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Optical Properties of Matrix-Isolated Tri- and Polyatomic Molecules

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ABSTRACT

This report presents a summary of the results of ultraviolet, visible, and infrared investigations of matrix-isolated tri- and small polyatomic radicals and molecules. The data is compiled from the literature through January 1969. Selected references appearing later than this date are also included. An attempt was made to make the report as comprehensive as possible, but it is almost certain that some data has been omitted, particularly for the polyatomic species. No effort was made to include organic species beyond single carbon containing molecules. Data on organics is contained elsewhere (B. Meyer, 70). Furthermore, data on pure solids are omitted.

This report consists of two parts. In the first, a written description of each triatomic species is presented. In the second, data for each molecule are presented in tabular form. Data for polyatomics are presented in tabular form

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only.

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The molecules covered in this report are listed alphabetically by formula. Triatomics with C_{2v} symmetry are, with few exceptions, written with the central atom first. Carbon containing molecules, also with a few exceptions, are written with the carbon atoms first. Where the possibility of ambiguity exists, the formulae are written to indicate the atomic arrangement. The following is a list of the molecules reviewed in the order presented in both the text and tables:

TRIATOMICS

Al_2O
BO_2
BaF_2
$BeBr_2$
$BeCl_2$
BeF_2
BeI_2
C_3
C_2H
CCO
CBr_2
CClBr
CCl_2
CF_2
CHCl
CHF
CH_2
CHO
CNN
COS
CS_2
CaF_2
$CdBr_2$
$CdCl_2$
CdF_2
CdI_2
Cl_3
ClCO
ClClO
ClO_2
ClOO
$CoCl_2$
$CrCl_2$
FCO
FNC
ClNC
BrNC
$FeCl_2$
GeF_2
HCN
H_2O
HCl_2
HNC
HNF
HNO
HNSi
HOBr
HOCl
HOF
HOO
$HgBr_2$
$HgCl_2$
HgF_2
HgI_2
KrF_2
Li_2O
LiON
LiO_2
MgF_2
$MnCl_2$
N_3
NCN
NCO
NH_2
N_2O
NO_2
$NiCl_2$
NiF_2
O_3
OCl_2
OF_2
OOF
PH_2
SO_2
S_2O
ScF_2
SeO_2
Si_3
SiCC
SiCSi
$SiCl_2$
SiF_2
SrF_2
TaO_2
WO_2
$XeCl_2$
XeF_2
$ZnBr_2$
$ZnCl_2$
ZnF_2
ZnI_2

TETRATOMICS

AlF_3
$(BO)_2$
CBr_3
CCl_3
CF_3
CF_2N
CF_2O
CH_2F
CH_2N
CH_2O
CH_3
CO_3
$(ClO)_2$
FNCN
$(HBr)_2$
$(HCl)_2$
HNCO
HNCS
HNF_2
HN_3
H_2O_2
Li_2F_2
NH_3
(NO_2)
NO_3
N_2H_2
O_2F_2
$SiCl_3$
$(SiC)_2$
SiF_3
WO_3

PENTATOMICS

B_2O_3

CBr_3Li

CCl_3Li

$CHCl_3$

CH_2CO

CH_2N_2

CH_3Cl

CH_3F

CH_3Li

CH_4

C_3O_2

NF_2CN

N_2O_3

N_3CN

SiH_2Cl_2

SiH_2F_2

SiH_3Cl

SiH_3F

XeF_4

OTHERS

CH_3LiBr

CH_3OH

C_2Br_4

$(HCN)_2$

N_2H_4

N_2O_4

$NbCl_5$

$CH_2(CN)_2$

N_2O_5

Al_2F_6

$(BF_3)_2$

$(CH_3)_3N$

$(CH_3)_2SiH_3N$

$CH_3(SiH_3)_2N$

$(SiH_3)_3N$

$Fe(C_5H_5)_2$

$Eu(C_5H_5)_3$

Part I

A Review of the Results of Optical Studies on Matrix-Isolated Triatomics Molecules

Al_2O

Linevsky et al. (64) have reported the infrared spectrum of Al_2O in argon and krypton matrices at 4.2°K. In dilute samples, only one prominent absorption is observed, but in more concentrated samples several bands appear. The former appears at 994 cm^{-1} in argon and 988 cm^{-1} in krypton and is assigned to ν_3. Bands at 715 cm^{-1} in argon and 709 cm^{-1} in krypton are assigned to ν_1. Results with ^{18}O substitution are consistent with the assignments. The observed shifts suggest a molecular bond angle of near 150° and a ν_2 bending frequency of 238 cm^{-1}. Also observed in the spectrum is a band near 1870 cm^{-1} which is assigned to an overtone of ν_3.

BO_2

Boron dioxide has been prepared for observation in matrices by Sommer, 1963, through the oxidation of B_2O_3 with ZnO. Mass spectroscopic analysis, however, shows BO_2 to be a minor constituent ($BO_2^+/B_2O_3^+ = 0.10$) so that spectral observation is limited to those regions unmasked by B_2O_3. The visible absorption spectrum of BO_2 in argon consists of a series of bands in the 380-580 nm region. The majority of these bands can be assigned to the transition $A\ ^2\Pi_u \leftarrow X\ ^2\Pi_g$ through comparison with the gas phase high resolution work of Johns (61). The gas to matrix shift is about 400 cm^{-1} and all but three bands appear to originate from the $^2\Pi_{3/2}$ sublevel. Two bands near 410 nm cannot be fitted to the Π-Π transition, but correlate closely with the (0,0) transition of the B state, the $B\ ^2\Sigma_u^+ \leftarrow X\ ^2\Pi_g$. These bands, along with three from the

Π-Π transition, appear to originate in the $^2\Pi_{1/2}$ sublevel.

The infrared spectrum of the molecule shows absorptions at 1276 and 1323 cm^{-1}. These bands are assigned to the asymmetric stretching frequency, ν_3, of the species $^{11}BO_2$ and $^{10}BO_2$ respectively. The additional fundamental frequencies were not observed because of overlap from the spectrum of B_2O_3.

BaF_2

The infrared spectrum of matrix-isolated barium fluoride at 4.2°K in the region from 4000-200 cm^{-1} was reported by Snelson in 1966, and more recently, by Calder et al. (69) in krypton at 20°K. The observation of an infrared absorption attributable to the symmetric stretching frequency substantiates the bent C_{2v} structure. Bands assigned to ν_3 and ν_1 appear in krypton at 413 and 390 cm^{-1} respectively. Assignments are based on the relative intensities. The bending mode was not observed but is calculated to be 64 cm^{-1}. A weak band at about 325 cm^{-1} appears in neon and argon matrices and is assigned to polymeric or agglomerate material. As the matrix is changed from neon to argon to krypton, the external heavy atom effect on both vibrational frequencies causes increasing red shifts. The apex angle is estimated to be 100°.

$BeBr_2$

$BeBr_2$ has been deposited directly from the solid into neon and argon matrices at 4.2°K by Snelson (68). The vapor is superheated to 975°K to reduce polymer concentrations. Infrared observations give two bands in neon at 993 and 207 cm^{-1}, but only one in argon, 985 cm^{-1}.

The band near 990 cm^{-1} is assigned to ν_3 and the low frequency band to ν_2. The latter is presumably shifted below the detection limit of 200 cm^{-1} in argon. The frequencies are consistent with a linear structure for the molecule. A calculation of ν_1 using the valence force field approximation gives a value of 230 cm^{-1}.

$BeCl_2$

Beryllium chloride in the rare gases at 4.2°K, shows infrared absorption bands at approximately 1120 and 240 cm^{-1} (Snelson, 66, 68). These bands are assigned to the asymmetric stretching vibration, ν_3 and the bending mode, ν_2, respectively. The former correlates closely with the gas phase ν_3 value of 1113 cm^{-1} (Büchler, 58). The gas phase band at 482 cm^{-1} previously assigned to ν_2 is not observed at low temperatures and is probably in error. Estimation of ν_1 suggests a value of 390 cm^{-1} (Snelson, 68). The absence of ν_1 is consistent with a linear structure for $BeCl_2$. Force constants are also reported.

BeF_2

Monomeric beryllium fluoride shows two strong infrared absorption features (Snelson, 66). These bands, at 1542 and 330 cm^{-1} in neon at 4.2°K, are assigned to ν_3 and ν_2, respectively. No bands corresponding to ν_1 are observed and the molecule is presumably linear. Additional weak bands at 830, 790, and 1250 cm^{-1} are attributable to dimers and polymers of BeF_2. Mass spectroscopic data (Hildenbrand, 64) indicates that up to one mole per cent of dimers may be present in the vapor at 600°C. Gas phase values for ν_3 and ν_2 are reported to be 1520 and

825 cm^{-1} respectively (Büchler, 58). The value for ν_3 in the gas phase and in matrices are consistent, however the results for ν_2 are in disagreement. It is possible that the gas phase band at 825 cm^{-1} is due to a polymeric species. Force constants and the symmetric stretching vibration, $\nu_1 = 680$ cm^{-1}, have been calculated using a valence force field method.

BeI_2

Only one vibrational fundamental of BeI_2 has been observed in matrices following vaporization of the solid (Snelson, 68). In both neon and argon at 4.2°K a band of multiplet structure appears near 870 cm^{-1}. The fine structure is presumed to be due to matrix effects. The band is assigned to ν_3 of the molecule. A calculated value of 160 cm^{-1} for ν_1 is obtained using the valence force field approximation.

C_3

The molecule C_3 has been studied extensively by several workers (Barger, 62, 64, 65; Brabson, 65; Weltner, 62b, 64a,b, 66) in a variety of solids. All workers have used trapped carbon vapor as the C_3 source. The vapor concentration of C_3 depends on the nature of the source. A tantalum Knudsen furnace has been reported by Weltner(64a) to give 50% C_3, 7% C_2, 38% C and 4% Ta at 2700°K. Langmuir sources at 2500°K give a composition of about 25% C_3, 25% C_2 and 50% C atoms.

The gas phase "4050 Å system" of C_3, assignable to the $A^1\Pi_u \leftarrow X^1\Sigma_g^+$ has recently been analyzed by Gausset _et al_. (63,65). The molecule has a very low ground state bending frequency (63 cm^{-1}) and a large Renner effect in the excited $^1\Pi_u$ state ($\epsilon = +0.537$). The gas phase analysis indicates that the upper state is also linear and that Franck-Condon factors allow transitions involving v_1', $2v_2'$, and $2v_3'$, if observed in this system.

The matrix absorption spectrum of C_3 also consists of the $A^1\Pi_u \leftarrow X^1\Sigma_g^+$ system. Table I gives the origins as well as other pertinent data on this system in each of the matrices studied.

Table I.

Characteristics of the C_3, $A^1\Pi_u \longleftarrow X^1\Sigma_g^+$ System in Various Matrices

Matrix	λ (nm)	μm^{-1}	Half-width (cm^{-1})	Gas to matrix shift[c] (cm^{-1})	References
CO_2	398.5	2.5085	500	-410	Barger 62, 64, 65
Ne[a]	405.7	2.4642	12-30	33	Weltner 62b, 64a,b, 66
N_2	405.8[b]	2.4635	250	40	Barger, Brabson 65
SF_6	407.0	2.4565	200	110	Barger
Ar	410.2	2.4370	11-50	305	Barger, Brabson, Weltner
O_2	410.2	2.4370	40	305	Barger
Kr	410.6	2.4350	200	325	Barger, Brabson
Xe	423.4	2.3610	100	1065	Barger

[a] After annealing.

[b] Brabson reports a value of 419.9 nm for the (0,0,0) band in N_2.

[c] Gas phase value 404.98 nm = 2.4675 μm^{-1}.

The appearance of the bands, as evidenced by the half-widths, depends on the matrix. Neon, argon and oxygen were all observed to give sharp structure. Neon and argon apparently give additional multiple sites on initial condensation. Weltner (66) reports that annealing of the C_3 neon system at 11-12°K for 0.5 hr leads to considerable simplification of the spectrum. It is noteworthy that, before annealing, the first strong band in neon occurs at 407.2 nm with the multiplet structure extending to about 405.0 nm and includes the strong band at 405.7 nm. Emission of this system (discussed below) also shows the first band at 407.2 nm, but the band structure is not a mirror image of the absorption (0,0,0) band and little other structure is present. Annealing leads to a loss of all structure with only the 405.7 nm band remaining. The annealing effect on emission is, unfortunately, not reported. It is not clear why the multiple sites are observed in absorption, but not in emission.

The absorption bands show progressions in v_1' and weakly $2v_2'$ in line with expectations. The values of ν_1' and ν_2' depend to a certain extent, on the matrix environment. Values reported for ν_1' are 1125 cm^{-1} in neon and 1095 cm^{-1} in argon. The upper state bending frequency ν_2' varies between 302 and 314 cm^{-1}. The values of ν_2' are less clear because the large Renner effect leads to uneven spacing of the vibrational levels in the upper state. Renner parameters, calculated from the observed band positions, are +0.52 by Brabson, 0.566 by Weltner, and 0.55 by Barger.

