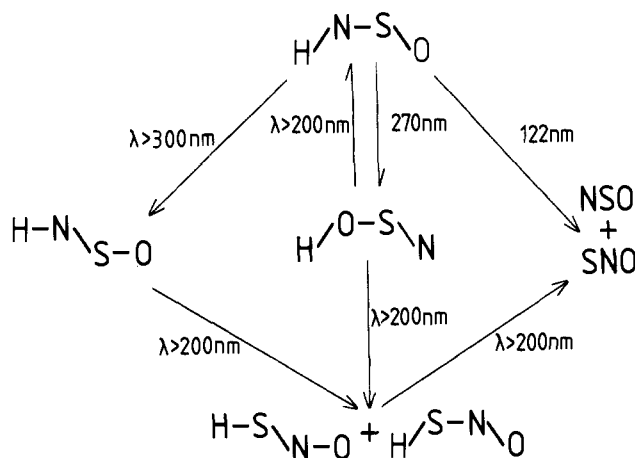
The same criticism can hardly be leveled at the experiments on the previously unknown bromine analogues. In this case Tevault showed that the isomerization proceeded in reverse!¹²⁵



Before the Tevault, Smardzewski (TS) work can be regarded as fully established, the ghost of a recent paper on cocondensation of halogen (Cl, Br, I) atoms with NO₂ must be laid to rest.¹²⁶ The authors of this paper did not consider the earlier work, or the possibility of isomerism, or photolysis, or ¹⁸O substitution. Their assignments for both ClNO₂ and BrNO₂ differ from TS drastically. Even the most intense bands of ClNO₂ differ and they include bands undetected by TS. The merit of this paper was the isolation of ClNO₂ direct from the gas phase, but that was marred by impurities.

The tetraatomic *cis*-HNSO is stable as a monomer in the gas phase. Photolysis in argon matrices with IR detection has proved a valuable source of isomers and molecular fragments reminiscent of the HCNO/HNCO/HOCN system (Scheme I).¹²⁷ The assignments were made with the aid of ²H and ¹⁵N substitution together with photolysis growth curves as a function of wavelength (Figure 7). The first isomers, *trans*-HNSO and *cis*-HOSN, are generated directly from *cis*-HNSO without prior bond rupture while the second pair, *cis*- and *trans*-HSNO, are probably formed via cleavage to

SCHEME I



HO + SN and recombination. Production of the triatomic SNO is most effective with VUV radiation; NSO is observed only the VUV photolysis. Selective photochemical interconversion of the isomers of HSNO has been demonstrated recently.¹²⁷

D. Chlorine-Oxygen and Bromine-Oxygen Compounds

Thirty-second irradiation of matrix-isolated chlorine dioxide is sufficient to convert it to another isomer (B) with inequivalent oxygen atoms (¹⁸OCl¹⁸O photolysis).¹²⁸ However, a third isomer (C) is detectable after short photolysis time, again with inequivalent oxygen atoms but with a lower O-O stretching and a higher bending frequency (isomer B, 1442, 407; isomer C, 1415; 435 cm⁻¹). Isomer C disappears on annealing above 4 K. The high efficiency of the initial isomerization suggests an intramolecular process, but I am doubtful about the suggestion that B and C represent isomers with slightly different bond angles. A cyclic structure for C would appear more plausible.

In an analogous reaction, laser photolysis (488 nm) of Cl₂O gives the ClClO isomer in addition to ClO (section IIC). Both IR and Raman spectra of eight isotopomers have been used to establish the identity of

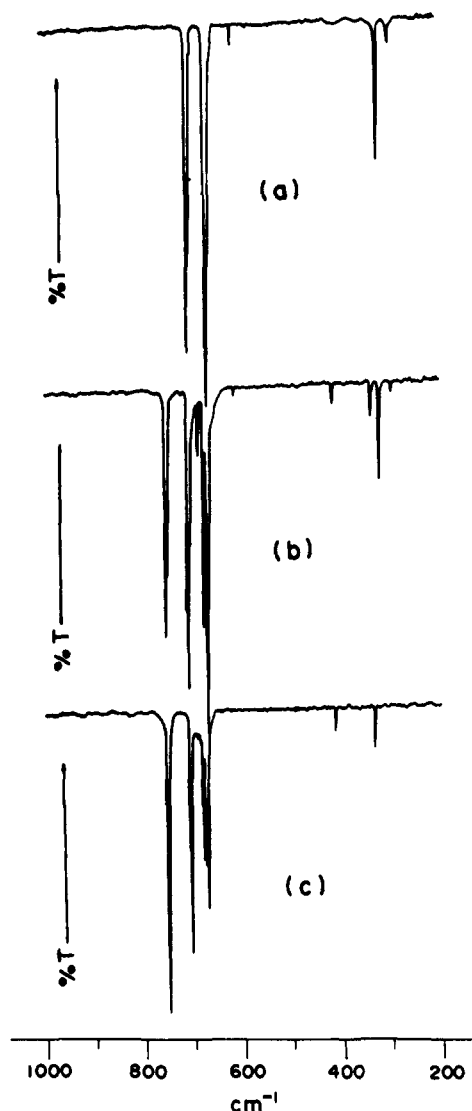
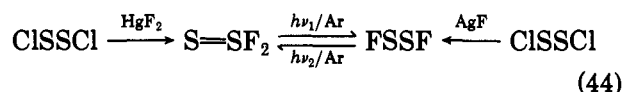


Figure 8. IR spectrum of (a) FSSF in Ar (1:500) before photolysis; (b) spectrum after 5 min UV photolysis of (a) or (c); (c) SSF₂ in Ar (1:500) before photolysis. Reproduced with permission from ref 130. Copyright 1979, Pergamon Press.

ClClO and to estimate a bond angle of $\sim 120^\circ$.⁶³ The bromine analogue BrBrO has been made by laser photolysis (632.8 nm) of Br₂/O₃/Ar matrices. Subsequent Nernst-glow photolysis converts it to the BrOBr isomer.¹²⁹

E. Disulfur Dihalides

Two isomers of S₂F₂ are known in the gas phase: the nonplanar chain FSSF isomer (cf. H₂O₂) slowly converts to the mixed oxidation state isomer F₂SS. The chlorine and bromine analogues exist exclusively as the XSSX isomers at room temperature. Haas and Willner have developed a method of preparing each isomer selectively and in high yield by fluorination of ClSSCl with AgF or HgF₂ immediately prior to deposition.¹³⁰ Photolysis of either isomer with an unfiltered mercury arc leads to the same photoequilibrium between isomers (Figure 8):



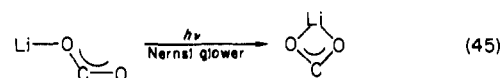
By using selective photolysis ($\lambda > 305$ nm) the SSF₂

isomer could be converted to FSSF quantitatively.¹³¹ Assuming that any photogenerated fluorine atoms could diffuse in the matrix, it follows that the photochemical reaction must be intramolecular. The same authors have also investigated the photochemical conversion of FSeSeF to SeSeF₂.¹³²

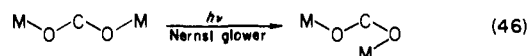
The isomerization of ClSSCl proceeds in the same direction on UV photolysis.¹³³ Similar isomerization by VUV photolysis of XSSX (X = Cl, Br) during matrix deposition has been observed,¹³⁴ although the matrices used here seem rather concentrated (150:1).

F. Carbon Dioxide-Alkali Metal Reaction Products

Cocondensation of alkali metals with CO₂ in inert matrices results in spontaneous formation of MCO₂, M₂CO₂, MC₂O₄, M₂C₂O₄, and M₂CO₃. For M = Li, the MCO₂ species exists as two isomers which react photochemically as in eq 45:¹³⁵



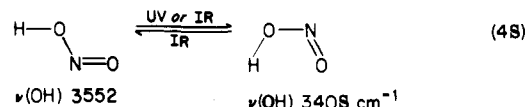
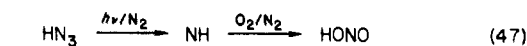
The molecule LiC₂O₄ is also photosensitive converting to LiCO₂-CO₂. For M = Na, K, Cs photochemical rearrangements of M₂CO₂ have been observed:



The stoichiometries and symmetries have been established by isotopic substitution but the detailed disposition of the metal atoms has not been established. The OCO angle is $\sim 126^\circ$ both in LiCO₂ (C_{2v}) and K₂CO₂ (C_{2v}).

G. Rotational Isomerization

1. **Infrared-Induced Isomerization.** The first infrared induced photochemical reaction was the cis-trans isomerization of nitrous acid generated by UV photolysis of hydrazoic acid in oxygen-doped nitrogen matrices:^{136,137}

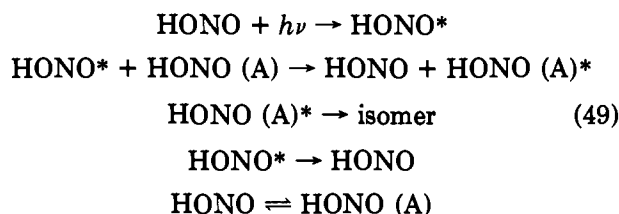


In recent years several more examples of *single-photon vibrational photochemistry* in matrices have been discovered. These reactions fall into three classes: isomerizations, treated here, bimolecular reactions, discussed in section IV, and photobleaching of ions (section VC3). The matrix observations are placed in the wider context of vibrational photochemistry in reviews elsewhere.^{138,139} Attention is drawn to the IR-induced isomerization of Fe(CO)₄ which is summarized in ref 138 but not here.

Baldeschwieler, Hall, and Pimentel demonstrated by using filters that the active frequencies were 3650–3200 for isomerization of HONO and 4100–3500 cm⁻¹ for DONO and that the rate of isomerization was reduced by ²H or ¹⁸O substitution. The position of the photo-stationary equilibrium was filter dependent and the quantum yield was of the order of unity.^{136,137} An explanation of this remarkable reaction, including how

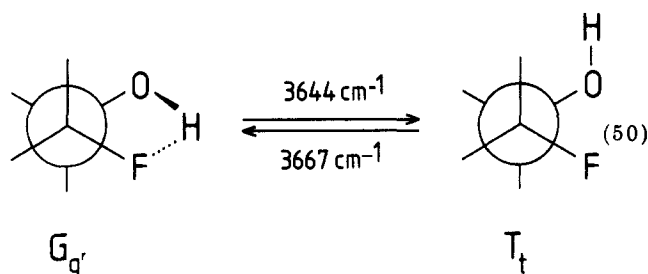
DONO can be affected by frequencies it does *not* absorb, has become possible with the advent of tunable lasers.¹⁴⁰

McDonald and Shirk have now shown that the most efficient isomerization occurs when irradiating into the OH stretching mode of either *cis*- or *trans*-HONO, but isomerization also takes place on irradiating modes of a third molecule such as H₂O at *higher* frequency than the HONO frequencies. Initially, it was thought that irradiation of lower frequency modes, whether of HONO or of third molecules (e.g. HN₃) has no effect.^{140a} More recently isomerization has been observed on irradiation of $2\nu_2$ of *cis*-HONO at 3236 cm⁻¹ and very weakly on irradiation of $2\nu_2$ of *trans*-HONO.^{140b} The rate is first order in light intensity, but approximately second order in [HONO]; polarized light fails to select particular orientations. The reaction is postulated to follow the mechanism:



where HONO (A) is an acceptor molecule in a cage appropriate for rapid isomerization. Thus, the reaction depends on efficient energy transfer between HONO molecules, or H₂O and HONO, or HONO and DONO (i.e., this is a good example of photosensitization). It also requires change to a minor but readily isomerized site. Even when normalized for the energy diffusion rate, the fraction of *cis*-HONO molecules which isomerize is 2–3 orders of magnitude greater than for *trans*-HONO. This difference is ascribed to a 100 cm⁻¹ difference in the torsional frequencies of the isomers.

A similar infrared-induced conformational isomerization occurs in substituted alcohols isolated in Ar matrices. Following the discovery of *gauche* to *trans* isomerization of 2-fluoroethanol,¹⁴¹ such rotational isomerization has been found for many related molecules (see Table IV).^{142–149} Laser studies of the 2-fluoroethanol isomerization showed that radiation in the O–H stretching region was required to effect the isomerization shown in eq 50:^{150,151}



While Pourcin et al. found excitation of C–H stretching modes to be ineffective,¹⁵⁰ Hoffman and Shirk observed $G_g \rightleftharpoons T_t$ isomerization and conversion to other isomers assigned as T_g and G_t .¹⁵¹ (G/T indicates the *gauche*/*trans* conformer about the C–C bond, g/t indicates the conformer about the C–O bond.) Evidence that photolysis with polarized light results in oriented samples with irradiation in the C–H stretching region is taken to indicate an intramolecular process. In contrast ir-

radiation in the O–H stretching region appears to result in energy migration in a similar manner to HONO.