Assignments are made by considering this splitting; (v_1', $v_2^{+'}$,0) and (v_1', $v_2^{-'}$, 0) bands are tabulated in the original references. The agreement between authors is excellent except for the assignment of the (0, 6^+, 0) band in argon for which Brabson and Weltner disagree. The value of the latter appears more probable. The assignments correlate well with calculated wavelengths based on the gas phase Renner parameter $\epsilon = +0.537$ and upper state bending mode $\nu_2' = 307.9$ cm^{-1}. Although bands involving $2v_3'$ are not forbidden, transitions involving this vibration are either not present or very weak. Weltner does, however, report two bands in neon at 379.8 and 364.7 nm which seem related but do not fit into the assignment scheme. These are proposed to involve v_3' with the 379.8 nm band (0,0,2) and the 364.7 nm band (1,0.2). This yields a value of 840 cm^{-1} for the ν_3' vibration. This value is extraordinarily low and is rationalized on the basis of similar anomalies in like molecules such as BO_2, CO_2^+, and CNN where large interaction force constants are observed. In addition, Douglas' (51) measurements of ^{13}C isotope shifts of the (0,0,0), (0,0,0) C_3 band in the gas phase requires a value for ν_3' of about 900 cm^{-1}.

When C_3 in Ne or Ar is excited with light of 405 nm or 365 nm wavelength, two distinct emissions are obtained (Weltner, 64a; Brabson, 65). The bluest emission has its origin near 407.2 nm and is assigned to the fluorescence associated with the $^1\Pi_u$ — $X^1\Sigma_g^+$ transition. This emission is characterized by a short progression with frequency differences of about 170 cm^{-1}, a second series of bands located about 1230 cm^{-1} away, and a third weak band 4046 cm^{-1} away. The difference of 1230 cm^{-1} is assigned to ν_1'', the 170 cm^{-1} difference represents $2v_2''$ giving a ν_2'' value of

85 cm^{-1}, and the 4046 cm^{-1} difference belongs to $2v_3''$ giving ν_3'' the value 2023 cm^{-1}. Direct infrared observations give a ν_3'' value of 2042 cm^{-1} thereby giving weight to the $2v_3''$ assignment.

The second emission originates at 585.6 nm in neon and 590.5 nm in argon. It shows progressions almost identical with the $A \rightarrow X$ system. The low frequency differences are 158, 164, 178, and 191 cm^{-1}, and the higher frequency is 1223 cm^{-1}. It is therefore likely that this system terminates in the C_3 ground state. Weltner determined a lifetime of 0.02 sec for this emission in neon. This value indicates that the transition is forbidden. The upper state is proposed to be the $a^3\Pi_u$ state, associated with the electronic configuration of the $^1\Pi_u$ state. Population of $^3\Pi_u$, because of excitation conditions, presumably results from intersystem crossing from the $^1\Pi_u$ state.

Although attempts were made to observe other transitions in the molecule, in particular, the $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$, none were found at least in the region down to 195 nm. Barger and Weltner have computed oscillator strengths for the $^1\Pi_u \longleftarrow {}^1\Sigma_g^+$ system. The values of 6×10^{-2} and 10^{-3}, respectively are reported for the 410.2 nm band in argon. In view of the inherent difficulty involved in measurements of this type in matrices, the agreement is excellent.

Barger and Broida (65) suggested the possibility of the presence of excited ground state vibrational levels of v_2'', in particular, levels 3, 4, and possibly 7. The suggestion is based on the presence of unassigned bands which fit the difference (0,3,0), (0,0,0); (0,7,0), (0,3,0) and (0,4,0), (0,0,0).

C_2H (HC_2)

The species C_2H has been shown by ESR to be produced when acetylene is photolyzed with vacuum ultraviolet radiation in an argon matrix (Cochran, 64). Very little, however, is known about the optical spectrum of the species. Milligan et al. (67a) have reported one vibrational fundamental of 1848 cm^{-1} when mixtures of acetylene and argon or nitrogen are photolyzed using H_2 or Kr discharge lamps. These sources are rich in vacuum UV light. Deuterium and ^{13}C substitution confirmed the assignment of the IR band at 1848 cm^{-1} to C_2H. Observations on the band indicate that C_2H is stable to further photolysis with wavelengths greater than 200 nm. Brabson, (65), suggested that a band at 405.4 nm, observed when carbon vapors are trapped in argon, may be due to C_2H.

CCO

The free radical CCO has been prepared in sufficient concentration for direct spectroscopic observation in two ways (Jacox, 65b). Carbon atoms, produced in the photolysis of matrix-isolated cyanogen azide at wavelengths shorter than 280 nm, were observed to react with carbon monoxide in the matrix with little or no activation energy, yielding directly CCO. The exact mechanism of CCO formation is not known, but several deductions can be made regarding it. Milligan (65d) showed that NCN is the initial photolysis product of N_3CN with radiation of wavelengths greater than 280 nm. Subsequent photolysis of NCN at wavelengths shorter than 280 nm yields N_2 and carbon atoms. The electronic state of the carbon atoms is not known although it is rationalized that ^3P and ^1D atoms may be produced, depending on the energy of the incident radiation.

Either is capable of reacting with CO to form CCO. Because of the nature of the CCO synthesis, this system also contains undesired impurities. Other species known to be present include: NCN, N_2, CO, N_3CN and C_3O_2. The latter is apparently formed through direct reaction of CCO with CO with little or no activation energy. The half-life of CCO in CO is about 3 minutes.

Vacuum ultraviolet photolysis of C_3O_2 also produces observable quantities of the radical CCO. Photolysis is effected using a xenon resonance lamp and wavelengths below 280 nm. This system has the advantage of fewer impurities than the above system; however, CO and unphotolyzed C_3O_2 as well as CCO are known to be present.

The CCO radical shows three distinct absorptions in the infrared. The three vibrational fundamentals attributable to CCO in an argon matrix occur at 381, 1074, and 1978 cm^{-1}. The use of carbon and oxygen isotopes confirm the identification. The data are consistent with a linear structure, as proposed by Walsh (53a,b). The ground state is probably $^3\Sigma$.

A continuous absorption assigned to CCO occurs in the visible region near 500 nm. The absorption appears as a broad structureless band and evidently results in the photodissociation of CCO:

$$CCO\ (^3\Sigma) + \underline{h}\nu \longrightarrow C(^3P) + CO.$$

$\underline{CBr_2}$

Andrews and Carver (68c) have reported two of the three vibrational fundamentals of CBr_2 in argon matrices at 15°K following the simultaneous deposition of lithium and CBr_4. Infrared absorptions at 641 and 595 cm^{-1} are assigned to ν_3 and ν_1 respectively of the dibromocarbene radical.

Warming of the matrix leads to the formation of C_2Br_4 thereby giving chemical evidence for the assignment. In analogy with CF_2 and CCl_2, the bond angle is assumed to be about 100°. The bending mode, ν_2, is not observed but presumably occurs below 200 cm^{-1}.

CClBr

This mixed dihalocarbene has been observed in the infrared following the reaction of lithium atoms with $CClBr_3$ and CCl_3Br in argon at 15°K (Andrews, 68c). The two stretching fundamentals appear at 739 and 612 cm^{-1}. The former is the C-Cl frequency while the latter is the C-Br frequency. The species disappears on warming of the matrix to 40°K.

CCl_2

Milligan (67c) and Andrews (68b,e) used two different methods for preparing CCl_2 in matrices for spectroscopic observation. Milligan reacted carbon atoms produced by the photolysis of cyanogen azide with chlorine in argon and nitrogen matrices at 14°K to form directly CCl_2. This method has the disadvantage that several unwanted species are simultaneously produced, thereby limiting the useful spectral range to those areas where overlap does not occur. The experiments consist of simultaneous depositions of $Ar:Cl_2$ and $Ar:N_3CN$ samples. The resulting solid is photolyzed with the entire spectrum of a cadmium lamp, with glass envelope removed. This treatment is known to result in the formation of excellent yields of the free radical NCN. The carbon atoms, used to form CCl_2 through reaction with Cl_2, are then produced through photolysis of the intermediate NCN with the full spectrum of a medium pressure mercury arc.

Andrews reported a more direct, but not less sophisticated, method involving the reaction of lithium atoms with carbon tetrachloride in argon matrices at 15°K. Lithium is deposited from a Knudsen cell while the carbon tetrachloride-argon mixture is deposited through a second jet. The reaction yields CCl_3 and LiCl as primary products. The CCl_2 is formed by secondary reaction of CCl_3 with excess lithium. This method also suffers from the presence of intermediates and impurities, which are inevitably present in a lithium beam.

Two infrared absorptions are reported for CCl_2. Andrews' assignments are based on isotope shifts and normal coordinate calculations. The bands at 746 cm^{-1} and 720 cm^{-1} are assigned to ν_3 and ν_1, respectively, of the $^{12}C^{35}Cl_2$ species in argon. These frequencies shift to 754 and 725 cm^{-1} in N_2. The assignment of ν_3 to the highest frequency band is consistent with previous observations for OCl_2, $HBCl_2$, and H_2CCl_2, where ν_3 is also higher than ν_1. It should be noted that $\nu_1 > \nu_3$ occurs in CF_2 and OF_2. The appearance of ν_1 in the infrared requires a bent structure for the molecule, with an almost certain C_{2v} symmetry. The calculation of the valence bond angle using ν_3 for $^{12}CCl_2$ and $^{13}CCl_2$ gives a value of 100° ± 9. From his data, Milligan estimated the angle to be 90° - 110°. The ν_2 bending mode is not observed.

In the visible region, 16 bands occurring between 440 and 560 nm are observed in absorption. These bands, because of analogous behavior with that of the infrared absorptions, are also assigned to CCl_2. The average spacing between bands is 305 cm^{-1}, and the system probably is a progression in v_2'. By analogy with CF_2, the lower state is concluded to be the $^1A_1$ ground state; the upper state is probably the first excited electronic configuration and presumably $^1B_1$, although $^1A_1$ is also possible. Herzberg (67) tentatively lists $^1A_1$ for the iso-valent CF_2.

CF_2

Photolysis of CF_2N_2 in matrices, reactions of carbon atoms from the photolytic decomposition of NCN_3 with molecular fluorine, and condensation of the products of a microwave discharge through C_4F_8/argon mixtures have all yielded sufficient quantities of the CF_2 radical for low temperature spectroscopic observation (Bass, 62; Milligan, 64c, 68a).

Only one absorption system of CF_2 is observed in the region 190 - 540 nm. This system, which corresponds to the gas phase transition $A(^1A_1) \leftarrow X^1A_1$, originates at 3.739 μm^{-1} and consists of at least 16 distinct bands. The transition consists of a single progression in v_2 with a vibrational spacing of 500 cm^{-1} and resembles the gas phase spectrum quite closely. The Franck-Condon maximum occurs near 248 nm, at the seventh band. Intensity in the origin region is sufficent to allow clear observation of the (0,0,0) band. Only in the case of the $NCN_3/F_2/Ar$ system is the spectrum overlapped. This is due to the CNN absorption in the same region.

The ground state vibrational frequencies of the radical have been observed directly in the infrared. All these vibrational modes appear as is consistent with the C_{2v} structure. Frequencies for $^{12}CF_2$ in argon are: $\nu_1 = 1222\ cm^{-1}$, $\nu_2 = 668\ cm^{-1}$, and $\nu_3 = 1102\ cm^{-1}$. Yields of the radical are sufficient to allow observations of ν_1 and ν_3 at 1191 and 1073 cm^{-1}, respectively, for the $^{13}CF_2$ species from ^{13}C natural abundance. These assignments have been confirmed using ^{13}C enriched samples. The frequencies are virtually identical in N_2 matrices. The 1222 cm^{-1} ν_1 band appears as a doublet in argon. The doubling is not totally clear although it may be due to multiple sites.

Results in CO and CO_2 matrices are essentially the same, indicating that CF_2 does not react with either under these conditions. Warm-up leads to the formation of C_2F_4. The dimerization of CF_2 to C_2F_4 is apparently accompanied by chemiluminescence because a "straw-yellow" glow is observed when diffusion becomes important.

Impurities or unwanted products depend on the preparative method; they include CF_3, C_2F_4, C_2F_6, $(CF_2N)_2$, and $CH_2N_2CF_2$, which is called perfluoroformadezine.

A bond angle of 108° is calculated from the observed $^{13}CF_2$ isotope shifts. This agrees favorably with Walsh's (53a,b) prediction that the molecule be strongly bent. CF_2, like several other halogen-containing species, has the asymmetric stretching fundamental at a lower frequency than the symmetric stretching fundamental. Force constants and thermodynamic functions are tabulated in the original references.

CHCl

The $A(^1A'') \leftarrow X(^1A')$ transition of the radical CHCl (HCCl) in the gas phase at 550 - 820 nm has been reported by Merer and Travis (66a). Jacox and Milligan (67b) have prepared CHCl in argon and nitrogen matrices at 14°K through the reaction of carbon atoms with HCl. The carbon atoms are produced by the photolysis of N_3CN.

The $A \leftarrow X$ absorption system is also observed in the solid, appearing as a series of bands between 560 and 750 nm. This observation confirms that the gas phase lower state is the ground state. These bands are relatively broad and weak and appear, in argon, to be blue shifted with respect to the gas phase by about 250 cm^{-1}. A red shift of 640 cm^{-1} could also explain the results if the gas phase numbering is wrong. Six of the bands can be correlated closely with the gas phase values. At 1.50 μm^{-1}, unassigned features appear between the principal bands. The bands show vibrational perturbations, as in the gas phase. The observed frequency is ~ 860 cm^{-1} corresponding most likely to ν_2'.

In the infrared, two fundamental vibrational modes are observed. These occur at 815 cm^{-1} for ν_3 and 1201 cm^{-1} for ν_2 in argon. The results of ^{13}C and D isotope substitutions are consistent with the assignment of these bands to CHCl. In addition to CHCl, bands at 753 and 1270 cm^{-1} attributable to CH_2Cl_2 are observed. These bands undergo considerable increases in intensity when diffusion is allowed to occur. The CH_2Cl_2 presumably results from the reaction of CHCl and HCl with little or no activation energy.

CHF

Vacuum ultraviolet photolysis of Ar:CH_3F or N_2:CH_3F mixtures yields CHF (Jacox, 69a). Four related bands between 470 and 546 nm correspond well with the most prominent gas phase band heads reported for CHF (Merer, 66b). The argon matrix shifts are approximately + 30 cm^{-1} from the gas phase bands of the $A(^1A'') - X(^1A')$ transition. The bands are assigned to the progression $(0, v_2', 0)$, $(0,0,0)$ and yield a ν_2' value of about 1010 cm^{-1}. Satellite bands approximately 110 cm^{-1} to the blue of the two strongest bands are attributed to site effects.

In argon, CHF shows an infrared band at 1182 cm^{-1} which can be assigned to ν_3'' on the basis of ^{13}C and D substitution. A band at 1405 cm^{-1} is assigned to ν_2''. The latter is based on the known ν_2'' derived from the gas phase by Merer (66b). Additional absorptions at 2918 and 3262 cm^{-1}, both in the C-H stretching region, show behavior expected for a fundamental of CHF but an assignment is not possible on the basis of the data. Force constant calculations indicate a C-F band stronger than normal, approaching the strength observed for CF.

CH_2

Numerous attempts have been made to prepare and stabilize the methylene radical in low temperature matrices for spectroscopic studies (Milligan, 58, 62a, 67d; Goldfarb, 60a,b; DeMore, 58; Moore, 64b, 65; Robinson, 60a, Jacox, 63a). Most of these attempts have utilized the photolysis of diazomethane CH_2N_2, which was expected to fragment into CH_2 and N_2. It was hoped that the back reaction between methylene and nitrogen would proceed slowly or not occur at 20°K or below. No unambiguous optical spectral observations on trapped CH_2 have been made. There are, however, several observations on reactions at low temperatures which indicate the formation of CH_2 from some photolytic processes. The CH_2 radical apparently has a very high reactivity in all systems yet studied.

CHO

The formyl radical, CHO has been produced via the photolysis of HI, HBr, or H_2S in CO matrices at 14-20°K, (Ewing, 60; Milligan, 64e) by condensation of the products of a discharge through methane-argon-oxygen mixtures (Robinson, 58b) or by condensation of the products of the reaction of atomic oxygen with C_2H_2 (McCarty,59b). The corresponding DCO can be produced using the appropriately deuterated precursor. More recently, Milligan and Jacox (69a) have succeeded in preparing HCO in argon matrices by reaction of H atoms with CO using as precursors HCl, H_2O, and CH_4, all of which photolyze in the vacuum ultraviolet to produce H atoms.

The UV and visible spectrum consists of a series of broad bands between 510 and 670 nm corresponding to the $^2A''\Pi - {}^2A'$ gas phase system (Johns,63; Ramsay, 53; Herzberg, 55) and a complicated series of absorptions between 210 and 260 nm corresponding to the hydrocarbon flame bands (see Vaidya, 64; Dixon, 67). The former spectrum consists of a progression in v_2' with a vibrational spacing of about 800 cm^{-1}. It involves the ground state, in which HCO is bent, and a linear upper state. The matrix bands, in CO, are shifted by about +220 cm^{-1} from the gas phase bands. The shift is about +400 cm^{-1} in Kr. The origin is not observed, so the assignments can be considered tentative. The lowest energy band reported in the matrix corresponds to the (0,8,0), (0,0,0) band. The "hydrocarbon flame bands" show simultaneous progressions in the upper state bending and C-O stretching vibrations in line with expectation from the gas phase rotational analysis by Dixon. The matrix spectrum leads to a new value for the origin of the transition of 3.867 μm^{-1} as compared to 3.948 μm^{-1} as originally suggested. The CO to Ar shifts are very small, of the order 10 cm^{-1} or less. The upper state vibrational frequencies determined from the spectrum are 1375 cm^{-1} for ν_2' , the bending mode and 1035 cm^{-1} for ν_3' the C-O stretching frequency. Using the new origin, the vibrational frequencies, and matrix shifts, a new tentative assignment of the gas phase bands has been made (Milligan, 69a).

The ground state vibrational fundamentals have all been directly observed. For HCO these are the C-H stretching mode, ν_1, at 2488 cm^{-1}, the C=O stretch, ν_3, at 1861 cm^{-1} and the HCO bending mode, ν_2, at 1090 cm^{-1}. The frequencies in Ar are shifted to 2481, 1863, and 1087 cm^{-1} respectively. All assignments are consistent with the ^{13}C and ^{18}O substitution results. The corresponding values for DCO are 1937, 1800, and 852 cm^{-1}. The results, except for the DCO C=O frequency, were reported by each group, although Ewing <u>et al</u>. did not make the C-H assignments. The C-H and C-D frequencies are lower than expected, but in line with ESR measurements (Adrian, 62). Intensity anomalies that occur in the DCO spectrum may be due to Fermi resonance interaction between the D-C and C=O stretching modes. In the CH_4 - O_2 - Ar system the bands as assigned (Robinson, 58) are shifted about -50 cm^{-1}. This implies that the "heavy atom effect" is violated, that the spectrum is perturbed by the presence of other species such as unreacted CH_4 or O_4 or that the assignment is wrong.

CNN

Robinson and McCarty, (60) made the first tentative spectroscopic identification of the radical CNN, when they suggested that bands at 424.8 and 423.4 nm produced in the photolysis of diazomethane in a krypton matrix might be due to CN_2 or HCN_2. Goldfarb and Pimentel (60a,b) at the same time studied the photolysis of diazomethane in nitrogen matrices and reported unassigned bands at 396.8 and 418.2 m. Warm-up behavior suggested that these bands were due to a reactive species and it was proposed that the methylene radical could be responsible for one or both. The 418.2 nm band presumably correlated with Robinson's 423.4 nm band. The 396.8 nm feature, however, could only be correlated to a band at 317.4 nm in krypton which Robinson assigned to CH. Milligan, et al (65d), in a study of the photolysis of N_3CN in N_2, reported bands at 418.9 and 396.4 nm. These corresponded very closely with those of Goldfarb and Pimentel, but a tentative assignment to CNN was made. A conclusive assignment could not be made on the basis of the data. In a subsequent investigation of the photolysis of N_3CN, aimed specifically at the identification of CNN, Milligan (66a) confirmed the assignment of the 396.4 and 418.9 nm features to CNN. The spacing between the bands corresponds to 1355 cm^{-1}, ν_3 of the upper state. The considerable intensity of the 396.4 nm band suggests that only a small change in bond length occurs in the transition. Weltner (64b) reported the presence of bands near 420 nm containing carbon and associated with depositions of carbon in neon and argon matrices. These bands were later (Weltner, 66) shown to be due to CNN formed through the reaction of carbon atoms, from vaporized carbon, with N_2 which had entered the system through a vacuum leak. Bands occur at 421.0-419.6 nm and 398.8-397.5 nm in neon and argon containing N_2. Weltner (66) reported an upper state vibrational frequency of 1325 cm^{-1}. ESR observations have led to the conclusion that the radical CNN is linear and that the ground state is triplet ($^3\Sigma^-$) (Wasserman, 65).

Milligan and Jacox (66a) have assigned all three fundamentals of the radical. Frequencies observed in an argon matrix and their assignments are $\nu_3'' = 1241$ cm^{-1}, $\nu_2'' = 393$ cm^{-1}, and $\nu_1'' = 2847$ cm^{-1} for the $^{12}C^{14}N^{14}N$ species. A frequency of 1235 cm^{-1} was observed in fluorescence in neon by Weltner (66) and correlates well with the ν_3''. This frequency is a counterpart of the 1325 cm^{-1} upper state frequency, therefore strengthening the latter's assignment as ν_3'. Identification of the absorber and the assignments are consistent with the observed isotope shifts on substitution of ^{13}C and ^{15}N atoms. A comparison of band structure on ^{15}N substitution in argon with substitution in nitrogen leads to the conclusion that CNN is formed from the reaction of carbon atoms with N_2. The asymmetric stretching frequency of 2847 cm^{-1} is anomalously high. This leads to the conclusion that the carbon-nitrogen bond has substantial triple bond character. Overtones or combination bands are ruled out as being responsible for this band by isotope substitution.

CNN is also observed in the vacuum ultraviolet photolysis of C_3O_2 in nitrogen matrices (Milligan, 66a; Moll, 66). The latter reports infrared absorptions of 2858, 1252 and 394 cm^{-1} for the species.

COS

Carbonyl sulfide has been studied in several matrices in the infrared (Venderame, 66; J. Smith, 68c) and in the vacuum ultraviolet (Roncin, 69). The vibrational frequencies observed directly in the infrared are $\nu_1'' = 2050$, $\nu_2'' = 518$ and $\nu_3'' = 857$ cm^{-1}. The former is in krypton and the latter two are for the pure solid, but the values in CO are essentially the same.

The vacuum ultraviolet absorption spectrum appears to consist of three separate transitions, two in the region 160-180 nm, and the third between 115 and 145 nm, with origins at 5.54, 5.96 and 6.75 μm^{-1}. The vibrational intervals for the three are 760, 495 and 511 cm^{-1} respectively. The transition at 6.74 μm^{-1} appears Rydberg-like; the other two are assigned to valence transitions. The bands are diffuse in neon, but sharpen on going to argon or krypton.

CS_2

The electronic spectrum of CS_2 is complex and not well understood in the gas phase. Furthermore, the matrix spectrum has not completely clarified the situation. CS_2 has been studied in the rare gases, and in nitrogen and methane, between about 2° and 20°K (Roncin, 69; Bajema, 70). Observations in the vacuum ultraviolet reveal a series of bands between 135 and 152 nm with an origin at 6.60 μm^{-1}. The best spectra are obtained in argon and krypton. The bands in neon are broadened to the point that they are nearly inseparable and xenon shows only one band. A vibrational spacing of 540 cm^{-1} occurs in neon and argon at the red end of the system. The assignment of the frequency ha: not been made. The Rydberg series appears to be suppressed.

A complex series of about six absorption bands is observed in the 290 to 330 nm region. Each band exhibits multiplet structure. The spectrum is interpreted as simultaneous progressions in v_1 and v_2 of the $^1B_2 \leftarrow {}^1\Sigma_g$ electronic system. Both matrix-isolated molecules and aggregates contribute to the observed absorption. The multiplet structure of the bands and the irregular spacings are attributed to a Renner-Teller effect. In emission, a weak broad phosphorescence excited at 250 nm appears between 360 and 550 nm. The lifetime has components, $\tau_1 = 0.8$ msec and $\tau_2 = 2.6$ msec in argon. This transition appears near 1.82 μm^{-1} and is tentatively assigned as $^3B_2$ or $^3A_2$, populated via intersystem crossing from $^1B_2$.

CaF_2

Snelson studied calcium fluoride in neon, argon, and krypton at 4.2°K and reported only one absorption in the infrared which could unambiguously be assigned to the monomeric species. This band appeared at 581 cm^{-1} in neon, 561 cm^{-1} in argon, and 565 cm^{-1} in krypton. Other bands appeared in argon at 370, 489, and 528 cm^{-1}. These bands were significantly weaker than the absorption at 561 cm^{-1}. The relative intensities at 370 and 528 cm^{-1} depended on deposition conditions and the bands were attributed to aggregates. More recently, Calder et al. (69) have examined CaF_2 in krypton at 20°K and observed all three vibrational fundamentals. These, for $^{40}CaF_2$ appear at 485, 163, and 554 cm^{-1} for ν_1, ν_2, and ν_3, respectively. Calcium-44 substitution results in red shifts of 2 to 12 cm^{-1}. The bands appearing near 520 and 370 cm^{-1} are assigned to the dimeric species. An apex angle of 140° is calculated from the isotope shifts and anharmonicities. The angle is in close agreement with the 145° suggested by Snelson.

$CdBr_2$, $CdCl_2$, CdF_2, CdI_2

The infrared spectra of the cadmium halides have been investigated in krypton at 4.2 and 20°K by Loewenschuss et al. (69). In addition, McNamee (62) has studied $CdCl_2$ in argon, krypton and xenon at 20°K. All can be conveniently vaporized from Knudsen furnaces. All are linear symmetric molecules (Büchler, 64) and thus are expected to have two infrared active fundamentals.

CdF_2 in krypton exhibits five bands in the infrared at 662, 475, 384, 377, and 123 cm^{-1}. The bands at 662 and 123 cm^{-1} are assigned to ν_3 and ν_2 respectively of the matrix-isolated monomer. The remaining three bands are attributed to polymers. The intensities of the latter bands relative to the monomer absorptions are dependent on deposition conditions.

$CdCl_2$ in krypton shows infrared absorptions due to the isolated monomer at 420 and 89 cm^{-1} and dimer bands at 371, 364, and 357 cm^{-1}. The former are assigned to ν_3 and ν_2 respectively. The ν_3 band appears as a multiplet due to isotopic splittings with components at 420, 419, 417, and 416 cm^{-1}. The dimer bands are assigned on the basis of "double-oven" experiments. These bands appear broader than the fundamental absorptions.

The ν_3 and ν_2 fundamentals of $CdBr_2$ appear at 319 and 62 cm^{-1} in krypton. A band at 270 cm^{-1} is assigned to the dimer and bands at 190 and 163 cm^{-1} to polymers.