An analogous reversible $G_g \rightleftharpoons T_t$ isomerization of 2-nitroethanol has been studied by irradiation of ν -(OH).^{146a} This process is first order in the alcohol, but its rate is strongly matrix dependent. The fastest rates are observed with Xe provided that the deposition temperature is below 20 K. Inhibition above that temperature is ascribed to Xe–alcohol complexation. The rate of vibration \rightarrow internal rotation transfer is probably rate determining and enhanced by more polarizable hosts. Further examples of this type of rotamerization include 1-propanol and 2-fluoroethylamine.^{146b} A short review including examples of related molecules which do not undergo IR-induced rotamerization has appeared recently.^{146c}

Infrared photorotamerization of allyl alcohol ($C_g \rightarrow G_g$, C = *cis*) is considerably faster than for other substituted ethanols and is also first order in alcohol and strongly matrix dependent (rate in Xe \gg Kr $>$ Ar \gg N₂ \sim CO).¹⁴⁸ Unlike most examples, photorotamerization may be effected by ν (OH) or ν (CH₂) radiation or even radiation below 2600 cm⁻¹. The high rate of isomerization and the lower photon-energy requirement are related to lower potential barriers for internal rotation than for 2-halo- or 2-nitroethanol.

Experiments on ethylene glycol in Ar using filters have demonstrated that radiation in the O–H stretching region isomerizes both gG_g' and tG_g' conformers to the tT_t conformer.¹⁴⁷ (The letters signify conformations about the O–C, C–C and C–O axes in sequence.) The O–H...N ($g'G_g'$) conformer of 2-aminoethanol is isomerized (Figure 9) to N–H...O bonded conformers.¹⁴³

Selective irradiation of 2,3-difluoropropene, one of the products of the vibrationally stimulated allene/fluorine reaction causes reversible interconversion of the *cis* and *gauche* conformers.¹⁵² The lowest frequency effecting reaction was 938 cm⁻¹ for one conformer whereas the other conformer required 1687 cm⁻¹ radiation. These differing thresholds were associated with different barriers to reaction. Using this argument Knudsen and Pimentel assigned the isomer with the higher barrier as the thermodynamically more stable *cis* conformer.

In conclusion, it is well established that IR radiation effects the rotamerization of substituted alcohols via intramolecular transfer of energy from stretching to torsional modes. The energy requirement of the majority of these single-photon reactions seems to be determined simply by the barrier height. However, the experiments on 2-fluoroethanol point to mode-selective chemistry and demand a more sophisticated model.¹⁵¹

2. UV/vis Induced Isomerization. The interchange of rotational isomers via absorption in an electronic transition represents a more conventional type of reaction than that discussed above. Indeed, UV radiation may be used as an alternative to IR radiation to effect rotamerization of HONO^{138,139} or O₂NCH₂C–H₂OH.¹⁴⁵ Other examples of UV-induced reaction include the *cis*/*trans* isomerizations of CH₃ONO (section IIH), HNSO and HSNO (section IIIC), HCO₂CH₃ (section IIF), (CF₃)₂CS, and FC(O)SCL.⁷⁶

H. Photochemical Hydrogen Migration

Photochemically induced hydrogen migration is observed occasionally in matrices. Most of the examples

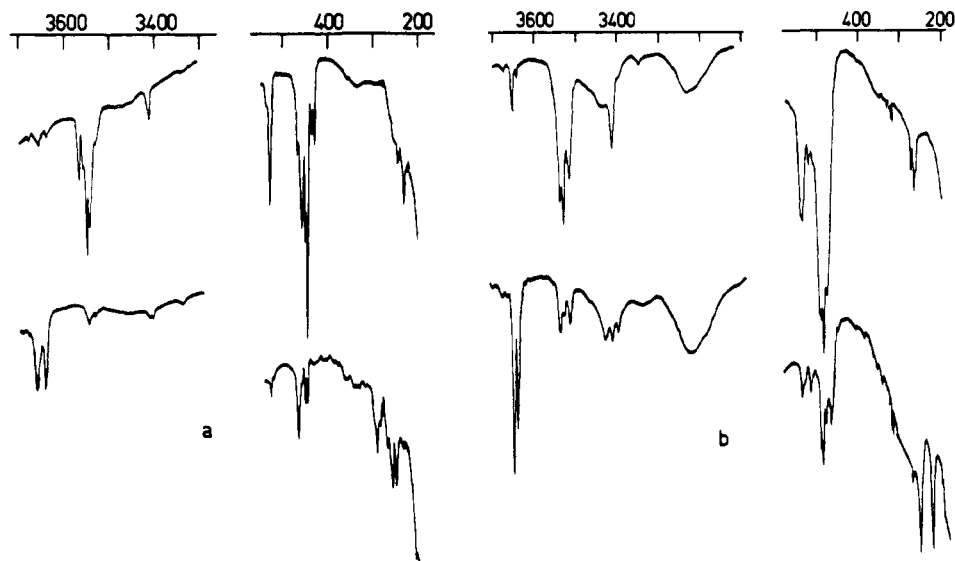
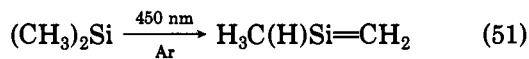


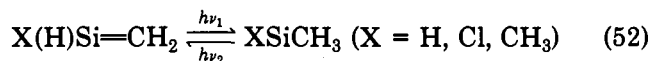
Figure 9. The $\nu(\text{OH})$ and $\tau(\text{OH})$ regions of the IR spectrum of 2-aminoethanol (a) in Ar (upper spectrum before photolysis, lower spectrum after 30 h Nernst glower irradiation); (b) in N_2 (upper spectrum before photolysis, lower spectrum after 100 h Nernst glower irradiation). Reproduced with permission from ref 143. Copyright 1982, Elsevier (Amsterdam).

have been mentioned elsewhere in this review, so I have simply collected them in Table V. An exception, however, is the isomerization of silaethenes to silylenes, a reaction of much current interest. Drahnak et al. generated $(\text{CH}_3)_2\text{Si}$ by photolysis (254 nm) of matrix-isolated $[(\text{CH}_3)_2\text{Si}]_6$. Subsequent visible photolysis caused isomerization to 2-silapropene.^{153a}



The observation of trapping products characteristic of $(\text{CH}_3)_2\text{Si}$ on annealing $\text{CH}_3(\text{H})\text{SiCH}_2$ in hydrocarbon matrices led initially to the postulate that reaction 51 was thermally reversible at 100 K. Recently, this conclusion has been revised following trapping experiments with N_2O .^{153b}

An isomerization similar to that of eq 46, but photochemically reversible, has been reported for this and other silaalkenes in Ar and N_2 matrices:



However, the spectral bands assigned to HSiCH_3 in Ar are so different from those observed in N_2 matrices that I find it unlikely that they belong to the same compound. It seems more plausible that HSiCH_3 reacts with N_2 to form $\text{HSi}(\text{CH}_3)\text{N}_2$.

IV. Intermolecular Photochemical Reactions: Molecular Transfer

The scope and mechanisms of photochemical atom transfer reactions were discussed at length in the previous review. Additionally, I collected examples of photoelimination of dimeric complexes such as $(\text{CH}_2\text{O})_2$ in section IIG of this review. Here it remains to consider examples of intermolecular group transfer in doped matrices. Some examples involving homonuclear diatomics are *not* readily distinguished from stepwise atom transfer; for these (e.g., $\text{Xe} + \text{F}_2 \rightarrow \text{XeF}_2$) the reader should consult the earlier review.¹ Like the section on rotational isomerization, this section is divided into infrared-induced reactions and UV/visible-

TABLE VI. Intermolecular Photochemical Reactions: Molecular Transfer

reactants	electronic/ vibrational excitation	ref
NO/O_3	vib	<i>a</i>
$\text{C}_2\text{H}_4/\text{F}_2$	vib	155–158
$\text{C}_3\text{H}_4/\text{F}_2$	vib	152, 155
$\text{C}_2\text{H}_3\text{Br}/\text{F}_2$	vib	159
UF_6/SiH_4	vib	160
$\text{SF}_6/\text{N}_2\text{O}_3/\text{NO}$	vib	161
BCl_3/CH_4	vib	162
$\text{H}_2\text{O}/\text{CO}$	elec	90
$\text{CH}_2\text{N}_2/\text{CO}$	elec	163a
$\text{CH}_2\text{N}_2/\text{O}_2$	elec	163b
$\text{CH}_2\text{O}/\text{O}_2$	elec	89b
$(\text{CHO})_2/\text{O}_2$	elec	164
$\text{CH}_3\text{I}/\text{O}_2$	elec	165
HN_3/O_2	elec	136, 140
$(\text{CH}_3)_2\text{N}_2/\text{O}_2$	elec	17
$(\text{SO}_2)_2/\text{O}_2$	elec	107
$\text{C}_4\text{H}_4\text{O}/\text{O}_2$	elec (near IR)	166
$(\text{CH}_3)_4\text{C}_3\text{H}_3\text{O}/\text{O}_2$	elec (near IR)	166
$(\text{CH}_3)_2\text{C}_4\text{H}_2\text{O}/\text{O}_2$	elec (near IR)	166
HN_3/CO_2	elec	167
$\text{Ga}, \text{Ga}_2/\text{H}_2\text{O}$	elec	168, 169
$\text{In}, \text{In}_2/\text{H}_2\text{O}$	elec	168, 169
$\text{Tl}, \text{Tl}_2/\text{H}_2\text{O}$	elec	168, 169
$\text{Si}/\text{H}_2\text{O}$	elec	170
Si/HF	elec	171a
$\text{CH}_2\text{N}_2/\text{C}_2\text{H}_2$	elec	163c
$\text{CH}_2\text{N}_2/\text{C}_2\text{H}_4$	elec	163a
$\text{HN}_3/\text{C}_2\text{H}_2$	elec	163c
$\text{HN}_3/\text{C}_2\text{H}_4$	elec	163c
HCl/AlCl	elec	171b

^a Frei, H.; Pimentel, G. C. *J. Phys. Chem.* 1981, 85, 3355.

induced reaction. The reactions are summarized in Table VI.

A. Bimolecular Vibrational Photochemistry

Interest in vibrational photochemistry is growing because of the possibility of selectivity in reaction and because of the development of IR lasers.^{138,139} Bimolecular matrix reactions which can be induced by IR radiation have proved very elusive, but three systems have been examined in detail: the $\text{Fe}(\text{CO})_4$ addition reactions (see ref 138), the NO/O_3 reaction (see ref 1,

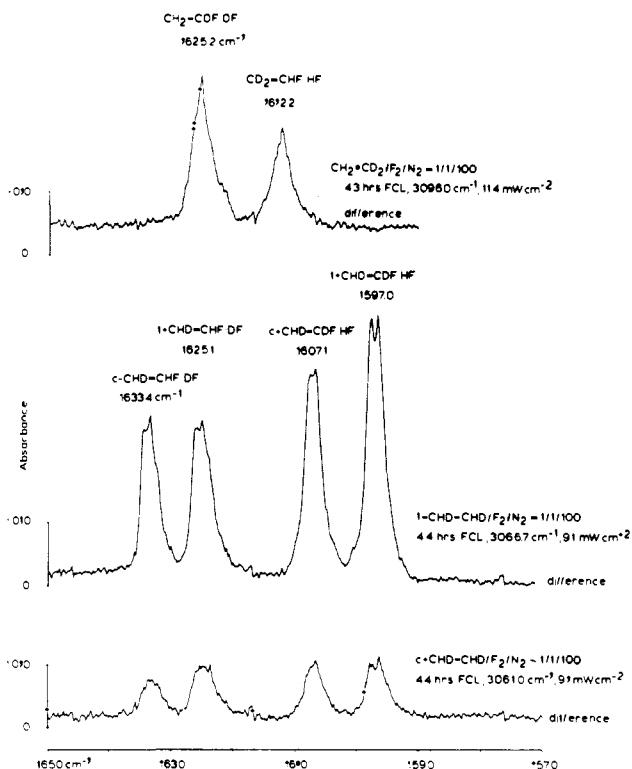


Figure 10. Growth of product absorptions in the C=C stretching region of the IR spectra after laser irradiation of the CH stretching mode, ν_9 , of three deuterioethylenes in matrices $C_2H_4D_2/F_2/N_2$ (1/1/100). Reproduced with permission from ref 157. Copyright 1983, American Institute of Physics.

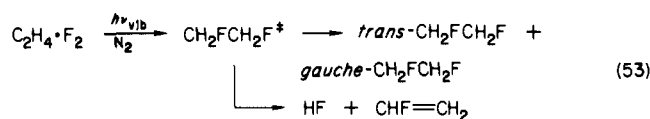
section VB2), and the reactions of F_2 with unsaturated hydrocarbons. A few other reactions have yet to be authenticated.

Hauge et al. investigated the reactions of hydrocarbons when cocondensed with F_2 or F_2/Ar mixtures. Among these, allene and ethylene stood out since they did not react on condensation but did react in the IR beam.¹⁵⁵ The products of reaction of $C_2H_4 + F_2$ were vinyl fluoride, HF, and 1,2-difluoroethane. The perturbation of the C_2H_4 vibrations by F_2 pointed to complex formation prior to reaction.