Only the asymmetric stretching mode, ν_3, of CdI_2 is observed. This band appears at 270 cm^{-1} in krypton. Bands at 222 and 217 cm^{-1} are assigned to dimers and bands at 140 and 127 cm^{-1} to polymers.

The intensity of the dimer and polymer bands are reduced by "superheating". Polymer formation is proposed to occur due to incomplete isolation rather than to the presence of molecular vapor phase species. Dimer bands are tentatively assigned as a stretching mode, possibly a b_{3u} mode associated with a D_{2h} symmetric halogen-bridged species. Calculated symmetric stretching frequencies, ν_1, are: CdF_2, 572 cm^{-1}; $CdCl_2$, 327 cm^{-1}; $CdBr_2$, 205 cm^{-1}; and CdI_2, 150 cm^{-1}.

Force constants and thermodynamic data have been calculated from the observed frequencies (Loewenschuss, 69).

Cl_3

Nelson and Pimentel,(967b), have proposed that bands occurring between 365 and 375 cm^{-1} in the infrared spectra of samples of $Kr:Cl_2$ mixtures (Kr/Cl_2 = 50 to 100) subjected to a microwave discharge before deposition are due to the radical Cl_3. The bands are explained as the ν_3 fundamental of a linear but slightly asymmetric ($C_{\infty v}$) species.

ClCO

Chlorine atoms produced through the photolysis of a suitable precursor are found to react with CO in argon matrices with little or no activation energy to give the radical ClCO (Jacox, 65a). Sources of Cl atoms reported, were HCl, Cl_2, Cl_2CO and $(ClCO)_2$. Hydrogen chloride was observed to give the most satisfactory yield of ClCO. Infrared spectra of the solids show the presence of CHO when HCl is used, and phosgene and oxalyl chloride when the other Cl precursors are used. The vibrational fundamentals of ClCO are observed at 281, 570 and 1880 cm^{-1}. The use of ^{13}CO, and identical results with and without hydrogen present confirm the assignment to ClCO. $Cl^{13}CO$ frequencies in agreement with observed values have been computed using a valence angle of 120° or 135° and bond lengths of $r_{C-Cl} = 1.75\mathring{A}$ and $r_{C=O} = 1.17\mathring{A}$ based on the values for phosgene. The computed force constant for the C=O stretching mode is significantly greater than that for phosgene. This leads to the conclusion that the carbonyl bond possesses some triple bond character. Similar behavior is observed in the radical CHO. Thermodynamic properties of the radical have been calculated using the vibrational fundamentals and the estimated structural parameters. No ultraviolet absorption for ClCO was observed in the region between 250 - 450 nm.

ClClO

When OCl_2 is photolyzed in N_2 or argon matrices at 20°K, several new bands near 960 cm^{-1} and 375 cm^{-1} appear (Rochkind, 67b). Growth plots of these bands indicate that three different molecules are produced. One species proposed to account for some of the bands between 952 and 962 cm^{-1} and 368 and 377 cm^{-1} is the ClClO molecule, with the nitrosyl halide type structure. The multiplet structure of the absorptions is presumably due to the ^{35}Cl and ^{37}Cl isotopic natural abundance. The magnitudes of isotopic shifts as well as relative intensities are consistent with the assignment to ClClO. The bands near 370 cm^{-1} are assigned to the Cl-Cl stretching vibration and the bands near 960 cm^{-1} to the Cl-O stretching frequency. The bonding in the molecule is apparently quite weak and resembles that in similar molecules, such as O_2F, FNO, and $(NO)_2$. The assignments must be considered tentative at best, because ClClO as well as the other species present are as yet uncharacterized. As in most photolysis experiments, several "impurities" are present in addition to the desired product. Definitely identified as being present are the molecules: N_2O, O_3, and unphotolyzed Cl_2O. In addition, the presence of $(ClO)_2$ is suggested to account for other observed spectral features.

ClO_2

The ground state vibrational frequencies for symmetrical chlorine dioxide, OClO, have been reported in argon and nitrogen matrices at 4.2 and 20°K, respectively, by Arkell (67) and Rochkind (67b) as parts of photolysis studies. The observed infrared absorptions are very close to the gas phase values determined from electronic spectra (Herzberg, 67). ν_1 is 940 cm^{-1}, ν_2 is 448 cm^{-1}, and ν_3 is 1100 cm^{-1} in argon at 4.2°K. The ν_1 and ν_3 bands appear as quartets, and ν_2 is a single band. In N_2, ν_3, is shifted to 1105 cm^{-1} at 20°K; the other frequencies, although presumably observed, were not reported. The corresponding gas phase frequencies are 946, 447, and 1111 cm^{-1}.

No report of the UV-visible spectrum of chlorine dioxide was made in the above studies. Norman and Porter (55) did, however, report an UV absorption in an isopentane, methyl cyclohexane glass at 77°K. In the liquid solution, the absorption consisted of distinct sharp bands between about 430 and 300 nm at 77°K. The structure of the absorption is retained on freezing but appeared almost entirely diffuse. Warmup and melting of the solvent again led to the original structure. The transition observed is probably $A \leftarrow X\ ^2B_1$. Herzberg lists the symmetry of the upper state as $^2A_2$. Because the purpose of the work was to look for ClO from the photolysis of ClO_2, no specific optical data on ClO_2 were presented.

ClOO

Asymmetric chlorine dioxide, ClOO, has been proposed as a precursor in the formation of ClO from Cl_2 and O_2 in the gas phase by Porter (53); but only later trapping experiments provided evidence for the existence of the ClOO molecule. Benson and Anderson (59) reported indirect and inconclusive evidence for ClOO. Mixtures of measured amounts of Cl_2 and O_2 were subjected to neon UV radiation and then trapped at 77°K. The amount of "trapped" oxygen over and above residual amounts was considered to exist as chlorine oxides. This amount of O_2 was determined by warming the sample to room temperature followed by direct measurement. Oxygen in amounts of 6 to 8 times of the blank runs were observed. Calculations based on estimated rate constants and activation energies seemingly rule out Cl_2O and OClO as being responsible for the "trapped" oxygen. The results can be interpreted in terms of either ClOO or ClO.

More recently (Arkell, 67), an infrared study of the photolysis of Cl_2 and O_2 mixtures and photolysis of OClO has resulted in direct observation of vibrational frequencies assignable to the fundamentals of ClOO. The photolysis of Cl_2, O_2 mixtures alone and in argon matrices at 4.2°K gave a band near 1440 cm^{-1} showing ^{16}O, ^{18}O isotope shifts appropriate for a O-O stretching vibration. Other fundamentals were too weak for observation in this system. Greater amounts of the desired species are obtained through photolysis of OClO in argon, nitrogen, or oxygen at 4.2°K. Intensity versus temperature characteristics of the observed peaks led to the assignment of bands at 373, 407, and 1441 cm^{-1}, at 4.2°K, in argon as the three fundamentals of ClOO, ν_3, ν_2, and ν_1, respectively. The assignments are strengthened by observation of isotope shifts and normal coordinate calculations. The low frequency, 407 cm^{-1}, for ν_2, and the Cl-O stretching frequency confirm the earlier suggestion of a weak Cl-O bond (Benson, 57). In addition to the absorptions assigned to ClOO, unassigned bands at 1415 cm^{-1} and 435 cm^{-1} in argon appear during the early part of the photolysis. Isotopic and decay-growth data led to the assignment of these bands to an intermediate designated ClOO* in the formation of ClOO. ClOO* is proposed to be a structural isomer of ClOO, which, because of the solid environment, is prevented from assuming its stable configuration.

Rochkind and Pimentel (67b) while studying the photolysis products of Cl_2O in N_2, photolyzed OClO as an impurity in the Cl_2O. Two bands that could be correlated to ClO_2 photolysis appeared at 1438 and 1428 cm^{-1}. These were tentatively assigned to the O-O stretching frequency in ClOO. These can be compared to the bands reported by Arkell (67) in N_2 at 1445 and 1424 cm^{-1}. A band at 1438 cm^{-1} observed by Arkell in argon, however, was not seen in N_2. The two results are therefore not in agreement on this point. The cause of discrepancy is difficult to determine because of the complexity of the systems on which the observations were made. Both studies report absorptions which cannot be unambiguously assigned. Furthermore, several "impurities" resulting from photolysis fragments and secondary reactions are present. Identified impurities include O_3, N_2O, α-O_2, Cl_2. It appears unlikely that experimental errors are to blame for the differences. It is conceivable that differences in photolytic procedures, wavelengths and temperatures result in the formation of different products. Also not totally ruled out are site effects.

$CoCl_2$

Matrix isolation spectra of $CoCl_2$ in the ultraviolet, visible and infrared regions have been reported (Clifton, 69; DeKock, 68; K. Thompson, 68; Jacox, 69). The molecule can be deposited by direct vaporization of the solid. The ligand field model gives a $^4\Phi_g$ ground state for the gaseous species. Strong transitions at 3.08, 3.20, 3.37, 3.50 and 3.64 μm^{-1} and weaker transitions at 3.95, 4.20, and 4.58 μm^{-1} were reported by DeKock and Gruen at 4.2°K, but only the 3.37 region, the 3.50 band and the weak absorption at 4.20 μm^{-1} were observed by Jacox and Milligan at 14°K. The 3.37 μm^{-1} system appears as a series of bands with a vibrational spacing of about 230 cm^{-1} and is assigned to a progression in v_1 of the upper state. The number of transitions observed is not consistent with the number expected from the ligand field model for a $^4\Phi_g$ ground state. Therefore, either the model, or the state designation or both may be in error. Clifton and Gruen (69) have obtained fluroescence spectra in argon and nitrogen.

$CoCl_2$ gives two bands in the infrared. A multiplet feature at 490 cm^{-1} corresponds to the asymmetric stretching vibration, ν_3, with the strongest component corresponding to $^{59}Co^{35}Cl_2$ at 493 cm^{-1} in argon. The bending mode, ν_2, occurs at 95 cm^{-1} in argon. The frequency ν_3 shows a heavy atom effect, shifting from 493 to 484 to 468 cm^{-1} from Ar to Kr to Xe.

$CrCl_2$

The ultraviolet and infrared spectra of $CrCl_2$ isolated in argon at 14°K have been reported by Jacox and Milligan (69b). Samples of $CrCl_2$ can be obtained by either direct vaporization of the solid or via the reaction of chlorine with a chromium surface at 1035-1095°K immediately prior to deposition. Samples were observed to be strongly absorbing at wavelengths shorter than about 260 nm. Thick deposits show, in addition, a weak absorption near 307 nm. Both absorptions appear unstructured. The gas phase systems reported at 3.623 and 4.960 μm^{-1} (DeKock, 66) do not appear in the matrix.

The infrared spectrum, down to 250 cm^{-1}, shows a strong complex group of bands near 490 cm^{-1} and several weak absorptions near 470 cm^{-1}. The former agree well with the spectrum expected from the natural isotopic abundance for the asymmetric stretching frequency ν_3 of linear $CrCl_2$. The latter bands are attributed to site effects. No evidence for a frequency assignable to ν_1 was obtained.

$FeCl_2$

$FeCl_2$ can be isolated in matrices by either direct vaporization of the solid, or by the reaction of chlorine with iron metal surfaces at 1085°K, followed by condensation on a cooled target (DeKock, 68; K. Thompson, 68; Jacox, 69b).

In the spectral range 200-550 nm several broad, structureless bands have been observed. In argon, 4.2°K, band maxima occur at 3.75, 3.98 (shoulder), 4.16, 4.41 (shoulder) and 4.76 μm^{-1} (DeKock, 68). At 14°K the bands are apparently less well resolved and the spectrum appears as a broad peak at 4.17 μm^{-1} superimposed on an increasing absorption below 4.00 μm^{-1}. Ligand field models predict a $^5\Delta_g$ ground state for $FeCl_2$ and five allowed one-electron transitions to $^5\Pi_u$, $^5\Delta_u$, and $^5\Phi_u$ states (DeKock, 68). Assignments to transitions is not, however, possible on the basis of the data.

Infrared observations yield directly 88 and 493 cm^{-1} for the ν_2 and ν_3 frequencies of the molecule. The asymmetric stretching frequency, ν_3, shifts to 447 cm^{-1} in N_2, an unexpectedly large shift. This has been rationalized in terms of N_2-$FeCl_2$ interactions. All evidence favors a linear ground state.

GeF_2

Infrared vibrational spectra of GeF_2 have been observed in neon and argon at 4.2°K following direct deposition of the vapor from a Knudsen furnace (Hastie, 68). The molecule can be prepared from GeF_4 and Ge at 575°K. The spectrum shows several groups of bands between 500 and 850 cm^{-1}. The general appearance is the same in neon and argon, however, the bandwidths in neon are less than in argon. Two vibrational fundamentals are observed; ν_1 at 685 cm^{-1} and ν_3 at 655 cm^{-1} in neon. These bands shift to 676 and 648 cm^{-1} in argon. The bands both show fine structure due to the germanium isotopes and the above frequencies are for the strongest component. Matrix bands are shifted from the gas phase by about -8 cm^{-1} and -15 cm^{-1} in neon and argon, respectively. The assignments are based on relative intensities and the computed band angle for the molecule, 94°.

Other bands near 600 cm^{-1} and 670 cm^{-1} are assigned to dimeric and polymeric species. A group of bands near 800 cm^{-1} is assigned to unreacted GeF_4. Since dimers and polymers exist in equilibrium with the monomer in the vapor phase, their appearance does not necessarily result from poor isolation.