The reaction of C_2H_4 with F_2 in nitrogen matrices has been examined very thoroughly by Frei, Fredin, and Pimentel¹⁵⁶⁻¹⁵⁸ using conventional and laser IR sources. This proves to be a single-photon reaction, first order in $C_2H_4 \cdot F_2$ pairs, with a threshold of 2000 cm^{-1} with a global source and 1896 cm^{-1} with a laser. The quantum yield, ϕ , shows a marked increase with frequency rising from 7×10^{-4} at 1896 cm^{-1} to 0.31 at 4209 cm^{-1} . However, excitation of $(\nu_2 + \nu_{12})$ at 3076 cm^{-1} gives a higher quantum yield than expected from the general trend. These and similar effects observed for *trans*-CHD=CHD, point to some mode specificity in the reaction. The general increase in ϕ with frequency is associated with access to $\nu > 1$ states of those deformation modes which facilitate reaction. The higher vibrational quantum number more than offsets an increased relaxation rate, so ϕ is increased. The quantum yield is also a function of isotope with ϕ for *trans*-CHD=CHD exceeding that for *cis*-CHD=CHD by a factor >10 for some modes (Figure 10). This isotope selectivity is interpreted in terms of slower nonradiative vibrational relaxation of the centrosymmetric molecule. It is suggested that only *ungerade* modes participate in the

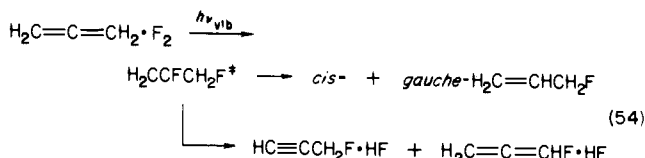
energy cascade of centrosymmetric isotopomers, but that all modes contribute in noncentrosymmetric isotopomers.

The analysis of products also holds important clues to the mechanism of reaction. Firstly, the absence of fluoroethane and C_4 products even from excitation of $(C_2H_4)_2 \cdot F_2$ complexes excludes the radical mechanism observed in the gas phase. Moreover, excitation of C_2H_4 in a $C_2H_4 \cdot CH_2CD_2 \cdot F_2$ complex does not result in any partially deuterated products. The branching ratio, b , defined as the ratio of addition products (*trans*- and *gauche*- $C_2H_4F_2$) to elimination products ($C_2H_3F + HF$) varies considerably according to the type of $C_2H_4 \cdot F_2$ complex excited. For $C_2H_4 \cdot F_2$ complexes $b \approx 0.04$ whereas it is about 100 times larger for $(C_2H_4)_2 \cdot F_2$ complexes. The branching ratio is also influenced by the deposition temperature but is independent of the vibrational mode excited. When different $C_2H_2D_2$ isotopomers are excited, the isotopomers of the vinyl fluoride products are consistent with $\alpha\beta$ elimination from 1,2-difluoroethane. The ratio of HF to DF is close to unity and independent of isotopomer. All these observations are consistent with a *four-center* mechanism resulting in vibrationally excited $C_2H_4F_2$ in its electronic ground state which is either deactivated to its ground vibrational state or undergoes elimination.



The second molecule of C_2H_4 in the complex $(C_2H_4)_2 \cdot F_2$ deactivates the hot $C_2H_4F_2$ so increasing the proportion of addition product. Although the quantum yield measurements are in line with the gas-phase activation energy of 1590 cm^{-1} , the change in mechanism reduces the significance of any comparison. The overall enthalpy of reaction to $C_2H_4F_2$ is -484 kJ mol^{-1} , so there is massive potential for vibrational excitation of the product. Interestingly, Frei has shown that $C_2H_4 \cdot F_2$ pairs can react following absorption by *different* aggregates. The spectra show that these reactions occur by nonresonant energy transfer and not by bulk heating.

The allene/ F_2 reaction follows a similar pattern to the C_2H_4/F_2 reaction with competing addition and elimination pathways.¹⁵² However, in this case there are two possible elimination products and the distribution between them and the addition product 2,3-difluoropropene varies considerably with the matrix material:



Active irradiation frequencies vary from 1679 to 3076 cm^{-1} , with similar variations in ϕ to the C_2H_4/F_2 reaction including indications of mode selectivity. The ratio of *cis*- to *gauche*-difluoropropene was altered by selective laser irradiation (see section IIG).

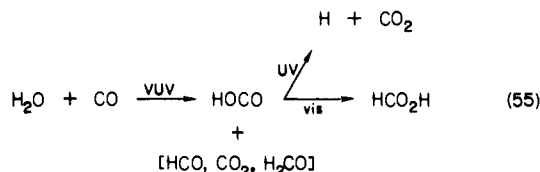
The reaction between vinyl bromide and F_2 has also been induced by laser IR radiation giving the addition product CH_2FCHBr and elimination products HF and *cis*- and *trans*- $CHFCHBr$.¹⁵⁹ Elimination of HBr does not take place. The quantum yield for reaction in-

creases by 3 orders of magnitude from 1605 cm^{-1} irradiation to 3116 cm^{-1} .

Catalano and Barletta have examined the IR laser photochemistry of several reactive matrices using laser powers appropriate to single photon absorption. Excitation of ν_3 of UF_6 (25 mW cm^{-2} or Nernst glower irradiation) in a SiH_4 matrix led to production of SiH_3F , UF_5 , and UF_4 .¹⁶⁰ Curiously the authors used alternate deposition of UF_6 and SiH_4 so calling into question the degree of isolation. Another system examined was SF_6 in a matrix of NO doped with N_2O_3 (see ref 121).¹⁶¹ Irradiation of ν_3 of SF_6 at 33 mW cm^{-2} for only 0.075 s gave product bands in the 3300–3700 cm^{-1} region and at lower frequency. The authors argued against the possibility that the product was H_2O by comparison with spectra of H_2O in N_2 matrices. Unfortunately, they did not dope their $\text{SF}_6/\text{N}_2\text{O}_3/\text{NO}$ samples with water deliberately. In a third system BCl_3 was irradiated in CH_4 giving HCl and possibly H_3CBCl_2 .¹⁶² In contrast to the reactions of F_2 discussed above, all of these reactions have high activation energies in the gas phase. The experiments fulfil the important photochemical criterion that bands of precursor decrease and bands of product increase. However, until the nature of the products and matrices is better defined, it will be difficult to explain the details of the photochemistry. The idea that activation energies could be reduced has also met scepticism elsewhere.¹³⁸

B. Bimolecular Reactions Induced by UV/vis Irradiation

1. **Reaction with CO.** When water is photolyzed (VUV) in a CO matrix a host of C_1 products is observed including two unfamiliar species assigned as the cis and trans isomers of HOCO .⁹⁰ On long-wavelength photolysis ($\lambda > 350$ nm) recombination with hydrogen atoms to HCO_2H is stimulated, while on shorter wavelength photolysis ($200 < \lambda < 300$ nm) hydrogen atoms are expelled to give CO_2 . The photolysis rates of the two isomers differ slightly but there is no evidence for isomerization.



Photolysis of diazomethane in CO-doped nitrogen matrices yields ketene.^{163a}

2. **Reaction with O_2 .** UV photolysis (unfiltered Hg arc) of diazomethane in oxygen-doped matrices yields formic acid, carbon monoxide, and oxygen.^{163b} On warming thermoluminescence is observed; some is ascribed to recombining oxygen atoms, some to formic acid. Among the pathways implicated is the reaction: $\text{CH}_2 + \text{O}_2 \rightarrow \text{HCO}_2\text{H} (\text{a}^3\text{A}') \rightarrow \text{HCO}_2\text{H} (\text{X}^1\text{A}') \quad (56)$

Formaldehyde is also subject to UV photooxidation, yielding CO , CO_2 , H_2O , H_2O_2 , O_3 , HCO_2H , HO_2 , $(\text{HO}_2)_2$, $\text{HC}(\text{O})\text{OO}$, and $\text{HC}(\text{O})\text{OOH}$.^{89b} In these experiments and in the photolysis of glyoxal, the carbon monoxide is generated as a complex with water.¹⁶⁴

Photolysis of iodomethane (low pressure Hg arc) in O_2 -doped matrices yields H_2O , H_2CO , CO , CO_2 , HI , HO_2 , and O_3 .¹⁶⁵ The reaction of photogenerated methyl

DMF/ O_2 /Ar = 1/15/85

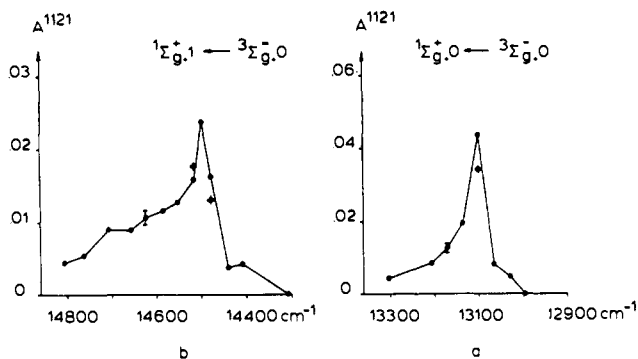


Figure 11. Laser reaction excitation spectra of (a) $\text{O}_2: 1\Sigma_g^+, 0 \leftarrow 3\Sigma_g^-, 0$ and (b) $\text{O}_2: 1\Sigma_g^+, 1 \leftarrow 3\Sigma_g^-, 0$ of matrices dimethylfuran/ O_2 /Ar (1/15/85) at 12 K. Each point in (a) and (b) shows the absorbance growth of dimethylfuran-endoperoxide at 1121.4 cm^{-1} during irradiation. Reproduced with permission from ref 166. Copyright 1983, American Institute of Physics.

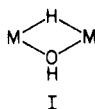
radicals with O_2 to form CH_3O_2 was discussed in section IID.¹⁷

Insertion of O_2 into NH , derived from HN_3 is the source of nitrous acid (see above).^{136,140} Photooxidation of $(\text{SO}_2)_2$ into SO_3 is observed in oxygen matrices.¹⁰⁷

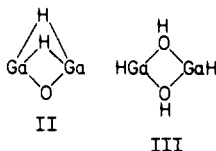
Singlet dioxygen is generated in solution reactions by photosensitization methods unsuitable for use in a matrix. However, Frei and Pimentel have recently demonstrated that $1\Delta_g$ and $1\Sigma_g^+$ states of O_2 may be obtained by direct excitation in a matrix, and their reactions with furan and substituted furans to form endoperoxides may be monitored by IR spectroscopy.¹⁶⁶ Although only the transition to $\text{O}_2(1\Delta_g)$ could be detected by absorption spectroscopy, the $v' = 0$ and $v' = 1$ components of the transition to $1\Sigma_g^+$ could be detected by their reactions. Thus, selective tunable, laser excitation together with IR monitoring resulted in a reaction excitation spectrum (Figure 11). Intriguingly, there appears to be a significant reduction (as much as 22 kJ mol^{-1} for furan) in the barrier to reaction of singlet oxygen with furans relative to the gas phase. The most satisfying explanation postulates that reaction of suitably oriented pairs of molecules imposes a smaller barrier than average. However, this contrasts with arguments advanced against changes in activation barriers in matrices.¹³⁸

3. **Reaction with CO_2 .** The reaction of HN_3 in solid CO_2 yields N_2 and CO_2NH (a molecule of unidentified structure)^{167a} as primary products, followed by $\text{CO} + \text{HNO}$ in a secondary reaction. Photolysis of CH_2N_2 in solid CO_2 yields unidentified products, perhaps isomers of H_2CCO_2 , followed by $\text{H}_2\text{CO} + \text{CO}$.^{167b}

4. **Reaction with H_2O .** Hauge et al. have taken up the challenging problem of the reaction of group 13 and 14 atoms with water. On condensation of Ga, In, and Tl atoms with water, photosensitive adducts are detected both by IR and UV/vis spectroscopy.^{168,169} Short irradiation ($\lambda > 330$ nm) caused reaction to HMOH (see ref 1, section IIB3), while more prolonged irradiation gave MOH . In corresponding experiments with aluminum, HALOH was formed without photolysis. Further bands in the IR spectrum of the Ga, In, and Tl deposits which responded to $\lambda > 530$ nm photolysis were ascribed to dimeric species, e.g., $\text{Ga}_2\cdots\text{OH}_2$ and I.



They photolyze to give several new IR bands in the 1000 cm^{-1} region and then in a subsequent step to give oxides M_2O . The authors argue that the 1000 cm^{-1} bands are H-bridging modes of I (in multiple trapping sites) and "of closely related structural isomers". However, a number of other possibilities come to mind, e.g., II and III, which could yield modes sensitive to deuteration.



Silicon atoms react with water on deposition to form $\text{Si}\cdot\text{OH}_2$ complexes which react slowly in the dark to form HSiOH .¹⁷⁰ However, the isotopic analogue $\text{Si}\cdot\text{OD}_2$ reacts only on $\lambda > 400$ nm excitation. The product is thought to be formed exclusively as a trans conformer for HSiOH but both cis and trans conformers are detected for HSiOD and DSiOD . On prolonged photolysis HSiOH decomposes to SiO .

5. Reaction with HX (X = Cl, F). The reaction of atomic silicon with HF in matrices also results in insertion.^{171a} The silylene product HSiF is formed spontaneously in low yield, but UV photolysis increases the yield appreciably. Both this reaction and the Si/OH_2 reactions suggest that the complexes $\text{Si}\cdot\text{HF}$ or $\text{Si}\cdot\text{OH}_2$ should be considered as discrete molecules with absorptions far removed from atomic silicon.

Photolysis of AlCl with HCl in matrices yields HALCl_2 .^{171b}

6. Reaction with C_2H_4 and C_2H_2 . The photochemical reactions of CH_2N_2 with C_2H_4 and C_2H_2 in matrices yield cyclopropane and allene, respectively.¹⁶³ The corresponding reactions of HN_3 are thought to yield ethylene imine ($\text{C}_2\text{H}_4 + \text{HN}_3$) and ketene imine, CH_3CN and CH_3NC ($\text{C}_2\text{H}_2 + \text{HN}_3$). The formation of ketene imine has been confirmed by synthesis from CH_3CN (section IIIA).¹¹⁴

V. Photochemical Generation and Reactions of Matrix-Isolated Ions

Since the field of matrix-isolated ions has been reviewed several times^{5,6} I will be concerned only with methods in which photochemistry plays a crucial role. Following a discussion of techniques, I will examine a selection of photochemically generated ions in detail, and finish with a discussion of charge stabilization and distribution in matrices. Photochemical experiments involving matrix-isolated ions during 1977–1983 are summarized in Table VII.

A. Methods

There are at least seven methods of generating ions in matrices. The use of multiple methods is often essential to the identification of matrix-isolated ions. (a) Vacuum-ultraviolet (VUV) photolysis through a LiF or other appropriate window. (b) Codeposition with matrix gas (particularly argon) which has passed through a windowless discharge. (c) Photoelectron transfer from

TABLE VII. Photochemically Generated Ions in Matrices^a

product	precursor	ref
C_2^-	C_2H_2	177, 185, 203, 204
CS_2^+	CS_2	178
BX_3^+ (X = Cl, Br)	BX_3	65
SF_n^- (n = 5, 6?)	SF_6	49, 50
SiCl_3^+	SiCl_4	66
HX_2^+ (X = Cl, Br)	halomethanes, SiCl_4	5, 6, 192, 66
HAr_n^+	halomethanes, CH_4	5, 6, 192, 185
CO^+	CO	197
H_2O^+	H_2O	197
NH_3^+	NH_3	197
CWXYZ^+	halomethanes ^b	5, 6, 9, 179–181, 192–195, c
CWXY^+	halomethanes ^b	5, 6, 9, 179–181, 192–195
CWX^+	halomethanes ^b	5, 6, 9, 179–181, 192–195
$\text{X}\cdot\text{H}\cdots(\text{CXYZ})^-$	halomethanes ^b	5, 6, 9, 179–181, 192–195
$\text{X}^-\cdots(\text{CHYZ})$	halomethanes ^b	5, 6, 9, 179–181, 192–195

^a 1977–1983 excluding "organic" ions. ^b W, X, Y, Z = halogen, hydrogen. ^c Andrews, L.; Kelsall, B. J.; Miller, J. H.; Keelan, B. W. *J. Chem. Soc., Faraday Trans. 2* 1983, 79, 1417.

alkali atoms codeposited into the matrix (see ref 1, section IIA). (d) Electron bombardment during deposition^{172–174} (in the most recent version the target is held at a positive potential relative to the source).¹⁷⁴ (e) Proton bombardment during deposition. (f) Cocondensation of a salt with a neutral molecule into a matrix (e.g., $\text{MF} + \text{SiF}_4 \xrightarrow{\Delta} \text{M}^+\text{SiF}_5^-$).^{175,176} (g) Two-photon ionization. I will discuss methods a, b, e, and g here.

1. Vacuum-Ultraviolet Photolysis through Window. In this section I discuss those experiments in which VUV radiation (usually from a H_2 or Xe discharge) is passed through a suitable window before reaching the target. We may be certain, therefore, that neither ions nor excited atoms from the discharge are involved in radiolysis. This method has been quoted many times in this review and ref 1 as a source of radicals; usually the radical yield greatly exceeds the ion yield. Since scattering of VUV radiation by the matrix is severe, it is usual to irradiate during deposition as in the generation of C_2^- from acetylene.¹⁷⁷ If the conversion is sufficiently effective and the method of detection sufficiently sensitive, in situ photolysis may be used. In one example Bondybey et al. photolyzed CS_2 (Ne or Ar matrices with either a H_2 or an Ar lamp) and detected CS_2^+ by laser-induced fluorescence.¹⁷⁸

The primary photochemical process in this method must be photoionization of the stable precursor or of radicals to give matrix-isolated cations. Anions are generated by subsequent electron-capture processes which are often dissociative (ref 1, section IIA).

2. The Windowless Discharge Technique. A popular technique involves cocondensation of a sample of precursor + Ar with Ar which has passed through a hole in a discharge tube. This method gives higher selectivity and higher yields both of radicals and ions than the conventional VUV photolysis method.⁵ For instance, it has been applied to the generation of BX_3^+ (X = Cl, Br) from BX_3 ,⁶⁴ and (using Ne instead of Ar) to generate CO^+ (see below). While Jacox argues that the major agents of reaction are 11.5–11.8-eV excited argon atoms,⁵ Andrews argues in favor of VUV photons of similar energy.⁶ The relative importance of excited argon atoms and argon resonance radiation probably varies substantially with the exact experimental con-

ditions and the molecule under study. However, the primary routes to ions must be simple electron loss and capture processes as in conventional VUV photolysis.

3. Proton Bombardment. If 2-keV protons from a RF discharge are focussed onto a matrix during deposition, they act as a potent radiolysis source in generating radicals and ions.¹⁷⁹⁻¹⁸¹ For instance, proton radiolysis of CCl₄/Ar gives CCl_n⁺ (*n* = 1-3), CCl_n⁺ (*n* = 2-4), and Cl_n⁺ (*n* = 3, 4). Either concurrent or subsequent exposure to thermal electrons from a bare tungsten filament not only neutralizes any gross charge accumulation but also bleaches the matrix-isolated ions and increases the concentration of radicals. A similar effect is obtained by Nernst glower photolysis, the most effective wavelengths being 500-3000 nm. This long-wavelength photolysis is thought to release electrons from anionic species. Only a small proportion of the protons are thermalized: they appear in the matrix as HCl₂⁻, Ar_nH⁺, CHCl₃, and CH₂Cl₂. The major mechanism of radiolysis must be via argon ions; indeed some of the protic species may be derived from adventitious water. Although the *matrix-isolated* ions are photo- and electrobleached in these experiments, the ion pairs are stable. One such ion pair is CCl₃⁺·Cl⁻, probably stabilized by the activation energy for distorting planar CCl₃⁺ and for moving the Cl⁻ counterion to a position appropriate for recombination.

4. Two-Photon Ionization. Kelsall and Andrews have shown that a high-pressure mercury arc will suffice to photoionize aromatics such as naphthalene isolated in matrices in the presence of CCl₄ as an electron trap.¹⁸² Filtered photolysis was used to show that ionization occurred *via* primary absorption to a long-lived excited state which absorbed a second photon to form the ion.

B. Examples of Ions in Matrices

This section includes discussion of several key matrix-isolated ions which were established some time ago, together with some species obtained recently. A major problem in this branch of matrix isolation is that of determining the charge carried by the matrix species. For some molecules it may be deduced from large shifts to high or low frequency in IR absorptions (e.g., NO₂/NO₂⁻).¹⁷² For others it is necessary to dope the matrix with suitable electron donors (e.g., alkali metals) or acceptors (e.g., chlorine) and look for enhanced production of the species. Another essential technique for determining charge is the photochemical behavior: isolated ions often are photobleached by long-wavelength radiation. Spectra of ions may be complicated not merely by the presence of cage complexes with neutral molecules (X⁺.....Y) but by ion pairing which may shift the spectrum considerably and alter the photochemistry (cf., CCl₃⁺·Cl⁻, section VA3, or e.g., C₂⁻ is photobleached but Cs⁺C₂⁻ is not).¹⁷⁹ Notice that molecular ions of one charge have been observed many times without evidence for ions of opposite charge so that this does not provide a criterion for identifying ions. The following examples illustrate these principles.

1. HAR_n⁺ and HKR_n⁺. When H₂ is passed through a discharge with Ar prior to condensation, an IR band is observed at 904 cm⁻¹. Its deuterium counterpart is shifted by a factor of 1.404 to 644 cm⁻¹; these bands are shifted a massive 52 and 37 cm⁻¹, respectively, when Kr

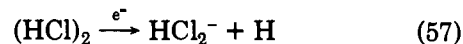
TABLE VIII. Effect of Counterion on the Absorptions of HCl₂⁻ in Argon Matrices^a

counterion	ν_3 , cm ⁻¹	counterion	ν_3 , cm ⁻¹
isolated	696	K ⁺	736
Li ⁺	760	Rb ⁺	729
Na ⁺	658	Cs ⁺	723

^a From ref 190.

replaces Ar but are not observed at all in Xe or Ne. The ³⁶Ar/⁴⁰Ar shift is only 0.2 cm⁻¹ indicating bonding to at least three and probably more Ar atoms.¹⁸³ This species is also observed on VUV photolysis of H/D containing species (e.g., HCl, HCCl₃) but not on mercury arc photolysis of H atom sources (e.g., H₂S, HI, etc.), nor on deposition of H atoms from an off-axis discharge tube.¹⁸⁴ However, it can be generated at lower energies if cations are already present as in the $\lambda < 260$ nm photolysis of HCCl₂⁺ or the $\lambda > 220$ nm photolysis of H₂CCl⁺ (see section VB3 and ref 192). It is considerably enhanced by doping the matrix with electron acceptors such as CO₂ or better Cl₂. The 644 cm⁻¹ band is observed weakly on D⁺ bombardment of Ar during deposition, but becomes 100% absorbing when the argon is doped with chlorine.¹⁸¹ The 904 cm⁻¹ band is not observed in H⁺ bombardment experiments. The most satisfying solution to the riddle is that this species is H⁺ (D⁺) solvated by a cage or four or six argon atoms. However, within the last year, arguments were advanced for reverting to the old assignments, namely the neutral HAR_n and HKR_n.¹⁸⁵ In these experiments, VUV photolysis of Kr/CO/CH₄ gave HCO, C₂⁻, and the HKR_n⁺ bands; on annealing the HCO increased, HKR_n⁺ decreased while C₂⁻ and other species were not affected. Similar results were obtained with argon matrices. In Pimentel's original experiments¹⁸³ HAR_n⁺ was photobleached by IR radiation suggesting very readily ionized, but unobserved, anions (H⁻, O₂⁻?). When Cl₂ is added to the matrix, long-wavelength photobleaching increased the HCO bands at the expense of HKR_n⁺.¹⁸⁵ Clearly, the conclusion of this story remains unwritten. Nevertheless, HAR_n⁺ and HKR_n⁺ play an important role in the photochemistry of other ions (e.g., halomethane ions).

2. HX₂⁻ and X₃⁻ (X = Cl, Br). Like HAR_n⁺ the species generated by VUV photolysis or glow discharge of Ar/HX/X₂ (X = Cl, Br) and Ar/Cl₂ mixtures were assigned originally to neutral radicals but have been shown subsequently to be anionic.¹⁸⁶⁻¹⁸⁸ Proof of the charge carried by the HX₂⁻ ions formed in the Ar/HX/X₂ discharge comes from (a) doping with Cs, when mercury arc radiation suffices for their production rather than VUV radiation,¹⁸⁸ (b) cocondensation of alkali halides with HX which gives the same species perturbed by alkali ions (Table VIII).¹⁸⁹ The probable source of HCl₂⁻ in discharge experiments with HCl has been shown to be dimeric species which undergo dissociative electron capture:¹⁸⁸



Cocondensation of Cl₂ with alkali halides has been used to demonstrate that the Cl₂/Ar discharge product is Cl₃⁻.^{190,191} These experiments are reviewed in more detail in ref 5 and 6.

3. Halomethyl Ions. The intensive investigations of halomethyl ions by Andrews et al. and by Jacox have

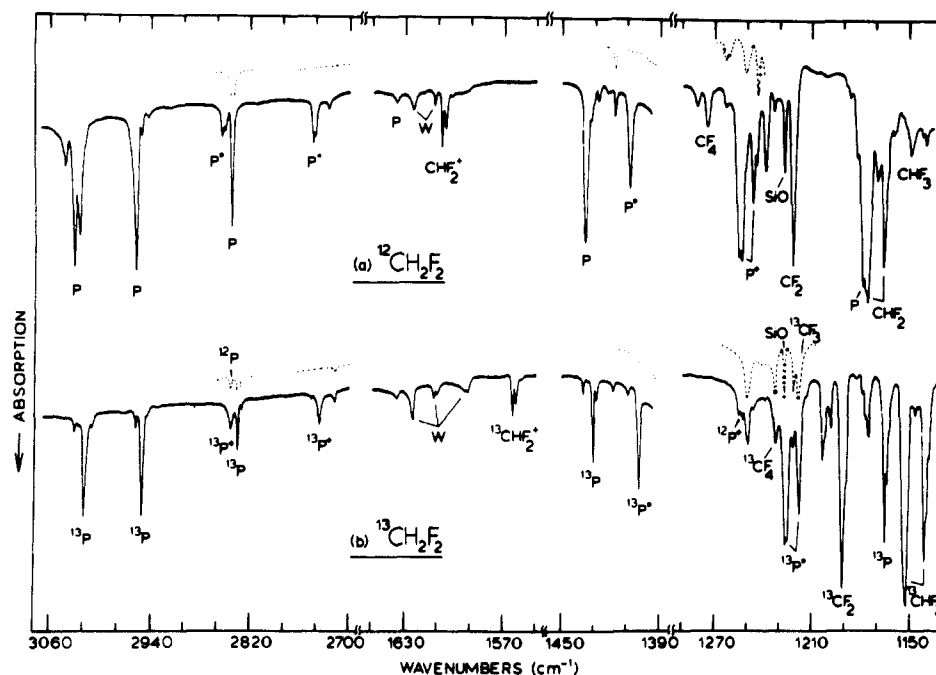


Figure 12. IR spectra of CH_2F_2 subject to windowless Ar resonance photolysis during condensation: (a) Ar/ CH_2F_2 (200:1), (b) Ar/ $^{13}\text{CH}_2\text{F}_2$ (400:1, 90% ^{13}C). Dashed traces show changes on mercury arc photolysis. P = CH_2F_2 , P⁺ = CH_2F_2^+ . Reproduced with permission from ref 9. Copyright 1979, American Institute of Physics.