HCN

C. King and Nixon (68) have examined the infrared and far infrared spectra of HCN in argon, nitrogen and CO matrices at 4.2 and 20°K. HCN forms aggregates in the gas phase and the spectra exhibit bands due to dimers and polymers as well as monomers. In general, the monomer peaks are sharper than the aggregate bands. The fundamental vibrational frequencies are observed at 3303, 720, and 2093 cm^{-1} in argon. These values are consistent with earlier results in nitrogen (Becker, 56; Moore, 65). The ν_2 band appears as a single peak in argon, but is a doublet in both nitrogen and carbon monoxide. Dimer peaks appear at 3301, 3202, 2114, 2090, 797, 792, and 732 cm^{-1}. The relative intensity of these and polymer peaks are lower in nitrogen than argon, presumably indicating a greater degree of isolation in the former.

H_2O

Infrared studies on matrix-isolated water have been made by several workers because of apparent free or nearly free rotation, even at 4.2°K (Catalano, 59; Glasel, 60; Harvey, 68; Hopkins, 68; Jacox, 61; Redington, 62, 63; D. Robinson, 63; Van Thiel, 57b). Van Thiel, Becker and Pimentel, in 1957, studied the hydrogen bonding of water in nitrogen at 20°K and reported the vibrational fundamentals of the monomer as well as bands attributable to dimers and polymers. The three fundamentals appeared at 3627, 1600, and 3725 cm^{-1} for ν_1, ν_2, and ν_3, respectively. Later Catalano and Milligan studied the ν_2 absorption band in argon, krypton, and xenon between 4.2 and 20°K as a function of temperature and concentration. This band appeared as a complex multiplet with six to eight sub-bands. The complexity was proposed to be due to rotation. Analysis of the ν_3 region by Glasel further supported rotation. High resolution studies have led to rotational assignments of the matrix spectra to low-J levels closely correlating with the gas phase values (Redington 62,63). The spectra exhibited bands due to both ortho and para spins. The presence of oxygen catalyzed ortho-para spin conversion. Several rotational levels were observed to be populated in spite of negligible Boltzman factors. This population has been explained using an ideal particle in a spherical box model and substitutional sites. The observed frequencies for the rotating molecule in argon are 3619, 1590, and 3733 cm^{-1}. D. Robinson has observed similar levels in the pure rotation region as Redington and Milligan in the vibration-rotation region thereby presenting support for the latter's assignments.

Similar results have been obtained for D_2O and HDO.

HCl_2

Condensation at 14°K of the products of a glow discharge through HCl, chlorine, argon mixtures led to infrared absorptions at 956 and 696 cm^{-1} which have been assigned to $(\nu_1 + \nu_3)$ and ν_3, respectively of the radical HCl_2 (Noble, 68a). These peaks showed parallel warm-up behavior and both disappeared at about 40°K. The 956 cm^{-1} absorption appears as a triplet with relative intensities consistent with chlorine isotopic splittings expected for a band involving ν_1 for a $D_{\infty h}$ ClHCl species. Results on deuterium substitution were also consistent. The 696 cm^{-1} band does not exhibit chlorine isotopic splittings, presumably because of the small magnitude, 0.19 cm^{-1}, expected. A value for the ν_1 fundamental of 260 cm^{-1} is obtained from the observed $(\nu_1 + \nu_3)$ and ν_3 bands. The bending frequency, ν_2, is probably below the limit of detection, 200 cm^{-1}. No evidence for HCl_2 formation was obtained when HCl, Cl_2, or HI, Cl_2 samples were photolyzed in nitrogen or argon at 20°K.

HNC

Milligan and Jacox (63c, 67b) have reported the infrared spectrum of the HNC molecule prepared by the vacuum ultraviolet photolysis of HCN in argon and nitrogen at 14°K and from the prolonged photolysis of methyl azide, CH_3N_3, in argon at 4.2°K.

The three fundamental vibrations of the molecule are observed at 477, 2029, and 3620 cm^{-1} in argon at high dilution. The presence of nitrogen in neighboring lattice sites apparently perturbs the (N-H) stretching frequency and the bending mode of the molecule. Frequencies obtained at low M/R's or in N_2 matrices are shifted significantly varying between 478 and 538 cm^{-1} for the bending mode and 3567 and 3620 for the (N-H) stretching frequency.

Isotope shifts for ^{13}C, D, and ^{15}N substituted species are consistent with the assignments. HNC is predicted (Walsh, 53a,b) to have a linear ground state and the computed isotope shifts suggest such a geometry. The computed force constants indicate that the carbon-nitrogen bond is a triple bond.

No ultraviolet-visible transitions have been observed. The photolysis of HCN, however, lead to sufficient CN concentrations for the observation of the (0,0) and (0,1) bands of the CN $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ system at 385 nm.

HNF

Jacox and Milligan (67a) have produced the radical HNF by the reaction of fluorine atoms with NH in argon matrices at 14°K. Fluorine atoms can be produced by the photolysis of F_2 or N_2F_2 and NH is prepared by the photolysis of HN_3. Photolytic production of both F and NH are required for HNF formation. Other species known to be present include NF, NF_2, NF_3, HNF_2, HF, NH, N_2H_2, as well as precursors.

HNF shows an electronic transition between 390 and 500 nm consisting of a progression of six bands in v_2' with a frequency of 1033 cm^{-1}. Walsh (53a,b) suggested that the progression is in the bending mode of the transition $^2A' \leftarrow {^2A''}$. The origin of the system appears at 2.034 μm^{-1}. The same system for DNF originates at 2.036 μm^{-1} and shows a progression with a frequency of 798 cm^{-1}.

Two vibrational fundamentals for HNF are observed in the infrared. The N-F stretching mode occurs at 1000 cm^{-1} and the HNF bending mode at 1432 cm^{-1}. The N-H stretching mode should occur between 2700 and 4000 cm^{-1}, but it is not observed. Presumably this mode is very weak. Deuterium and ^{15}N isotope shifts confirmed the identification. The HNF bond angle is about 105°, in analogy with NH_2 and NF_2. Force constants and thermodynamic properties have been computed.

HNO

The HNO molecule was among the first trapped free radicals (Robinson, 57a, 58a,b,d). It was obtained as a by-product following condensation of the products of a discharge through hydrazine, argon mixtures containing water as an impurity. Shortly thereafter, the sustained photolysis of nitromethane and methyl nitrite in argon was also found to give observable amounts of HNO (H. Brown, 58). Subsequently, HNO has appeared in other systems often as the result of impurities (McCarty, 59b; Harvey, 59; Baldeschwieler, 60; Milligan 62c). Of particular note is its formation in the photolysis of HN_3 in CO_2 (Milligan, 62c) via the reaction of NH with CO_2. This system gives a moderately clean sample, spectroscopically.

Eight bands of HNO are observed in the visible spectrum originating at 1.312 μm^{-1} and extending to 1.740 μm^{-1}. Only the first three have significant intensity. These bands correlate well with the gas phase bands initially reported by Dalby (58). The bands are assigned to the transition $^1A'' \leftarrow X^1A'$ and involve simultaneous progressions in v'_2 and v'_3. The observed frequencies are $\nu'_2 = 1422\ cm^{-1}$ and $\nu'_3 = 982\ cm^{-1}$. The matrix bands are shifted from the gas phase bands by about $-54\ cm^{-1}$.

The infrared spectrum of matrix-isolated HNO has been reported by several worker (H. Brown, 58; Harvey, 59; Milligan, 62c). Agreement as regards the ν_2 and ν_3 fundamentals, the molecular bending mode and the N = O stretching frequencies among workers is excellent and the values observed in argon are: $\nu_2 = 1570\ cm^{-1}$ and $\nu_3 = 1110\ cm^{-1}$. The use of deuterium and oxygen isotopes confirm these assignments. There is, however, a discrepancy regarding the value for ν_1, the H-N stretching mode. Brown and Pimentel (58) observed a band at 3300 cm^{-1} which they tentatively assigned to HCO; Milligan, et al. (62c) report a value of 3380 cm^{-1} in CO_2 and N_2O; whereas Harvey and Brown (59) report a value of 3592 cm^{-1} in argon. In all cases, deuterium substitution has been used. Deuterium shifts are all within reasonable limits. There is no aspect in any of the experiments that would tend to reject the observations. All systems are, however, complex, and contain species other than HNO. The value reported by Harvey and Brown of 3592 cm^{-1} does correlate best with the gas phase value, 3596 cm^{-1} (see Herzberg, 67).

The high frequency observed for ν_2 indicates a molecular angle of 110°. This is in good agreement with the 109° from the gas phase data (see Herzberg, 67).

HNSi

Irradiation of SiH_3N_3 in argon near 4°K with a high pressure mercury lamp is reported to produce infrared observable quantities of the species HNSi (Ogilvie, 66). Frequencies assigned to the molecule are ν_1 = 3583 cm^{-1}, ν_2 = 523 cm^{-1} and ν_3 = 1198 cm^{-1}. Calculated and observed isotope shifts with deuterium are consistent. The structure is linear and a large k_2 force constant is taken as an indication of a singlet ground state. The (N-H) stretching frequency, ν_1, is identical with the equivalent mode in the species HNC in argon containing nitrogen (Milligan, 63c, 67b).

HOBr

Photolysis of argon, HBr, ozone mixtures at 4.2°K are observed to produce HOBr (Schwager, 67) presumably by the reaction $O_3 + HBr + h\nu = HOBr + O_2$. No evidence for intermediates such as OH is obtained so that a detailed mechanism is not available.

All three fundamental vibrational frequencies are observed. For $H^{16}OBr$ these appear at: $\nu_1 = 3590\ cm^{-1}$, $\nu_2 = 1164\ cm^{-1}$ and $\nu_3 = 626\ cm^{-1}$. The DOBr counterpart bands appear at 2153, 854 and 621 respectively. ^{18}O isotopic substitution in both HOBr and DOBr has been used to assist in the assignments. The molecular bond angle was estimated to be 110° for the calculation of force constants and isotopic frequencies.

HOCl

Similar to HOBr, HOCl has been prepared in argon matrices via the photolysis of Ar, HCl, O_3 mixtures at 4.2°K (Schwager, 67). The vibrational fundamentals of HOCl, ν_1, ν_2, and ν_3, appear at 3581, 1239 and 729 cm^{-1} respectively. ^{18}O isotopic substitution was used to verify assignments and to calculate force constants. The molecular bond angle is 113° as determined from the gas phase data (see Herzberg, 67).

HOF

The photolysis of condensed mixtures of water, fluorine, and nitrogen at 20 or 14°K has led to infrared observable quantities of the radical HOF (Noble 68b). Bands attributable to the three fundamentals were observed at 3483, 1393, and 884 cm^{-1} for ν_1, ν_2, and ν_3, respectively. Similar, but more complex bands were obtained when argon was substituted for nitrogen. An additional band in the hydrogen stretching region at 3772 cm^{-1} was assigned to HOF hydrogen bonded to an adjacent HF. A normal coordinate analysis based on structural parameters from H_2O and OF_2 verified the assignment. Experiments with D_2O and $H_2{}^{18}O$ were also consistent with the identification of HOF and the frequency assignments. Thermodynamic properties have been calculated. The bonding in the molecule is apparently similar to the bonding in H_2O and OF_2.

HOO

Milligan and Jacox (63b, 64a) have succeeded in observing the vibrational fundamentals of the species HO_2 following the reaction of H atoms, produced in photolysis of HBr or HI, with oxygen in argon matrices at 4.2°K. Yields of the radical are apparently greater with HI than HBr. Bands attributable to HO_2 are observed at 1101, 1389, and 3414 cm^{-1}. The use of ^{18}O and D isotopes as well as comparisons with spectra of H_2O_2 lead to the assignments $\nu_1 = 3414$, $\nu_2 = 1389$, and $\nu_3 = 1101\ cm^{-1}$. The spectrum indicates that the oxygen atoms are non-equivalent casting doubt on an isosceles triangle structure. The data is insufficient to permit calculation of an accurate value for the molecular angle. At wavelengths < 220 nm, HO_2 appears to also undergo photolysis.

Giguere (54) had earlier assigned a band observed at 1305 cm^{-1} to HO_2 following condensation of the products of a discharge through water vapor. He subsequently showed (56) that the band was due to N_2O_3 produced from nitrogen as an impurity.

$HgBr_2$, $HgCl_2$, HgF_2, HgI_2

The infrared spectra of the mercury di-halides in krypton at 4.2 and 20°K have been reported by Loewenschuss et al. (69). The chloride, $HgCl_2$, has also been investigated in argon, krypton, and xenon at 20°K by McNamee (62). All are prepared by vaporization of the solids. Monomer yields are greatest with a double-oven arrangement. The spectra are consistent with linear structures (Büchler, 64) with only two fundamentals appearing in the infrared for the matrix-isolated monomers. Spectra of each species also show additional bands attributable to dimers, polymers, or other species. Table II summarizes the observed frequencies for the monomers.

Table II

Infrared Frequencies of Mercury Di-halides in Krypton (cm^{-1})

	ν_3	ν_2
HgF_2	642, 639	172
$HgCl_2$	407, 403, 398	107
$HgBr_2$	294	73
HgI_2	238	63

The multiplet appearance of the $HgCl_2$ ν_3 band is apparently due to isotopic splittings.

Dimer bands appear at 586 cm^{-1} for the fluoride, 286 cm^{-1} for the bromide, and 229 cm^{-1} for the iodide. These are tentatively assigned to a stretching mode of a D_{2h} halogen-bridged species. Other bands appearing and due to polymers or other unidentified species are at 660 and 384 cm^{-1} for HgF_2, 412 cm^{-1} for $HgCl_2$, 261 cm^{-1} for $HgBr_2$, and 220 and 234 cm^{-1} for HgI.