TABLE IX. IR Absorptions of $\text{CH}_2\text{F}_2^{n+}$ and CHF_2^{n+} ($n = 0, 1$)^a

	$\nu_a(\text{CH}_2)$	$\nu_s(\text{CH}_2)$	$\delta(\text{CH}_2)$	$\nu_a(\text{CF}_2)$
CH_2F_2	2958	3032	1436	1079
CH_2F_2^+	2744	2854	1408	1255
CHF_2				1175
CHF_2^+				1608
$^{11}\text{BHF}_2$				1402

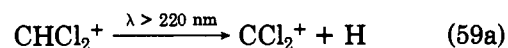
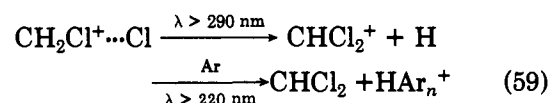
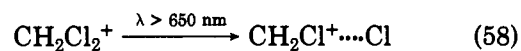
^aFrom ref 9, in cm^{-1} .

been summarized in their reviews.^{5,6} I will examine one example in some detail, the photolysis of CH_2F_2 , and add further examples only where they introduce different principles.

Cocondensation of CH_2F_2 with argon which has passed through a discharge⁹ yields four groups of product bands in IR and UV/vis spectra which are distinguished by (i) photolysis with a variety of wavelengths, (ii) annealing experiments, and (iii) changing the orifice of the discharge tube. The groups of product bands are assigned with the aid of ^{13}C and ^2H substitution: (a) The well-known radicals CHF_2 , CHF , CF_2 , and CF are all stable to mercury-arc photolysis. The major progression observed in the visible spectrum is photosensitive and is assigned to CHF perturbed by HF . (b) The parent cation, CH_2F_2^+ (Figure 12) has IR bands which show a photolysis threshold between 500 and 650 nm, but the reaction product is not identified. The C-H stretching and bending fundamentals of CH_2F_2^+ are shifted by up to 200 cm^{-1} to low frequency of CH_2F_2 while the antisymmetric C-F stretching mode is raised 176 cm^{-1} (Table IX). This is in accord with calculations which show that the HOMO of CH_2F_2 is C-H bonding and C-F antibonding. CH_2F_2^+ is thought to arise by direct photoionization of CH_2F_2 by Ar resonance radiation. (c) The bands of CHF_2^+ are photosensitive only with the unfiltered mercury arc and destruction is limited to 20%. The massive increase in the CF_2 antisymmetric stretching band of CHF_2^+ rela-

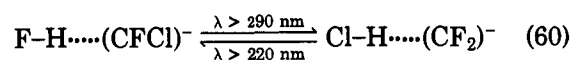
tive to CHF_2 (>400 cm^{-1} , Table IX) is attributed to the change from pyramidal to planar structure on ionization. Not only has an antibonding electron been removed but π bonding is now enhanced. The frequency is 200 cm^{-1} above that for BHF_2 suggesting stronger π bonding in the cation. The most likely source of CHF_2^+ is photoionization of the radical CHF_2 . (d) The fourth group of bands consist of 2 broad bands at 3243 and 3214 cm^{-1} with no ^{13}C shift and sharper bands in the 750–850 cm^{-1} region. This species, which is photobleached by 500–1000-nm radiation, is assigned to the anion $\text{FH}\cdots\text{CHF}^-$. It is probably formed by electron capture by CH_2F_2 but the photobleaching product is unidentified.

The photolysis of CH_2F_2 provides an example of one type of anion and some of the photochemical pathways. Other possibilities are illustrated by CH_2Cl_2 , CHCl_3 ,¹⁹² and CHF_2Cl .^{192–194} The products of photolysis of CH_2F_2^+ were not established but more details are known for CH_2Cl_2^+ and CH_2Cl^+ :^{192,195}



Notice the dissociation of the proton as HAr_n^+ .

The anion $\text{F-H}\cdots(\text{CHF})^-$ observed in the CH_2F_2 experiments is one of a group in which HX is hydrogen-bonded to a CHX^- or CX_2^- ion. The corresponding anions derived from CHF_2Cl show a remarkable photochemical isomerization.^{193,194}



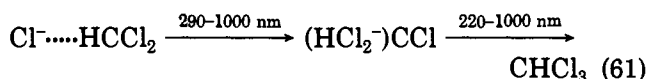
Two further types of anion are observed. The major

TABLE X. Comparison of Hydrogen-Stretching Frequencies for Intramolecular Hydrogen-Bonded Anions Identified in Haloform Studies^a

species	absorptions, cm ⁻¹	species	absorptions, cm ⁻¹
Type III		Type I	
F-N...(CF ₂) ⁻	3562, 3599	Cl ⁻ ...HCFC1	2762
F-H...(CFCl) ⁻	3456	Cl ⁻ ...HCCl ₂	2723
F-H...(CCl ₂) ⁻	3308, 3478	Cl ⁻ ...HCClBr	2681
F-H...(CFBr) ⁻	3444	Cl ⁻ ...HCClI	2670
F-H...(CBr ₂) ⁻	3287, 3441	Cl ⁻ ...HCBBr ₂	2640
F-H...(CFI) ⁻	3380	Br ⁻ ...HCFBr	2782
F-H...(Cl ₂) ⁻	3158	Br ⁻ ...HCCl ₂	2795
Cl-H...(CF ₂) ⁻	2688	Br ⁻ ...HCClBr	2764
Cl-H...(CFCl) ⁻	2518	Br ⁻ ...HCBBr ₂	2730
Br-H...(CF ₂) ⁻	2406	I ⁻ ...HCF ₂	2874
		I ⁻ ...HCFI	2865
		I ⁻ ...HCCl ₂	2863

^a From reference 193 and 194.

anion obtained from CH₂Cl₂ is the familiar HCl₂⁻ ion. The anion from chloroform shows the typical H-bonding characteristics of a broad low frequency stretching mode (2723 cm⁻¹) and an intense overtone mode (2499 cm⁻¹). With the aid of ¹³C and ²H substitution this ion is assigned to Cl⁻...HCCl₂. In contrast to the F-H...CHF⁻ ion the proton is not transferred to the halide ion. The Cl⁻...HCCl₂ ion is photosensitive too.



The range of anions observed in the halomethane experiments is shown in Table X.

4. BX₃⁺ (X = Cl, Br) and SiCl₃⁺. Proton radiolysis of BX₃ (X = Cl, Br) yields HCl₂⁻, HBX₂, and BX₂. In windowless Ar discharge experiments BX₃⁺ ions are observed in addition to BX₂ radicals⁶⁵ (see section IIC). Their IR absorptions are shifted 100–150 cm⁻¹ to high frequency of the neutral molecules and are destroyed by photolysis in the region of their near-ultraviolet absorption bands (300–400 nm). The photoproducts have not been identified. Although the HOMO of BX₃ is a halogen nonbonding orbital, π bonding must be enhanced in the cation (contraction of the halogen p orbitals) resulting in the high frequency shift in the vibrational fundamentals. The windowless discharge technique has also been used to generate SiCl₃⁺, HCl₂⁻, and other neutral products (see section IIC)⁶⁶ from SiCl₄ and SiHCl₃. The SiCl₃⁺ ion showed chlorine isotopic structure in its IR spectrum consistent with its formulation. Limited evidence was also obtained for the MCl₄⁺ cations (M = Si, Ge, Sn).

5. SF_n⁻ (n = 5 or 6) Ions. The generation of SF_n⁻ (n = 5 or 6) has been mentioned in section II2 and in ref 1. One of the features observed on codeposition of discharged argon and SF₆/Ar was assigned to SF₅⁻ because of a coincidence with the absorption of Cs⁺SF₅⁻.⁴⁹ Simpler spectra were obtained by photolysis of SF₆ in the presence of electron donors Na, NO, and K, or by VUV photolysis with a hydrogen lamp.⁵⁰ In this case the same feature (595 cm⁻¹) was assigned to SF₆⁻. Clearly the experiments with electron donors establish the negative charge, but the stoichiometry remains uncertain. On intuitive grounds I prefer SF₅⁻ to SF₆⁻. Both ions are generated by electron attachment in the gas phase but SF₅⁻ has a much higher electron affinity

TABLE XI. Changes in Ionization Potential Induced by Matrices in eV^a

	matrix	matrix			
		Ne	Ar	Kr	Xe
guest	C ₂ H ₄	-0.08	-1.38	-1.63	-2.37
	CH ₃ I	+0.02	-0.91	-1.36	
	C ₆ H ₆	-0.06	-0.74	-1.07	-1.50
	Xe	+0.02	-1.59	-1.73	-2.8 ^b
	H	-2.1	-3.9	-4.4	-4.9

^a All values except those for H from ref 198. The values for H are gas-phase proton Affinities from ref 199. ^b This is the photoelectron emission threshold of solid xenon.

than SF₆ (3.6 and 0.8 eV, respectively).¹⁹⁶

6. ESR Studies of Nonmetal Cations: CO⁺, N₂⁺, H₂O⁺, NH₃⁺. Knight et al. have had considerable success in producing molecular ions in matrices for study by ESR. The ions CO⁺, NH₃⁺, and H₂O⁺ were generated in Ne matrices by an open discharge technique in which only Ne passed through the discharge region.¹⁹⁷ In contrast, N₂⁺ was generated by electron bombardment.¹⁷⁴ All of the ions generated by photoionization were bleached rapidly by visible irradiation, a useful distinction from the neutral radicals. The massive ¹³C isotropic hyperfine coupling in ¹³CO⁺ (A_{iso} = 1573, A_{dip} = 46 MHz) demonstrates that a sensitive ion parameter shifts very little compared with the gas phase (A_{iso} = 1506, A_{dip} = 48.2 MHz).¹⁹⁶ Both NH₃⁺ and CO⁺ proved to rotate in the matrix, producing nearly isotropic ESR spectra.

C. Charge Stabilization and Distribution in Matrices

This section addresses questions concerning (i) the energetics of formation and distribution of ions in matrices, (ii) the ability of the matrix to support electrons, holes, and protons, and (iii) the elusive nature of counterions and the nature of photobleaching reactions.

1. Energetics and Distribution of Ions. Two important features of the energetics of ion formation in matrices are that (i) the matrix must remain very close to electrical neutrality, (ii) the matrix can alter the energetics of ion formation relative to the gas phase by (a) solvation and (b) ion pair formation.

A study of VUV absorption spectra in matrices has shown that molecular and atomic ionization potentials are reduced substantially by the matrix.¹⁹⁸ These shifts, which are induced largely by solvation of the cation and electron (Table XI), illustrate the importance of obtaining more VUV spectra in matrices. The values for the proton have not been obtained experimentally, but it is safe to assume that they exceed the gas-phase proton affinities (also listed in Table XI).¹⁹⁹ The observation of Ar_nH⁺ (n = 4/6) rather than ArH⁺ supports this contention.

Direct measurements of ionization energies (IE) of matrix-isolated molecules in solid xenon by photoelectron spectroscopy suggest somewhat less dramatic reductions relative to the gas phase.^{200,201} The reduction in IE for N₂ is 1.2 eV, for the A²Π state of CO⁺ 1.2 eV, for Ni atom d⁹s¹ → d⁸s¹ ionization ~2 eV, for Cu atoms 1.3 eV.

The role of electrostatic energy in stabilizing ion pairs formed by photoelectron transfer from alkali metals has

TABLE XII. Ionization Potentials (Gas-Phase) of Molecules Exhibiting Ion Photochemistry in Matrices

IP, eV		IP, eV		IP, eV	
H	13.6	HB ^r a	11.7	CO ^a	14.0
C ₂ H ₂ ^a	11.4	Cl ₂	11.5	NH ₃ ^a	10.2
CH ₂ F ₂ ^a	12.7	BCl ₃	11.6	CCl ₄ ^a	11.7
HCl ^a	12.7	SF ₆ ^a	15.5	CS ₂ ^a	10.1
				H ₂ O ^a	12.6

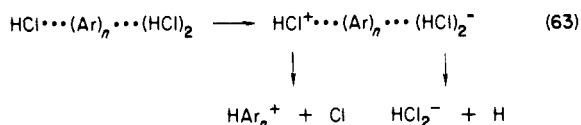
^aVertical ionization potentials from: Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy"; Wiley: London, 1970.

been stressed by Kasai²⁰² and Jacox⁵ (see also ref 1, section II4). It is pointed out less often (but see ref 203) that this coulombic term and the electron affinity of an acceptor may be important in ionization processes using discharge lamps, if the electron tunnels from the highly excited state of one guest through to the next guest. The energy of a process such as



is given by $\text{IE} - \text{EA} - e^2/(4\pi\epsilon_0\epsilon r)$. The separation of two nearest neighbor sites in Ar is 7.5 Å giving a coulomb stabilization of ~ 1.3 eV in addition to the electron affinity which is likely to be favorable. Thus, pairs of molecules which are too far apart to affect each other's vibrational spectrum, may stabilize ion pairs.

The two sources of stabilization of ions go far in explaining the processes occurring on VUV photolysis. The gas-phase ionization potentials of some atoms and molecules which exhibit matrix ion chemistry are listed in Table XII. For comparison the major emission of a hydrogen discharge lamp is 10.2 eV, while the argon resonance radiation is mostly in the 11.6–11.8-eV range. Since the ionization potentials often exceed the photon energies, solvation and/or ion-pair formation must be essential in many of these ionization processes. It also follows that the ionization must take place in the matrix, not in the gas phase (prior to deposition). A reaction might typically follow a course of the type



The alternative explanation of sequential photochemical processes involving ionization of daughter radicals has rarely been subjected to experimental test and may be important in some ionization processes.

The importance of solvation and electrostatic terms will depend on host and guest. For instance, assuming that C₂⁻ is generated together with C₂H₂⁺ on 122-nm photolysis of acetylene, solvation effects are sufficient to explain the photolysis in Ar, Kr, and Xe matrices but electrostatic attraction is probably needed in Ne. Using this argument, which assumes similar solvation energies for C₂H₂ (unknown experimentally) and C₂H₄ (Table XI), Brus and Bondybey postulate that C₂⁻ is formed in Ne by electron tunnelling from excited C₂H₂ to a C₂ molecule $\lesssim 20$ Å away (Figure 13).²⁰³ On the other hand, experiments in Ar matrices suggest that there is a limiting concentration of C₂⁻ of about 1 ppm corresponding to ion separations of 350 Å and that electron transfer between anion and cation destroys the ions at closer separation.²⁰⁴ Return electron tunnelling is also

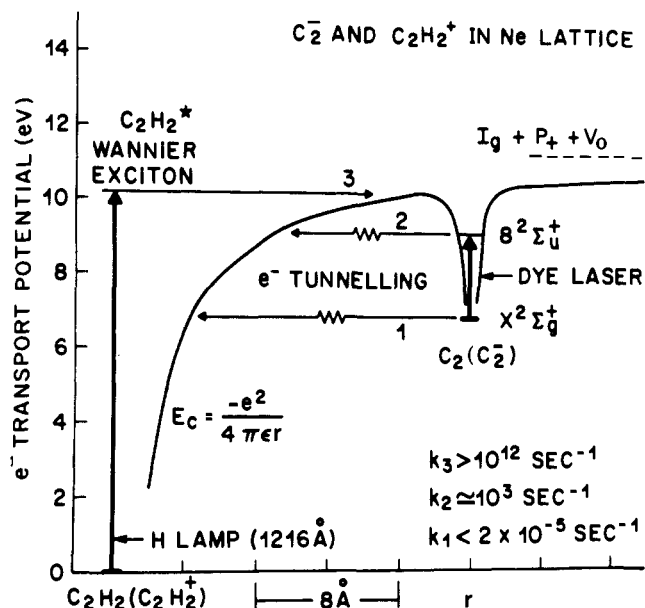


Figure 13. Electron transport potential between C₂H₂⁺ and C₂⁻ separated by 20 Å in Ne matrix. The Rydberg-like Wannier excitation state of C₂H₂^{*} is a weakly bound electron-ion pair screened by the dielectric host. k_2 is the rate constant for photobleaching, k_3 the rate constant for photoproduction, k_1 the rate constant for thermal bleaching. Reproduced with permission from ref 203. Copyright 1975, American Institute of Physics.

invoked to explain the photobleaching of C₂⁻(B²Σ_u⁺) in Ne²⁰³ (see section VC3).

2. Protons, Electrons, and Holes. As has been shown by experiment (section VB1) it is straightforward to support a solvated proton in an Ar or Kr matrix. Energetic considerations (section VC1) suggest Xe_nH⁺ should also be highly stable, but intriguingly it has never been detected. Milligan and Jacox¹⁸⁴ suggest that it may be unstable with respect to Xe₂⁺ and H, but this simply moves the question to the nondetection of Xe₂⁺ (see below). I attribute its absence to absorption by Xe matrices instead of hydrogen atoms: the onset of absorption by Xe is at 148 nm.²⁰⁵ Use of a dilute Xe/Ar matrix would seem to avoid this problem, but this method has not been successful with Kr/Ar mixtures.¹⁸³

In contrast to the stability of solvated protons, it seems to be assumed by most authors that any electrons or holes would migrate rapidly through a noble-gas mixture until they were captured by a guest molecule. Thus, it is argued that the absence of a counterion spectrum indicates that the ions are not detected, rather than that the opposing charge is carried by electrons or holes. In support of this contention no ESR or optical spectrum of either holes or electrons has been detected in a noble-gas matrix. However, a closer examination of the experimental evidence shows that this assumption, although justified for electrons, is probably incorrect for holes.

Three types of experiment give information on electron mobility in noble-gas matrices: (i) mobility of excess electrons, (ii) VUV absorption by rare gases, (iii) photoconductivity measurements. I will summarize the results of all three in turn. Measurement of the residence time of excess high-energy electrons in rare-gas solids gives a direct measurement of electron mobility in the conduction band.²⁰⁶ The values of the low-field electron mobilities range from 600 (Ne) to 4000 (Xe) cm² V⁻¹ s⁻¹, a high value comparable to that of Ge (4500

$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$). Remarkably, the values decrease by a factor of only about 2 in liquid Ar, Kr, and Xe, suggesting that they are not dependent on high order. The mobility of electrons in liquid neon is reduced drastically relative to the solid.

VUV spectra of pure rare-gas solids show a series of exciton bands to low energy of the conduction band edge.²⁰⁵ While the first two bands for Ne, Ar, Kr, and Xe are close to the free atom absorptions, the higher energy bands correlate with atomic spectra only for Ne. There are two extreme theories of exciton spectra. At the Frenkel extreme, there is an excited atom at a given lattice site and the transition energies are perturbed only slightly from the free atom spectra. At the delocalized extreme, a Wannier exciton is a weakly interacting electron-hole pair extending over a distance much greater than the lattice constant. The spectrum of a Wannier exciton shows a series of hydrogen-like bands which are not found in the free atom. The picture obtained for Ar, Kr, Xe is of a Frenkel-type $n = 1$ state with $n = 2, 3$ states closer to the Wannier limit. Neon can be described adequately by the Frenkel theory. The presence of these Wannier excitons is good evidence of the delocalization of electrons in Ar, Kr and Xe.

Pure xenon shows an onset for photoconductivity at about 9.2 eV,^{205,206} but xenon doped with a suitable donor shows photoconductivity in the near UV and visible. Xenon doped with aniline, methylaniline, or dimethylaniline ($M/R = 100\text{--}300$) exhibits photocurrents which peak in the 300–260-nm region compared to ionization potentials above 60000 cm^{-1} (165 nm).²⁰⁷ More recently Gründler et al. have observed photoconductivity using Na in Xe ($M/R < 6000$) with a threshold of 630 nm.²⁰⁸ I conclude from these various experiments that it is unlikely that trapped electrons are stable in noble-gas matrices, but that the matrices should be excellent mediators of interionic electron transfer.

Although some authors have argued that holes would be highly mobile in argon matrices,²⁰³ this is not in accord with direct measurements of hole mobilities which are $\sim 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for solid Ne, Ar, Kr, and Xe.²⁰⁶ The low mobility is interpreted in terms of self-trapping to form R_2^+ ions which are able to hop slowly. While Ar_2^+ has been detected only as a transient in the gaseous and liquid phases, Xe_2^+ is a stable species in SbF_5 solutions.²⁰⁹ Xe_2^+ should be very conspicuous on account of its green color (absorption bands, 335, 710 nm), intense resonance Raman scattering ($\nu = 123 \text{ cm}^{-1}$), and ESR signals. The possibility of Xe_2^+ or Xe_n^+ in matrices must therefore be taken quite seriously. Circumstantial evidence for the production of Ar_2^+ in experiments with HCCl_2F has been found by Jacox and Milligan.²¹⁰ Usually anion production is enhanced by doping with alkali metals. However, higher anion yields were obtained with a windowless Ar discharge than with sodium photoionization, and no cations were detected. The authors argued that the anion concentration was too high for the molecular cations to go undetected. They suggested that Ar atoms in higher Rydberg states could be photoionized and that Ar_2^+ would then be trapped in the matrix. A repeat of this experiment using ESR detection would be valuable, although identification of Ar_2^+ would be hampered by the lack

TABLE XIII. Possible "Invisible" Anions and Electron Affinities of the Corresponding Neutral Species (eV)^a

anion	electron affinity	anion	electron affinity
H^-	0.80	Cl^-	3.61
O^-	1.47	Br^-	3.36
O_2^-	0.45	I^-	3.06

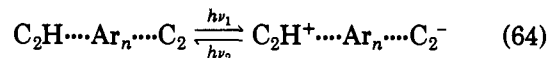
^aFrom CRC Handbook of Chemistry and Physics.

of argon isotopes with nuclear spin.

3. Counterions and Photobleaching. As has been mentioned in the previous sections, one ion is frequently detected in a matrix spectrum without evidence for an ion of opposite charge. In considering the nature of these phantom ions, we need to consider another enigma of this branch of matrix isolation, the nature of photobleaching processes.

In some situations molecular ions become conspicuous because of exceptionally intense absorptions. Any molecular counterions are then likely to be undetectable. If Allamandola et al.²⁰⁴ are correct in arguing a limiting concentration of 1 ppm of C_2^- in Ar, it seems reasonable that counterions such as C_2H^+ , C_2H_2^+ , and possibly HAr_n^+ would remain unobserved. When concentrations are higher we must consider species which have no sharp absorptions derived either from the guests or from H_2O and O_2 impurities. Possible anions together with the relevant electron affinities are listed in Table XIII. In contrast to the anions, almost all cations except O_2^+ and R_2^+ ($\text{R} = \text{Ar, Kr, Xe}$) should be detectable in the IR. As shown above, the R_2^+ ions should absorb in the visible spectrum and be conspicuous in ESR spectra.

Further deductions about counterions may be made from the wavelengths active in photobleaching ions. Photobleaching of isolated ions is very widespread but a glance at the preceding pages will show few well-documented processes. There is the photodissociation of $\text{CH}_2\text{Cl}_2^{+192}$ and the isomerization of $\text{F-H}\cdots(\text{CFCl})^-$,¹⁹³ but the simpler process of electron return is harder to document. The photobleaching of C_2^- is thought to be a return process involving electron tunnelling (see above), but there is no chance of detecting the products when the C_2^- concentration is very low. This bleaching of $\text{C}_2^-(\text{B}^2\Sigma_u^+)$ is specific for each of the sites observed in Ne matrices and has a quantum yield of $10^{-4}\text{--}10^{-5}$ (see Figure 13).²⁰³ Intriguingly, C_2^- can be regenerated in Ar following photobleaching even if longer wavelength radiation (6.2–7.4 eV) is used than in the original generation from acetylene (10.2 eV).¹⁷⁷ This has been explained by reaction of daughter radicals assisted by electrostatic stabilization:²⁰³



Photobleaching of cations sometimes occurs on long-wavelength irradiation suggesting ready electron photodetachment from anions. The two "invisible" ions most likely to supply return electrons on IR irradiation are H^- and O_2^- (Table XIII). Electron return from Cl^- requires UV irradiation as has been observed for $\text{HAr}_n^+\cdots\text{Cl}^-$ ion pairs.¹⁸¹ The bleaching of "isolated" HAr_n^+ proceeds with light of 650–1200 cm^{-1} corresponding to absorption by HAr_n^+ .¹⁸³ Is this electron return and, if so, what is absorbing the light; if not, does Ar_nH^+ dissociate to $\text{Ar}_2^+ + \text{H}$? This phenomenon is

surely ripe for study by selective laser photolysis.

VI. Energy Transfer and Laser-Induced Fluorescence In Photochemical Fragments

The use of pulsed lasers has added enormously to our knowledge of dynamic processes and of spectroscopic constants in matrices. The visible absorptions associated with many radicals make these molecules especially amenable to study by laser-induced fluorescence. In the technique developed and applied mainly by Bondybey et al., a dye laser is used to excite an emission spectrum which is often extremely sharp because of the site and isotope selectivity of the narrow laser line. The resulting time-resolved emission gives information about excited-state energies and lifetimes, and ground-state vibrational energies. By scanning the laser and examining a constant emission frequency, one obtains an excitation spectrum. This corresponds to selected bands of the absorption spectrum and gives excited-state vibrational properties. Often all the emission originates from the ground vibrational state of the upper electronic state ($v' = 0$) indicating that the vibrational relaxation rate is faster than the rate of emission. In other cases vibrational relaxation is slower and emission is detected from excited vibrational states ($v' > 0$). In this way information is obtained about vibrational relaxation in the excited state. Further data may be obtained by using a dual laser arrangement. In addition to the usual pump laser, a probe laser fired after a slight delay is used to excite the electronic transition from excited vibrational states of the ground electronic state (e.g., $v'' \geq 1 \rightarrow v' = 0$). The $v'' \geq 1$ states are populated by emission following the initial laser pulse. The perturbations in the resulting emission spectrum allow the vibrational relaxation times in the ground electronic state to be deduced.