Calculated symmetric stretching frequencies, ν_1, are: HgF_2, 588 cm^{-1}; $HgCl_2$, 348 cm^{-1}; $HgBr_2$, 219 cm^{-1}, and HgI_2, 158 cm^{-1}. Force constants and thermodynamic functions have been computed from the data (Loewenschuss, 69).

KrF_2

Infrared absorptions at 580 cm^{-1} and 236 cm^{-1} occurring when 1:70:220 mixtures of F_2:Kr:Ar are condensed at 20°K and photolyzed with an AH-4 medium pressure mercury lamp, have been assigned to ν_3 and ν_2 respectively of the molecule KrF_2 (Turner, 63a,b). At higher F_2:Kr ratios, these bands shifts to 575 and 245 cm^{-1}. The shifts are believed to be due to aggregations. Force constants derived for the molecule indicate that the bond energies are similar to those in XeF_2.

Li_2O

Condensation of the vapors from solid Li_2O with krypton under conditions where the vapor consists of predominately Li_2O, yields, infrared bands at 112 and 987 cm^{-1} assignable to ν_2 and ν_3 of the molecule (Seshadri, 66; White, 63b). Substitution of ^6Li in the molecule shifts the bands to 118 cm^{-1} and 1029 cm^{-1} respectively. Isotope ratios are consistent with a linear structure, but the accuracy of measurements are not sufficient to make the conclusion unambiguous. They are, however, sufficient to exclude large deviations from linearity. On the basis of force constant data, a value for ν_1 of 685 cm^{-1} is calculated.

LiON

Andrews and Pimentel (66a) report the appearance of new infrared bands when co-depositions of lithium, nitric oxide and argon are made at 15° and 4.2°K. The isotope shifts with ^6Li, ^{18}O and ^{15}N are consistent with their assignment to a triatomic species containing one each Li, O, and N atoms. The observed isotope shifts and a normal coordinate analysis favor the molecular arrangement LiON in which the molecule is bent with an angle of 100° ± 10°. The observed frequencies for the natural isotopic species, assuming the structure LiON, are: ν_1, the NO stretching motion, 1352 cm^{-1}, ν_2, the bending mode, 333 cm^{-1} and ν_3, the LiO stretching frequency, 650 cm^{-1}. The latter is the strongest of the three bands. The NO stretching frequency suggests a bond order of about 1.7. The bonding of the species is not clear. The molecular arrangement is not unambiguous and must be considered tentative.

LiO_2

Low frequency infrared bands at 231 and 685 cm^{-1} appearing in the spectrum of matrix-isolated Li_2O vapors under conditions where the predominant vapor species is Li_2O_2 have been assigned to the ν_2 and ν_3 fundamentals of the species LiO_2 (White, 63b; Seshadri, 66). Isotope substitution indicates the presence of only one Li atom in the species and calculated isotope ratios are consistent with the assignment to LiO_2. Best fit is obtained when a symmetrical molecule with an angle of 170° is assumed. It is conceivable that the molecule is linear. A calculated value for ν_1 of 340 cm^{-1} is reported.

MgF_2

Magnesium difluoride can be deposited by direct vaporization from a Knudsen furnace at temperatures in the range 1500 - 1575°K (Calder, 69; Mann, 67; Snelson, 66). The infrared spectrum of MgF_2 in krypton shows several bands between 200 and 900 cm^{-1}. Bands at 478, 242, and 837 cm^{-1} are assigned to ν_1, ν_2, and ν_3 respectively of the most abundant species of the molecule. Isotope shifts for ^{24}Mg and ^{26}Mg are in agreement with the assignments. The direct observation of ν_1 requires that the molecule be bent. The apex angle giving the closest agreement between observed and calculated isotope shifts is 158° (Calder, 69). Spectra in neon and argon appear essentially the same, but the frequencies are shifted as expected.

Other bands occurring in the spectrum are assigned to other species. A band at 740 cm^{-1} is assigned to MgF and bands near 450 and 480 cm^{-1} are assigned to polymeric species.

$MnCl_2$

$MnCl_2$ can be deposited for matrix spectral studies by either direct vaporization of the solid or via the reaction of chlorine with manganese metal surfaces at 995 - 1085°K. (DeKock, 68; K. Thompson, 68; Jacox, 69b).

The ultraviolet-visible spectrum of $MnCl_2$ in argon gives three broad unstructured bands at 4.39, 4.57, and 5.00 μm^{-1}. $MnCl_2$ is linear and is suggested to have a $^6\Sigma_g^+$ ground state (DeKock, 68). The transitions may involve upper $^6\Sigma_u^+$ and $^6\Pi_u$ states, but no definite assignments have been made. The asymmetric stretching frequency, ν_3, and the bending mode, ν_2, appear in an argon matrix at 477 and 83 cm^{-1} respectively.

N_3

Milligan et al. (56) assigned a band appearing at 2150 cm^{-1} in condensed films of discharged nitrogen, at 20°K, to the asymmetric stretch of a linear N_3 radical. ^{15}N enriched samples gave additional bands confirming that the absorbing species contained nitrogen. Bands appearing at 962 and 737 cm^{-1} in the same samples were assigned to polymeric species greater than N_3. All these bands disappeared on warming to 35°K as expected for a reactive species. Becker et al. (57) observed a band at 2140 cm^{-1} in argon following the photolysis of HN_3 which they correlated to the N_3 radical. Harvey and Brown (59), however, failed to duplicate the results using discharged nitrogen condensed at 4.2°K. Both systems are complex and often contain impurities.

Peyron et al. (59b,c) have proposed a different type of N_3 species to account for the observed emission features in condensed, discharged nitrogen. This species is proposed to be a loosely bound N-N_2 complex in which the observed emission is viewed as simple combinations of electronic transitions of the nitrogen atoms and vibrational transitions of the N_2 molecules. Results of isotopic experiments with ^{15}N are consistent with this interpretation. This N_3 species is not the same molecule as that proposed by Milligan et al. in spite of the fact that the observed vibrational frequency of about 2200 cm^{-1} is similar.

NCN

The free radical NCN has been prepared by the photolysis of cyanogen azide, N_3CN, in a variety of different solvents. Infrared observations yielded two of the three vibrational fundamentals. The third was deduced from the first two. The gas phase bands at 329 nm (Herzberg, 64) and a new UV absorption system between 240 and 300 nm were observed by Milligan, et al. (65c,b, 66c, 69c).

The gas phase rotational analysis of the (0,0,0) band of the 329 nm system shows the molecule to be linear and symmetric with a $^3\Sigma_g^-$ ground state (Herzberg, 64).

Cyanogen azide has two distinct UV absorptions at 275 nm ($\epsilon = 103$) and 220 nm ($\epsilon = 2157$) (Marsh, 64), and irradiation of the molecule in either band leads to photolytic cleavage to give NCN and N_2. Because of the characteristics of the absorption, the 228.8 nm line of a cadmium lamp has proved to be the best photolysis source for the production of NCN. Its yield is, for all practical purposes, quantitative. If light of 250 nm is used, NCN itself will also photolyze, but photolysis apparently does not occur with the 228.8 nm cadmium line.

The 329 nm gas phase $^3\Pi_u \leftarrow {^3\Sigma_g^-}$ absorption system is, in the solid, shifted to 330.4 nm in nitrogen and to 334.4 nm in argon. This system normally appears as a single broad unstructured band. In solids containing large amounts of NCN an additional band appears about 1140 cm^{-1} toward the blue. Assuming this band belongs to the transition, the frequency of 1140 cm^{-1} is assigned to ν_1 of the $^3\Pi_u$ state.

In addition to the $^3\Pi_u - {}^3\Sigma_g^-$ transition, a second and previously unreported transition appears. This system consists of a series of bands extending from 300 nm to 240 nm and separated by about 1040 cm^{-1}. Each major absorption is accompanied by a weaker second component located 35 cm^{-1} toward the blue in argon, or 50 cm^{-1} toward the blue in N_2. The exact cause of the substructure is not known. The 1040 cm^{-1} vibrational frequency, assignable to $\nu_1{}'$, and the number of vibrational bands observed, about 10, suggests that the upper state is also linear and involves an appreciable change in the carbon-nitrogen bond length. Using the arguments of Walsh (53a,b) the transition is assigned to $B^3\Sigma_u^- \longleftarrow X^3\Sigma_g^-$.

Schoen(66) has employed flash photolysis of N_3CN, N_2 mixtures at 20°K to study the photolytic process. He observed an absorption band at 335 nm which he assigned to the NCN $^1\Pi_u \leftarrow {}^1\Delta_g$ system. This band appears as the only absorption attributable to NCN immediately following the flash. Delay time measurements indicate a mean lifetime of about 500 μsec for the $^1\Delta_g$ state. Subsequently, the $^3\Pi_u \leftarrow {}^3\Sigma_g^-$ absorption appears as the NCN ($^1\Delta_g$) decays to the ground state.

Infrared observations give directly the frequencies 423 cm^{-1} for $\nu_2{}''$ and 1475 cm^{-1} for $\nu_3{}''$. Samples containing large amounts of NCN also show a band at 2672 cm^{-1} which is assigned to the combination band ($\nu_1 + \nu_3$). This then gives a value of $\nu_1{}''$ equal to 1197 cm^{-1}. The use of the isotopes ^{13}C and ^{15}N supports all assignments. Force constants and thermodynamics data for the species have been calculated. The C-N stretching force constant is near that of a carbon-nitrogen double bond.

Small amounts of NCN have also been produced during the vacuum ultraviolet photolysis of C_3O_2 in N_2 (Moll, 66).

NCO

Robinson (58b) and McCarty (59b) tentatively observed a band near 440 nm in the condensation products of a methane-argon discharge containing nitrogen and oxygen impurities. They assigned it as the $(0,0,0) \leftarrow (0,0,0)$ band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of NCO. This band was shifted by about +70 cm^{-1} from the gas phase band (Holland, 58). In light of more recent work (Milligan, 67e), this assignment of Robinson and McCarty is questionable. However, there is no doubt now that NCO has been isolated in low temperature matrices.

Two transitions of the radical have been observed (Milligan, 67e) in neon, argon, nitrogen, and carbon monoxide matrices at 4.2 and 14°K. The first of these is the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition originating near 2.28 μm^{-1}. The bands correlate with the more recent gas phase data of Dixon (60a,b). The matrix spectra are shifted with respect to the gas phase with neon showing a -38 cm^{-1} shift, argon -64 cm^{-1}, N_2 + 156 cm^{-1}, and CO + 119 cm^{-1} for the (0,0) band. Band half-widths vary from 40 cm^{-1} in neon to 500 cm^{-1} in CO. All three frequencies for the upper state ($A^2\Sigma^+$) can be derived from the spectra. They are, in neon, $\nu_1' = 2325$ cm^{-1}, $\nu_2' = 687$ cm^{-1} and $\nu_3' = 1270$ cm^{-1}. The second system observed is the $B^2\Pi \leftarrow X^2\Pi$ system with its origin near 3.16 μm^{-1}. The matrix bands are shifted from the gas phase bands by -122 cm^{-1}, -301 cm^{-1}, -400 cm^{-1} and -768 cm^{-1} in neon, argon, nitrogen and CO, respectively. Vibrational frequencies observed for the $B^2\Pi$ state are approximately 2300 for ν_1' and 1040 cm^{-1} for ν_3'. The $B \leftarrow X$ transition is a much more extensive band system than the $A \leftarrow X$ transition. Nearly 40 bands are observed in neon for $B \leftarrow X$ vs. 5 bands for the $A \leftarrow X$ system.

Analysis of the spectra is complicated by an appreciable Renner effect for the NCO-ground state. In addition, the molecule has a large spin splitting (Dixon, 60a). As a result, transitions are expected from the $^2\Pi_{3/2}$ level only at 14°K when paramagnetic impurities are present to depopulate the $^2\Pi_{1/2}$ level.

Infrared observation on NCO produced by several reactions has led to the assignment of all three vibrational fundamentals of the ground state. These appear at 1922, 487, and 1275 cm^{-1}, respectively, for ν_1, ν_2, and ν_3. The assignments are consistent with ^{13}C and ^{15}N isotopic substitution. Force constant calculations indicate that the CO bond is somewhat stronger than the CN band.

Continued photolysis of NCO at wavelengths near 254 nm led to disappearance of the molecule. It is concluded that NCO photolyzes to give N atoms and CO. No evidence for the species with atomic arrangement CNO was obtained.

$\underline{NH_2}$

The electronic spectrum of the radical NH_2 has been carefully investigated in argon matrices at 4.2 and 14°K and to a lesser extent in Kr and N_2 (Milligan, 65e; Keyser, 60; Robinson, 58a,b,c, 59, 62c). NH_2 appears following discharges through nearly any system containing nitrogen and hydrogen, for example, N_2H_4 in argon, following vacuum ultraviolet photolysis of NH_3 in argon, or via photolysis of HN_3 in matrices. The spectrum in argon appears as an extensive series of 67 sharp bands between 345 nm and 790 nm. The bandwidth of many of the "lines" is less than 3 cm^{-1}, suggesting that the radicals are situated in equivalent, and possibly, well ordered lattice sites. In N_2 the absorption appears as a series of broad features with bandwidths of nearly 100 cm^{-1}. The principal transition involved is $A^2A_1(\Pi) \leftarrow X^2B_1$.