The simplest theory of radiationless transitions involves coupling to the lattice phonons, i.e., a multiphonon relaxation process. The relaxation rate should then decrease exponentially with the energy gap of a particular relaxation step, and should also be a function of the coupling to the lattice. Such relaxation should be strongly dependent on the isotopes involved because of the resulting changes in the energy gap. Since it is an intramolecular process, it should be concentration independent. I have selected two examples (C_2^- and NH) to illustrate upper and lower state vibrational relaxation times, relaxed and unrelaxed emission, and molecules which do and do not follow the energy-gap law. I then pick out trends in relaxation processes of linear triatomics and dihalocarbenes.

Table XIV gives a summary of LIF results on photochemical fragments. The reader is also referred to the discussion of LIF in other molecules in ref 1.

A. Examples of Laser-Induced Fluorescence (LIF)

1. C_2^- . The LIF spectrum of C_2^- shows the characteristic progression with each member consisting of a sharp zero phonon line (ZPL) and a broader low frequency wing (Figure 14).²⁰³ While the ZPL represents transitions with no change in phonon number, the wing is a superposition of transitions involving an increased phonon quantum number in the ground state. Thus,

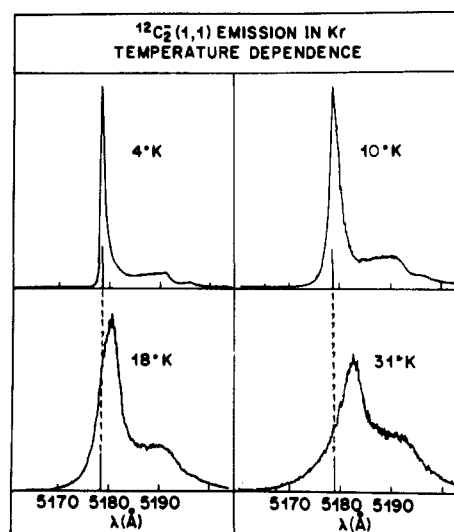
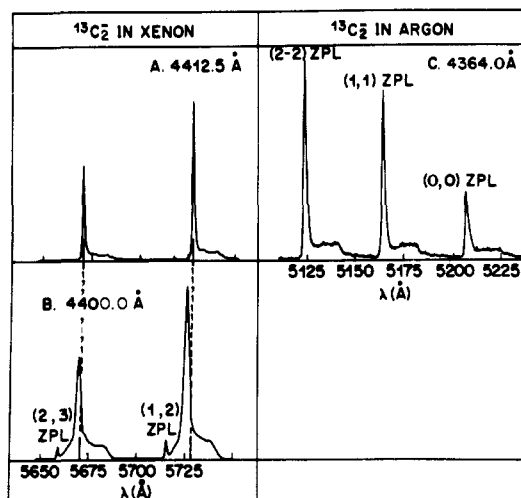


Figure 14. (Above) Laser-induced emission spectra of $^{13}C_2^-$ in (A) Xe matrix, excitation 4412.5 Å; (B) Xe matrix, excitation 4400.0 Å; (C) Ar matrix, excitation 4364.0 Å. In each case $v' = 2$ is excited and emission from $v' = 2, 1$, and 0 are shown. (Below) Laser-induced emission of $^{12}C_2^-$ in Kr show $v' = 1 \rightarrow v'' = 1$ emission as a function of temperature for threshold excitation of $v' = 1 \leftarrow v'' = 0$. Reproduced with permission from ref 203. Copyright 1975, American Institute of Physics.

the LIF spectrum shows considerable line narrowing relative to the inhomogeneously broadened absorption spectrum. The radiative lifetimes for the $B(^2\Sigma_u^+) \rightarrow X(^2\Sigma_g^+)$ emission ($T_e = 19107 \text{ cm}^{-1}$) are strongly dependent on the matrix material, the carbon isotopes, and the temperature (Figure 14, $\tau_f = 18\text{--}64 \text{ ns}$ for $v' = 0$). When $v' = 1$ is excited more than 95% of emission is from $v' = 1$, since the lifetime for $v' = 1 \rightarrow v' = 0$ is 0.6–6 μs , 1–2 orders of magnitude longer than the radiative lifetime. Even the $v' = 2 \rightarrow v' = 1$ lifetime exceeds τ_f . These nonradiative vibrational transitions in the upper state follow an energy-gap law in which B state relaxation proceeds via $^4\Sigma_u^+$ levels which have a much smaller vibrational frequency and overlap the B-state energies (X: $\omega'' = 1805$; B: $\omega' = 1986$; a: $\omega' = 1093 \text{ cm}^{-1}$).

While the upper state vibrational lifetimes are in the microsecond range, the ground-state $v'' = 1$ lifetime is long enough to permit significant reexcitation by the laser. Consequently, emission from $v' = 1$ to $v'' = 0$ is

TABLE XIV. Laser-Induced Fluorescence Experiments on Photochemically Generated Molecules

molecule	precursor	transition	upper state vibrational relaxation	comments	ref
NH	NH ₃	A(³ Π) → X(³ Σ)	contrary to energy-gap law; strong isotope and matrix dependence; acceptance by rotational modes	also ground-state relaxation contrary to energy-gap law	212-213
OH	OH ₂	A(² Σ ⁺) → X(² Π)	violation of energy-gap law; acceptance by mixed rotational/lattice modes	H bonding and charge-transfer interaction with rare gases	218
C ₂ ⁻	C ₂ H ₂	B(² Σ _u ⁺) → X(² Σ _g ⁺)	follows energy-gap law; isotopic and temp dependent; interstate cascade	ground-state relaxation concn dependent and very slow; photobleaching	203, 204, 211
CN	HCN	A(² Π) → X(² Σ ⁺)	follows energy-gap law; dominated by internal conversion in interstate (A and X) cascade	also ground-state relaxation	219
IF	CHF ₂ I or CHFI ₂	B(² Σ) → X(² Σ ⁺)			55
XeF	XeF ₂ or CF ₄ /Xe	B(³ Π ₀) → X(¹ Σ ⁺) D(¹ / ₂) → X(² Σ ⁺)		260- and 350-nm excitation; ground-state potential; see ref 1	220
XeO	H ₂ O or O ₂ discharge + Xe	B(¹ / ₂) → X(² Σ ⁺) E(¹ Σ) → C(¹ Π)		220-nm excitation; well depth in excited state; see ref 1	221
C ₃	H ₂ CCCH ₂	E(¹ Σ) → B(¹ Σ) a(³ Π _u) → X(¹ Σ _g ⁺)	picosecond relaxation involving ν ₂ (65 cm ⁻¹)		214
CCN	CH ₃ CN	A(² Δ ₁) → X(² Π ₁)	all emission vibrationally relaxed; strong coupling to lattice		113
CNN	CH ₄ /N ₂	A(³ Π) → X(³ Σ ⁻)	some unrelaxed emission; relaxation via bending mode	note ν ₁ ^{''} = 2824; ν ₁ ['] = 1807 cm ⁻¹	215
NCO	HNCO or NH ₃ /CO or N ₂ discharge/CO	A(² Σ ⁺) → X(² Π)	slow relaxation; unrelaxed emission except for levels coupled by Fermi resonance		216
CS ₂ ⁺	CS ₂	A(² Π) → X(² Π)		perturbed by Ar not by Ne	178
CF ₂	H ₂ CF ₂		unrelaxed emission following ν ₂ ['] excitation		222
FCCl	HCCL ₂ F or FCCl ₃		relaxed emission from ν ₂ ['] ; some unrelaxed from ν ₃ ['] ; preferential relaxation within one vibrational mode; contrary to energy-gap law		217
CCl ₂	CH ₂ Cl ₂ or CCl ₄ + alkali atom		vibrationally relaxed emission		223
FCBr	HCBBr ₂ F or H ₂ CBrF			broad emission	12
ClCBr	H ₂ CBrCl				11
CBr ₂	H ₂ CBr ₂ or CBr ₄ + alkali atoms				11, 224

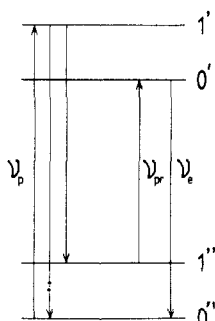


Figure 15. Simplified energy level diagram illustrating the method of probing vibrational energy transfer in the ground electronic state of C_2^- . ν_p = pump laser, ν_{pr} = probe laser, ν_e = emitted beam. Adapted from ref 204.

TABLE XV. Lifetimes of $v = 1$ of NH ($X^3\Sigma^-$) from ref 213^a

	NH	ND
Ne	0.5	240
Ar	180	24000
Kr	2300	210000

^a In microseconds.

observed as an anti-Stokes line (to high frequency of the exciting line) following $v' = 0 \leftarrow v'' = 0$ excitation.²¹¹ This ground-state radiationless relaxation has been studied directly by Allamandola et al. using a dual-pulse laser system in which a probe pulse modifies the population of $v'' = 1$ following the original excitation of $v' = 1 \leftarrow v'' = 0$ (Figure 15).²⁰⁴ The time dependence of B-state emission from $v' = 0$ gives the radiationless lifetime of $v'' = 1$. This lifetime is very long and does not follow an energy-gap law as is shown by strong dependence on the concentration of acetylene precursor but no dependence on temperature (e.g., 1.3 ms at $M/R = 100$ increasing to 147 ms at $M/R = 20\,000$ in Ar). That this concentration dependence involves energy migration to acetylene, not to C_2^- , is shown by the strong effect of deuterium on the lifetime (147 ms for C_2H_2 , 93 ms for C_2D_2 at $M/R = 20\,000$). Indeed, there is no evidence for energy migration between C_2^- ions in ground or upper electronic states.

2. NH. The LIF spectrum of NH shows some very different features from that of C_2^- .²¹² The emission lifetime ($A^3\Pi \rightarrow X^3\Sigma^-$) for $v' = 0$ (200–350 ns) is temperature independent (Ne and Ar matrices), little affected by deuteration but strongly matrix dependent. When $v' = 1$ of ND is excited in Ar no emission from $v' = 0$ is detected, but with NH about 35% of the emission is relaxed. The slower relaxation of ND is entirely contrary to the energy-gap law, but it can be understood if the energy is accepted by rotational modes of NH rather than phonon modes of the lattice. (Rotation is almost free in the ground state but NH librates in the $A^3\Pi$ state.)

A dual-pulse system has been used to examine the ground-state vibrational relaxation of NH^{213} in a similar way to C_2^- . The lifetimes of $v'' = 1$ are strongly matrix dependent, independent of concentration or temperature and are increased $\sim 10^2$ by deuteration (Table XV). They are more than 10^2 greater than in the A state of NH. Again the violation of the energy-gap law is explained by transfer of energy to rotational modes, since the rotational spacings change faster with reduced mass than the vibrational spacings.

Recently, Esser et al. have obtained emission spectra of NH showing the $a^1\Delta \rightarrow X^3\Sigma^-$ transition by chopping the iodine discharge lamp which they use to generate NH from HN_3 or $HNCO$ and examining the emission during the dark intervals.⁷⁴ The lifetime of NH ($a^1\Delta$) ranged from 0.2 to 1.0 s according to matrix and temperature. Unlike Bondybey's data which were obtained from annealed matrices, Esser et al. observed considerable restriction of NH rotation by interaction with the other photofragment, N_2 , except in Xe matrices. The strong temperature dependence of the relaxation time of NH ($a^1\Delta$) in Xe matrices fits an energy-gap law for multiphonon relaxation, but no data on ND have been reported.

3. Linear Triatomics. The series of linear triatomics C_3 , CCN, CNN, and NCO show remarkable changes in the characteristics of vibrational relaxation. The ground-state bending mode of C_3 is so low (63 cm^{-1}) that it is strongly mixed with the lattice modes. The resulting relaxation in the upper state is fast enough (picoseconds) that any emission bands involving this mode show lifetime broadening.²¹⁴

In CCN all emission is vibrationally relaxed indicating upper state relaxation times faster than the radiative lifetime of 180 ns.¹¹³ This fast relaxation is caused by a moderately low frequency bending mode and, more importantly, strong coupling to the lattice which gives gas-matrix shifts as large as 37 cm^{-1} in the vibrational fundamentals.

The CNN radical shows some unrelaxed emission although still only a small proportion.²¹⁵ The relaxation proceeds intramolecularly via the low frequency bending mode (radiative lifetime of $v' = 0$ is 220 ns, vibrational lifetime of (0,1,0) level of the A state is 52 ns).

The final member of the series, NCO, has such a long vibrational relaxation time, compared to the A-state lifetime of 180 ns, that most emission is unrelaxed (e.g., lifetime of (0,1,0) level of the A state $> 20\ \mu\text{s}$).²¹⁶ The exceptions are those levels which are linked by Fermi resonance which show only relaxed emission.