Clearly visible in the spectrum in argon are transitions involving rotational levels as well as vibrational levels. This has led to the conclusion that NH_2 undergoes nearly free end-over-end rotation in the matrix. In the ground state the four lowest rotational levels are: $0''_0$ at 0.00 cm^{-1}; $1''_{-1}$ at 21.11 cm^{-1}; $1''_0$ at 31.87 cm^{-1}, and $1''_{+1}$ at 36.65 cm^{-1}. At 4.2°K, approximately 99,9% of the molecules are in the lowest rotational level, $0''_0$. As a result, the strongest features in the absorption spectrum involve transitions from this level (Ramsay, 57). The matrix spectrum correlates very closely with the gas phase spectrum (Ramsay, 57; Dressler, 59) and shows a progression in the excited state bending mode, $(0, v_2', 0) \longleftarrow (0,0,0)$. Only those bands where v_2' is even are observed with significant intensity, and the first strong band is assigned to (0,4,0). The alternating appearance of the spectrum results from the fact that odd v_3' levels cannot combine with $0''_0$.

The upper state of NH_2 apparently consists of vibronic levels with Π vibronic bands for even v_2' and Δ subbands for odd v_2'. Robinson (59) has given a tentative rotational assignment for the strongest bands. The results of Milligan and Jacox (65e) are in excellent agreement with the results of Robinson. Many of the weaker lines can be attributed to transitions from excited ground state rotational levels such as $1''_0$. The observed intensities are somewhat greater than expected on the basis of thermal distribution alone. The excess population can be rationalized in terms of optical pumping via either absorption followed by emission to levels other than $0''_0$ or via direct absorption of and transitions between rotational levels.

In addition to the principal progression, bands attributable to (1,6,0), (0,0,0) and (1,8,0), (0,0,0) transitions are observed. These transitions arise via Fermi resonance with the (0,10,0) and (0,12,0) bands, respectively. Measurements of the relative intensities have led to calculated values for the interaction constants of $W_{(1,6,0)} = 72\ \mathrm{cm}^{-1}$ and $W_{(1,8,0)} = 76\ \mathrm{cm}^{-1}$. These values are in excellent agreement with the gas phase values of Dressler (59).

An extrapolated origin of about $1.02\ \mu\mathrm{m}^{-1}$ is obtained, and a vibrational frequency ν'_2 of $680\ \mathrm{cm}^{-1}$; because the origin region is not observed, these values are highly tentative.

Two of the three ground state vibrational fundamentals of NH_2 have been directly measured by Milligan and Jacox (65e). The use of ^{15}N and D isotopes confirmed the assignment of bands appearing at 1499 cm^{-1} and 3220 cm^{-1} in argon following the vacuum uv photolysis of NH_3 to ν_2 and ν_3, respectively, of NH_2. These results contradict an earlier tentative assignment of 1290 cm^{-1} for ν_2 (Becker, 57). The complexity of the absorption pattern near 1499 cm^{-1} is consistent with the conclusion that NH_2 is free to rotate in the solid.

N_2O

Several ultraviolet absorption systems of N_2O have been reported, both for the pure solid and in neon, argon and krypton matrices over the temperature range 1.5 - 63°K, (Sibleyras, 68; Romand, 52; Granier-Mayence, 53). The A system, appearing in the gas phase near 3.85 μm^{-1} appears in the solid at 20°K also as a broad, structureless feature, half-width of 3000 cm^{-1}, but reportedly shifted by +1500 cm^{-1}. The gas phase system B at 5.954 μm^{-1} appears in the solid shifted by +2500 cm^{-1}. This system shows vibrational structure; however, the origin is not observed, and the upper state vibrational frequency cannot be deduced with accuracy. An average spacing of 590 cm^{-1} is observed for those bands appearing in the solid. The progression appears to be in v'_2.

The B bands as well as four other systems further in the vacuum ultraviolet are observed in matrices (Sibleyras, 68). The B system shows more extensive vibrational structure than in the pure solid. Fifteen bands are reported in argon. As in the pure solid all transitions are reported to have very large gas to matrix shifts varying from 2000 to 5400 cm^{-1}. The transitions can be correlated to the gas phase systems B, C, D, E, and F (Herman, 67) appearing at 5.959, 6.895, 7.790, 8.490, and 8.680 μm^{-1}, respectively. Bands C and D are both continua.

Infrared spectra give the values for ν_1 and ν_3 of the ground state molecules as 2222 and 1290 cm^{-1}, respectively, in nitrogen (DeMore, 59a).

NO_2

The radical NO_2 has been studied on several occassions and under a variety of conditions (Bass, 56; Becker, 56; Broida, 57b, 58c; DeMore, 59a; Fateley, 59; Harvey, 58; Peyron, 59a; Robinson, 57a).

It is one of the earliest radicals to be studied by matrix-isolation methods. Bass and Broida (56) observed a series of diffuse bands in the region 300-470 nm following the trapping of nitrogen discharges at 4.2°C which they assigned as NO_2 bands. These bands were later observed in the warm-up glow by Broida and Peyron (57b) and found to depend on the presence of small amounts of oxygen impurity (Broida, 58c). Experiments using ^{18}O isotope confirmed the assignment to NO_2 (Peyron, 59a). Robinson <u>et</u> <u>al</u>. (57a) studied argon, NO_2 mixtures at 4.2 and 1.5°K and reported a complex series of bands in the region 340-700 nm. These bands correlated with the corresponding gas phase bands but exhibited shifts of +55-70 cm^{-1}. A sharp decrease in intensity above 620 nm may indicate the presence of more than one transition. The complexity of the low temperature spectrum at both 4.2 and 1.5°K is interpreted as evidence that the excited state structure leading to the bands below 620 nm is non-linear.

An accurate vibrational analysis was not given, but frequency differences of 620 cm^{-1}, presumably corresponding to ν_2 commonly occur.

Infrared studies have been made on NO_2 in O_2, N_2, Ar, H_2, CO_2, and N_2O at 4.2 and 20°K. Both monomeric and dimeric NO_2 are observed. The number of bands observed depends on the degree of isolation. Fateley <u>et</u> <u>al</u>. (59), for example, report three types of dimers and 16 absorption bands.

Vibrational fundamentals are observed at 1611 and 750 cm^{-1} in oxygen at 4.2°K. These correlate with the ν_3 and ν_2 gas phase fundamentals of 1616 and 750 cm^{-1}, respectively (see Herzberg, 67). The ν_1 gas phase frequency of 1320 cm^{-1} is not observed. The ν_2 fundamental varies from 1608 cm^{-1} in N_2O_4, to 1624 cm^{-1} in CO_2 with the order being $N_2O_4 < Ar < O_2 < N_2 < H_2 < N_2O < CO_2$. Dimerization occurs readily upon warming of the matrix.

$NiCl_2$

The matrix spectrum of $NiCl_2$ in argon consists of at least six distinct electronic transitions in the region from 260 to 500 nm (DeKock, 68; Gruen, 68; Jacox, 69b; Milligan, 65a, K. Thompson, 68). Structured progressions are observed with origins near 2.02, 2.13 3.05, 3.35, and 3.69 μm^{-1} as well as a broad unstructured band at 2.12 μm^{-1}. In addition a very weak structureless feature at 4.15 μm^{-1} has been reported by DeKock and Gruen (68). The system appearing at 3.05 μm^{-1} is the most intense, with the bands at 3.35 and 3.69 μm^{-1} somewhat weaker. The bands at 2.02, 2.13 and 2.12 μm^{-1} are observed only after long depositions. The observed vibrational frequencies for each of the three bands, 3.05, 3.35, and 3.69 μm^{-1}, are near 250 cm^{-1}, the individual average values being 256, 249 and 283 cm^{-1} respectively. These values are assigned to ν_1 of the excited state. The system at 2.02 μm^{-1} shows four bands with an average spacing of 114 cm^{-1}. This frequency is unassigned.

The band at 2.13 μm^{-1} shows a vibrational spacing of 350 cm^{-1}, also assigned as a ν_1 frequency. This transition also shows fine structure, with three apparent parallel progressions. The second-most intense features are shifted with respect to the strongest by -95 cm^{-1}, while the least intense bands appear at approximately 55 cm^{-1} higher energy than the strong bands. The exact reason for this is not clear, but it may be due to multiple sites, overlap of transitions, or Renner splitting in a linear degenerate upper state.

A detailed assignment of the absorption spectrum of $NiCl_2$ is not possible, even in the gas phase work (DeKock, 67). Previously, the observed matrix spectrum (DeKock, 68) had been interpreted in terms of an axial ligand field model including spin-orbit coupling. The transitions of 3.05, 3.35, 3.69, and 4.15 μm^{-1} were believed to correspond to the four lowest allowed one-electron allowed transitions to the $^3\Sigma_u^+$, $^3\Sigma_u^-$, $^3\Pi_u$ and $^3\Delta_u$ molecular states. The observation by Jacox and Milligan (69b) of the bands at 2.02, 2.13, and 2.12 μm^{-1} cannot be interpreted easily with this model. Consequently, Jacox and Milligan (69b) have proposed a revised energy relationship between the orbitals on the nickel and chlorine atoms in a molecular orbital treatment based on a covalent $NiCl_2$. This treatment results in four low lying allowed transitions not involving charge-transfer and therefore likely to show structure ($^3\Pi_u$, $^3\Sigma_u^+$, $^3\Sigma_u^-$, and $^3\Delta_u$). Two of these states, $^3\Pi_u$ and $^2\Delta_u$ might be expected to show Renner splittings. The transitions at 2.02, 2.13 and 2.12 μm^{-1} presumably involve these states. Two higher energy transitions are also predicted, these being $^3\Sigma_u^+$ and $^3\Pi_u$ states. The model falls short, however, because four transitions are observed. Expansion to include all the transitions, involve other possible levels due to different electron configurations and possible spin forbidden transitions.

Irradiation of $NiCl_2$ in argon at 3.20 or 2.70 μm^{-1} is observed to result in green emission from the molecule. Three band systems have been reported (Gruen, 68) although only two could be reproduced (Jacox, 69b). These band systems originate near 2.13 and 1.95 μm^{-1} with a very weak one near 1.72 μm^{-1}. The first two show clear vibrational frequencies of 360 cm^{-1}, very close to the expected ground state frequency ν''_1. The appearance of three absorption systems in this region, particularly the two at 2.02 and 2.13 μm^{-1} suggests that the two stronger emission systems may be the corresponding fluorescences. Gruen (68) postulated that all but four of the observed bands resulted from emission from a $^3\Sigma_g^+$ upper state to various lower lying states.

Infrared observations have yielded directly two of the three ground state vibrational frequencies. The band attributable to ν_3 of the most abundant species appears at 521 cm^{-1}. The bending mode, ν_2 is at 85 cm^{-1}. Additional bands near 440 cm^{-1} have been assigned to the dimer $(NiCl_2)_2$. Calculations of ν_1 based on the values for ν_2, ν_3 and the isotope spacings give a value of 351 cm^{-1} in good agreement with the 360 cm^{-1} observed in the emission spectrum.

NiF_2

The asymmetric stretching fundamental of the molecule NiF_2 appears near 780 cm^{-1} in argon at 14°K, with the most intense component at 780 cm^{-1} corresponding to the most abundant isotopic species (Milligan, 65a). The failure to observe ν_1 along with the correlation between observed spacings to those calculated tend to support the hypothesis that NiF_2 is linear. A group of bands near 715 cm^{-1} is tentatively assigned to dimers. A calculated value for ν_1 of 606 cm^{-1} of obtained from ν_3.

No absorption in the region 220 - 500 nm attributable to NiF_2 have yet been observed in matrices.

O_3

Ozone has been studied in nitrogen, oxygen, and carbon dioxide matrices and as a solid film at 4.2°K and 20°K (Bass, 58; DeMore, 58; Harvey, 58; and Moll, 66). It can be produced by a discharge through purified molecular oxygen or prepared conventionally and deposited directly. Ozone shows a visible absorption extending from 400 to 670 nm, with the first band near 1.90 μm^{-1}. When produced by condensation of an oxygen discharge, the spectrum is overlaid with bands due to α-oxygen. Also observed is an infrared band at 3030 cm^{-1}, which has been assigned as $3\nu_3$ (Bass, 58).

Infrared studies of the pure solid and in oxygen and carbon dioxide yield the three fundamental frequencies: $\nu_1 = 1120$, $\nu_2 = 705$, and $\nu_3 = 1050$ cm^{-1}, in oxygen. These values are shifted toward slightly higher frequencies in nitrogen at 20°K. Overtone or combination bands are observed at 3060, 2800, 2150, 2110, and 2060 cm^{-1}.

OCl_2

The species OCl_2 has been investigated in the infrared at low temperatures by Rochkind.(65) Spectra have been recorded in N_2 and argon matrices at 20°K and in the pure solid at 77°K. The pure solid shows all three normal modes; ν_1, ν_2 are observed in N_2 matrices. The values reported for the fundamentals are: $\nu_1 = 631\ cm^{-1}$, $\nu_2 = 296\ cm^{-1}$, and $\nu_3 = 671\ cm^{-1}$. Under high resolution, the ν_3 band is observed to be a triplet. In a nitrogen matrix, ν_1 occurs at 640 cm^{-1} and ν_3 at 680 cm^{-1}, ν_1 is shifted to 639 cm^{-1} in argon. The bands are sufficiently sharp in matrices to reveal isotope shifts. In addition to the fundamental frequencies, overtone bands are observed in pure OCl_2 at 965 cm^{-1} $(\nu_2 + \nu_3)$, 1294 cm^{-1} $(\nu_1 + \nu_3)$, 1328 cm^{-1} $(2\nu_3)$, and 1976 cm^{-1} $(3\nu_3)$. All of these bands show multiplet structure. The assignments are based upon isotope shifts, band contours, intensity and separate observations on rotational structure in the gas phase. The assignments differ from earlier references quoted by Rochkind, particularly as relates to ν_3. The band at 972 cm^{-1} previously assigned as ν_3 is calculated to be due to the combination $\nu_3 + \nu_2$. This reassignment results in a lower value for the force constant associated with the Cl-O stretching mode. This force constant correlates with the relatively long Cl-O bond length of 170 nm. As a further result, revision of the calculated thermodynamic functions has been carried out.