4. Dihalocarbenes. Lifetime data are now available for the excited electronic states of six dihalocarbenes. Surprisingly, the lifetime increases with the mass of the halogens (Table II); the reason is as yet unclear.¹¹ It was mentioned above that relaxation can proceed rapidly in a cascade between electronic states (e.g., C_2^- and CN). It might be expected that relaxation between different vibrational modes of the same electronic state would be efficient too. However, in C_3 the stretching modes relax orders of magnitude more slowly than the bending modes. In ClCF Bondybey showed that relaxation was rapid for ν_2' but slower for ν_3' .²¹⁷ The ν_2' levels did not relax via ν_3' even though a ν_3' level was often closer in energy than the next ν_2' mode (Figure 16): yet another violation of the energy-gap law.

VII. Comparisons with Methods Used in Studying Mobile Phases

Many of the key differences between photochemical matrix-isolation techniques and those used in mobile phases have been documented in earlier reviews^{4,5} or elsewhere in this review. Following a brief summary of these points, I will outline some of the newer techniques used for detecting unstable species in the gas phase and in solution.

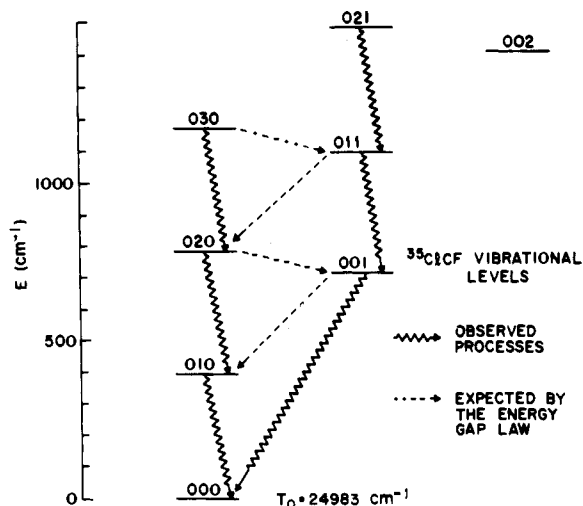


Figure 16. Schematic diagram of the low vibrational energy levels of the upper state of $^{35}\text{ClCF}$. The observed relaxation processes are shown by the wiggly arrows. Reproduced with permission from ref 217. Copyright 1977, American Institute of Physics.

The cage effect plays a much more conspicuous role in matrix isolation than in solution (see ref 1, section VC4) with the result that many simple photochemical reactions are unobservable in matrix experiments. However, the cage effect can be put to advantage in the observation of cage complexes prior to bimolecular reaction (ref 1, sections VC2 and VC3), and subsequent to photodissociation (this review, section IIIH).

While thermal processes usually remove the primary photochemical product rapidly at room temperature, the stability of matrix-isolated species opens up the possibility of *secondary photolysis*. Although such reactions may complicate the relationship to room-temperature chemistry, many remarkable species have been revealed by secondary photolysis (e.g., $\text{H}_3\text{NBH}_3 \rightarrow \text{HNBH}$, section IIA). As a result of the cage effect and secondary photolysis, it is usually safe to argue that *primary products observed in matrices will be significant in mobile phases under similar photolysis conditions but not vice versa*.

Some of the methods which dominate room-temperature photochemistry are rarely available in matrix experiments, most notably *kinetics*, *quantum yield determinations*, and *photosensitization*. The IR-induced reactions discussed in sections IIIG and IVA provide some notable exceptions. For instance, the IR-induced isomerization of HONO has been followed kinetically and proves to be an example of photosensitization.^{137,140} Frei and Pimentel followed the kinetics of the $\text{C}_2\text{H}_4 + \text{F}_2$ reaction and measured its absolute quantum yield as a function of wavelength by making suitable assumptions about extinction coefficients of $\text{C}_2\text{H}_4\text{F}_2$ pairs.¹⁵⁷ In other situations, only relative quantum yields have been measured (e.g., for UF_6 , section IIB).⁴⁵ Some further examples of photosensitization in matrices are given in ref 1, section III.

The great strength of matrix photochemistry lies in the ability to detect unstable photoproducts by a variety of spectroscopic techniques (ref 1, section I) which supply considerable structural information. In addition to its intrinsic value, such information is essential to the identification of unforeseen products. Notable advantages of matrix isolation have accrued from the measurement of IR, Raman, magnetic circular di-

chromism, and ESR spectra and the simplification of UV/vis and IR spectra on cooling. Recently, additional selectivity and sensitivity have been obtained from laser-induced fluorescence.

The traditional methods of detecting short-lived species in mobile phases divide into two categories according to their timescale. Longer lived species ($>10^{-4}$ s) were examined by steady-state experiments using UV/vis, microwave, or ESR detection. Shorter lived species required the use of pulse radiolysis or flash photolysis followed by detection with UV/vis spectroscopy. However, several new techniques have increased the range of methods of detection both in steady state and in pulsed experiments. Some of these techniques are outlined below together with examples of their application. The growth of these new methods holds out great promise for the more effective correlation of matrix results with those in mobile phases. However, the generality of the matrix method, the simplicity of the spectra, and the range of detection wavelengths remain unsurpassed. I anticipate that matrix-isolation will continue to maintain its importance, particularly for the detection of unstable polyatomic molecules.

A. Laser Magnetic Resonance (LMR)

In the LMR experiment a steady-state concentration of radicals is generated in a discharge within a laser cavity.²²⁵ Absorption is detected as a dip in laser power as the laser is tuned into resonance by a magnetic field. The observed transitions occur between Zeeman-split rotational sublevels in the far IR,²²⁵ or between vibrational-rotational levels in the IR.²²⁶ This method is more sensitive than gas-phase ESR and gains selectivity by its tuning method. It has been used for detecting a variety of diatomics and triatomics (OH, OP, CF, OF, NH_2 , HO_2 , CH_2).²²⁵⁻²²⁹ One pentaatomic, OCH_3 , has also been examined.²³⁰ In an intriguing example, McKellar et al. were able to detect singlet CH_2 as well as triplet CH_2 because mixing with the levels of the triplet ground state rendered it magnetically active. In this way they established the singlet-triplet separation as 3165 cm^{-1} .²²⁹

B. Steady-State Laser IR Spectroscopy

Infrared lasers confer an enormous increase in signal to noise ratio compared to conventional IR sources making it possible to detect radical species present in low steady-state concentrations in discharges. Suitable tunable radiation can be obtained from diode lasers,²³¹⁻²⁴³ color-center lasers,²⁴⁴ or by generating a difference frequency from visible laser sources.²⁴⁵⁻²⁴⁹

Like LMR this method has been used only for molecules with four or fewer atoms: ClO, CS, CF, NS, CCl, SiO, BF, NF, CN, NeH^+ , ClO, NH, OF, SF, AlF, KF, NF_2 , CF_2 , CH_2 , NH_2 , HO_2 , ClBO, CH_3 , CF_3 .²³¹⁻²⁴⁹

Since such lasers have a very narrow line width (often narrower than the Doppler width of approximately $.001 \text{ cm}^{-1}$) but can be tuned over a limited frequency range, this method is appropriate for obtaining extremely high-resolution IR spectra over a narrow frequency range. For instance, Amano et al. observed about 200 transitions in the ν_1 and ν_3 bands of NH_2 over a range from 3126 to 3399 cm^{-1} with an accuracy of $.003 \text{ cm}^{-1}$

using a Zeeman-modulated cell and tunable difference frequency laser.²⁴⁷ Whereas the matrix method can give an overall picture of a reaction, this method can give far more detail concerning a particular molecule. However, it has not yet proved possible to tackle more complex molecules such as have often been observed by matrix isolation methods.

C. Infrared Spectroscopy In Liquid Rare Gases

One of the obstacles to comparison of matrix and solution results has been the lack of inert and transparent cryogenic solvents. By using quite modest pressures (<15 atm) and a range of mixtures of N₂, Ar, Kr, and Xe, a full liquid range from 77 to 230 K can be obtained. The range can be extended to 289 K if a pressure of 58 atm can be tolerated. Using a high-pressure IR cell Turner et al. have obtained solution spectra and reaction kinetics of several of the metal carbonyl dinitrogen species previously observed in matrices.²⁵⁰⁻²⁵² They have also detected Cr(CO)₅Xe in liquid xenon, a complex previously observed in Xe matrices.²⁵³ Since these solvents have no absorptions, long pathlengths and low concentrations may be employed. This steady-state method should be appropriate to many of the more stable species observed in matrices, which are nevertheless too reactive to observe by more conventional means.

D. Photoelectron Spectroscopy

Photoelectron spectroscopy is another spectroscopic method which can be applied to the steady-state study of radicals present in discharges, or to high-temperature species.²⁵⁴ Recent examples include the spectra of FCO, BF, CrO, and NF.²⁵⁵⁻²⁵⁷ Photoionization of anions usually requires visible or UV radiation rather than VUV energies. With a visible laser as a source, photoelectron spectra of mass-selected anions such as CH₃⁻, Fe(CO)₄⁻, and Ni(CO)₃⁻ have been obtained, yielding important information about the corresponding neutral molecules.²⁵⁸⁻²⁶⁰

E. Time-Resolved IR Spectroscopy

The growth of laser technology has enabled great advances in time-resolved IR spectroscopy to be made since the early experiments by Pimentel.²⁶¹ However, there have been some successes even without lasers. Forster et al. used modulated electronic excitation with IR detection to detect the OH stretching band of the 2-hydroxyphenoxy radical following photolysis of catechol. These experiments were conducted in conjunction with modulated ESR and established the lifetime of the radical to be 7 ns.²⁶²

Herrmann et al.^{263,264} have used standard flash-photolysis techniques but with a global IR source and monochromator as the kinetic monitor to obtain time-resolved IR spectra of the metal carbonyls M(CO)₅ (M = Cr, Mo, W, Mn) and Mn₂(CO)₉. Lifetimes of these transients fall in the range 10⁻⁵-10⁻² s.

A remarkable approach has been developed by Sorokin et al.^{265,266} Light from a *broad-band* dye laser is converted into a pulsed IR continuum of similar bandwidth by stimulated broad-band electronic Raman scattering in Rb vapor. After probing the sample the

IR beam is mixed with light from a narrow-band laser in a second Rb vapor cell, so converting it up to the visible region. The visible light is dispersed conventionally and photographed. The IR beam has a frequency range of 3200 ± 500 cm⁻¹ and is dispersed to ~0.5 cm⁻¹ resolution with a time resolution of ~10 ns. By using this method (time-resolved infrared spectral photography, TRISP) the authors have followed the decomposition of HN₃ in a laser-initiated explosion. They have also observed a C-H stretching band of (CH₃)₃C at 2833 cm⁻¹ following photolysis of (CH₃)₃C-NO (cf., 2825 cm⁻¹ in matrix). The *t*-Bu radicals decay bimolecularly with a rate constant of ~10¹⁰ dm³ mol⁻¹ s⁻¹. In another application of the method ClOClO₃ was detected on flash photolysis of ClO₂.²⁶⁷

Infrared spectra of Fe(CO)_{*n*} (*n* = 2-4) have been measured at microsecond intervals by photolysis of Fe(CO)₅ with a pulsed UV laser, and monitoring of the products with a CW IR laser.^{268,269} A similar method but with a conventional flash lamp has found application in the flash photolysis of [(⁷5-C₅H₅)Fe(CO)₂]₂.²⁷⁰

The most striking of recent applications of flash photolysis with IR detection is probably the study of singlet CH₂ generated by pulsed UV laser photolysis of ketene. The IR spectrum was monitored with a difference frequency laser (see above) which allows the detection of radical concentrations of ~10¹³ cm⁻³ at Doppler-limited wavenumber resolution.²⁷¹

F. Time-Resolved Resonance Raman Spectroscopy

Resonance Raman spectroscopy offers a high degree of selectivity, but nevertheless allows vibrational spectra to be recorded over a full frequency range. It is limited to those molecules with suitable chromophores which, for preference, are photostable and do not show broad fluorescence. Only those vibrational modes which are associated with the chromophore are enhanced. The extra sensitivity conferred by resonance enhancement is sufficient to detect radicals both in the steady state (e.g., [*p*-(Me₂N)₂C₆H₄]⁺)²⁷² or in a time-resolved mode following flash photolysis or pulse radiolysis. Examples in the time-resolved mode include (SCN)₂⁻ (*t*_{1/2} = 1.6 μs) detected following pulse radiolysis of SCN⁻ solutions,²⁷³ and the photodissociation product of carbonmonoxyhemoglobin. In the latter case spectra have been obtained from a flash with a duration as short as 30 ps,²⁷⁴ which both generated the transient and excited the resonance Raman spectrum.

G. Time-Resolved Chemically Induced Dynamic Electron and Nuclear Polarization (CIDEP and CIDNP)

Detection of ESR spectra under steady-state or modulated conditions is well established,²⁷⁵ but ESR signals may also be detected following flash photolysis or pulse radiolysis. The flash results in a nonequilibrium distribution of free radicals among their electron spin states so that the ESR signal may appear in emission (CIDEP). By this method, for instance, Ph₂COH radicals have been observed following flash photolysis of benzophenone.²⁷⁶ The nuclear analogue of this method has been developed more recently and has been applied, for instance, to the flash photolysis

of benzyl phenyl ketones monitored by CIDNP in $\sim 10^{-7}$ s.²⁷⁷

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- (278) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.