OF_2

The molecule OF_2 has been studied in nitrogen, argon and oxygen at 4.2 and 20°K in connection with production of the O_2F radical (Arkell, 65a,b; Spratley, 66a,b). Samples were prepared by direct deposition or by photolysis of oxygen fluorine mixtures. Two of the three vibrational fundamentals are reported. The asymmetric stretching fundamental, ν_3, appears as a doublet at 926 and 915 cm^{-1} in nitrogen; the symmetric stretching frequency, ν_1, is 812 cm^{-1}. The latter is reportedly shifted to 822 cm^{-1} in argon; other frequencies are not reported in this matrix. The bending fundamental, ν_2, is not observed, but from the gas phase value of 461 cm^{-1} (Harmony, 62) should appear at or near this frequency.

OOF

The infrared spectrum of the radical O_2F has been observed following photolysis of OF_2,O_2 or F_2,O_2 mixtures in N_2, Ar, or O_2 at 4.2° and 20°K (Arkell, 65b; Noble, 66; Spratley, 66a,b). All three vibrational fundamentals have been reported. All observations give essentially the same results of 1495 cm^{-1} for ν_1, 858cm^{-1} for ν_2 and 376 cm^{-1} for ν_3. The early interpretation of the spectral features was complicated by unexpected results on ^{18}O substitution. Instead of a quartet feature, the ν_1 band near 1500 cm^{-1} was a triplet whereas the ν_2 mode at 585 cm^{-1} was a doublet. Normal coordinate analysis showed that the observed bandwidths could exceed the isotope splitting thereby leading to unresolved structure. Later experiments (Noble, 66) confirmed this behavior.

The bonding of O_2F apparently is the same as in O_2F_2. The O-F bond length is unusually long, as in O_2F_2, and the bond angle is 109.5°.

PH_2

McCarty and Robinson (59b) have reported five bands in the spectrum of condensed products from a discharge through argon phosphine mixtures which correlate well with the gas phase bands of PH_2 (Ramsay, 56; Herzberg, 67) These bands show matrix shifts of about -80 cm^{-1} with regard to the gas phase. They have been assigned to a progression in v'_2 with the first band observed at 1.91 μm^{-1} corresponding to (0,1,0), (0,0,0) of the $A\ ^2A_1 \leftarrow X\ ^2B_1$ transition. The observed vibrational frequency is 930 cm^{-1}. They have estimated ν'_1 as 2320 cm^{-1} from a force constant calculation. The data indicates an upper state angle of approximately 125° and a ground state angle of 97°.

SO_2

Sulfur dioxide has been studied in a wide variety of matrices and in a solid film over the temperature range of 4.2° to 110°K. Infrared observations on SO_2 in krypton matrices give the three ground state vibrational fundamentals as: $\nu_1 = 1150$, $\nu_2 = 519$ and $\nu_3 = 1351$ cm^{-1}. Isotopic substitution with ^{34}S and ^{18}O verify the assignments (Allavena, 69). The ν_1 and ν_2 frequencies are also observed in the phosphorescence spectrum (Meyer, 68; Phillips, 69a,b).

The ultraviolet absorption spectrum consists of several bands attributable to the $A\ ^1B_1 \leftarrow X\ ^1A_1$ transition in the region 280 to 310 nm (Phillips, 69). The origin of the system is not observed; the first band corresponds to (2,4,0), (0,0,0). The system consists of overlapping progressions in v'_1 and v'_2. The frequency differences are 720 and 220 cm^{-1} respectively for the first bands, but because of the failure to observe the origin, these cannot be compared to the gas phase $^1B_1$ frequencies. The origin is estimated to occur at about 2.96 μm^{-1}. In addition, estimates for the origins of the C and D systems are 4.15 and 4.23 μm^{-1} respectively.

Excitation of SO_2 with ultraviolet light into the systems A, C or D and with x-rays leads to strong phosphorescence, a $^3B_1 \rightarrow {}^1A_1$, in the region 390 to 470 nm. The lifetime of this phosphorescence varies from 0.55 msec in O_2, where strong quenching occurs, to 17.5 msec in neon. The lifetime is relatively independent of temperature over the range of 4.2° to 110°K, but the phosphorescent intensity decreases by a factor of up to 100 over the equivalent range. This intensity decrease is interpreted in terms of a temperature dependent intersystem crossing rate (Meyer, 68). A completely analogous behavior is observed with $^{34}S^{18}O_2$ (Phillips, 69b). The emission bands are well resolved in SF_6 and can be assigned to progressions in v''_1 and v''_2 with differences equal to 1126 and 518 cm^{-1}, respectively. Other matrices do not yield separation of the two frequencies. Synthesized spectra based on the observed values of ν''_1 and ν''_2 shift from matrix to matrix, but the shifts do not show the same trend. The origin of the system appears at 2.56 μm^{-1}. The intensity and lifetime measurements lead to the conclusion that radiationless processes in SO_2 are very small under the conditions of the experiments. Even pure SO_2 and SO_2 in oxygen show phosphorescence.

Zeeman experiments on the phosphorescence of SO_2 produce two lifetimes and a broadening of several emission bands (Conway, 69). At fields greater than 20kG, a second, about 15% longer lifetime component representing 20-30% of the total intensity appears. The contribution of this component is independent of field up to 90kG, however at about 80kG a Paschen-Back effect occurs. The results are believed to be due to a combination of factors, including spin lattice relaxation, kT imbalance and triplet level splitting.

S_2O

The ultraviolet absorption spectrum of the molecule S_2O has been observed in argon, krypton, xenon, and nitrogen matrices at 20°K, and the infrared spectrum in a solid film at 77°K (Phillips, 69a; Blukis, 64). S_2O can be prepared by passing a mixture of $SOCl_2$ in rare gas through a column of Ag_2S heated to 160°C. In absorption, only one transition of S_2O is observed. The spectrum consists of a progression of 18 bands originating near 2.90 μm^{-1} with a vibrational spacing of 415 cm^{-1}. All 18 bands fit the formula

$$G(v'_3) = 29.070 + 426\ (v'_3 + 1/2) - 4.80\ (v'_3 + 1/2)^2 + 0.075\ (v'_3 + 1/2)^3$$

The matrix spectrum is very similar to that of the gas phase (see Herzberg, 67). The predissociation limit, however, is suppressed in the solid. Two bands to the red of the reported gas phase origin are observed indicating that the gas phase numbering is incorrect, if the heavy atom effect holds. A reevaluation of the gas phase data in light of the matrix observations leads to estimated excited state frequencies $\nu_1 \sim 720$ and $\nu_2 \sim 286$ cm^{-1}. In addition some previously unassigned bands are accounted for.

Infrared observations in solid films of S_2O give directly values for the three vibrational fundamentals in the solid at 77°K. These values are $\nu_1 = 1165\ cm^{-1}$, $\nu_2 = 388$, and $\nu_3 = 679\ cm^{-1}$.

ScF_2

McLeod and Weltner (66) have reported the observation of a series of ultraviolet absorption bands and several infrared bands, following condensation of vaporized ScF_3 into a neon matrix at 4.2°K, which they have tentatively assigned to ScF_2, ScF_3 or both. The UV band system extends from 280 to 320 nm with the origin at 318 nm and a vibrational frequency of 580 cm^{-1}. Five infrared bands appear at 726, 709, 661, 482 and 446 cm^{-1}. It is proposed that the bands at 726, 482 and 446 might be due to $ScF_3(D_{3h})$ and the bands at 709 and 661 cm^{-1} to ν_3 and ν_1, respectively, of a slightly bent ScF_2.

SeO_2

The UV visible spectrum of selenium dioxide has been reported by Voigt et al. (Voigt, 70) in argon, krypton, xenon, SF_6, CH_4 and C_4F_8 matrices at 20°K. Two absorption regions are observed. A strong absorption originating at about 3.10 μm^{-1} shows fine structure in argon and xenon, but appears as a broad, unresolved system in SF_6, CH_4 and C_4F_8. The resolved spectrum consists of vibrational bands forming an extended Franck-Condon curve with two close lying maxima. The absorption could result from two different progressions or from overlap of bands. Site effects are ruled out because the structure is identical in all matrices. If the spectrum consists of two progressions, it can be due to absorption in two electronic transitions, both with progressions in v'_1, or a single transition involving progressions in $(v', 0,0)$ and $(v',1,0)$. The data does not allow distinction, but the latter is preferred. The spacing between adjacent bands averages 310 cm^{-1} and between alternate bands 620 cm^{-1}. These are reasonable values for ν'_2 and ν'_1, respectively. This transition is assigned to the gas phase B state (see Herzberg, 67) which is analogous to the C state of the isovalent molecule SO_2.

A second, considerably weaker absorption appears in the region between 320-410 nm as a broad system with no distinct Franck-Condon maximum. This transition is tentatively assigned to $S_1 \leftarrow S_o$, where S_o represents the ground state, and S_1, the first excited singlet state in the molecule. The latter state is, in all likelihood, analogous to the A^1B_1 state of SO_2. It is also believed that the lowest triplet state, T_1, may contribute to the absorption in this region. The weak intensity of this absorption leads to the conclusion that S_1 and T_1 are very strongly mixed.

Depending on the wavelength of excitation, two emissions from SeO_2 are observed. With excitation into the strong absorption near 275 nm, or with X-rays, a weak, blue, generally structureless emission originating at 3.10 μm^{-1} appears. This emission is interpreted as resonance fluorescence of the strong absorption. With light of 365 nm wavelength, a strong yellow emission with origin at 2.20 μm^{-1} is obtained. The system appears as an extensive progression in v''_2 with vibrational spacing of 365 cm^{-1}. The lifetime of this transition has been measured in Xe, SF_6 and C_4F_8 and found to be < 0.2, 2.5 and 2.0 msec respectively. This transition is assigned to the phosphorescence $T_1 \rightarrow S_o$ with T_1 corresponding to the gas phase C state and analogous to the a^3B_1 state of SO_2. Population of T_1 occurs either via direct excitation through $T_1 \leftarrow S_o$ or by intersystem crossing following the weak $S_1 \leftarrow S_o$ absorption. $S_3 \leftarrow T_1$ intersystem crossing is apparently absent.

$\underline{Si_3}$

Trapping of silicon vapors in a neon matrix at 4.2°K has given a series of 7 weak bands between 420 and 470 nm which do not fit the scheme of Si_2 absorptions. These bands have been tentatively assigned to a $^3\Sigma^-_u \leftarrow {}^3\Sigma^-_g$ transition of Si_3(Weltner, 64c). The bands appear in groups of three, separated by 310 cm^{-1}. The separation of individual components in a group is 110 cm^{-1}. The 110 cm^{-1} splitting within groups has been attributed to site effects. The frequency of 310 cm^{-1} is suggested to be ν'_1. This value is not unreasonable when compared with a value for the ground state ν'_1 of 358 cm^{-1} as computed by Drowart (58).

SiCC

Weltner and McLeod (64c) report the appearance of 11 bands assignable to SiCC in the absorption spectrum of silicon carbide vapors trapped in neon or argon at 4.2°K and 20°K. The bands appear in the same region as the previously observed blue-green stellar bands (Kleman,56). The bands originate at 497 nm in neon and extend to about 400 nm. The intensity is highest near the origin and decreases abruptly at higher energies indicating little change in internuclear distance. In analogy with C_3 (Weltner 64a,b) the molecule is expected to be linear in both the ground state and the excited state. Transitions occur in which Δv_1 and Δv_3 take integral values and $\Delta v_2 = 0,2,4$ etc. The vibrational frequencies derived from the spectrum are: $\nu'_1 = 1461$; $\nu'_2 = 230$; $\nu'_3 = 1015$ cm^{-1}. The vibrational structure in the upper state apparently requires positive values for x'_{13} and x'_{23}. That is, the frequency ν'_3 increases with higher vibrational quanta of ν'_1. No evidence for Renner splittings, as in C_3, was observed. The transition is assumed to be $^1\Pi_u \leftarrow X^1\Sigma_g^+$.

The emission spectrum of this same system has been recorded, but the interpretation is not complete. Vibrational frequencies for the ground state of 836 cm^{-1} and 1745 cm^{-1} are obtained from the emission. The former is assigned to ν_3 and the latter to ν_1. The remaining frequency, ν_2, is listed as 300 cm^{-1} as obtained from the gas phase data.

Infrared measurements confirm the ν''_1 and ν''_3 frequencies, giving 1751 and 835 cm^{-1}, respectively, in neon. No observation of ν''_2 was made. All features are also observed in argon.

SiCSi

A few bands appearing in the absorption spectrum of silicon carbide vapors trapped in neon and argon at 4.2 and 20°K have been proposed to arise from the molecule SiCSi (Weltner, 64c). These bands overlap the long wavelength end of the A bands of SiCC. The bands originate near 530 nm in argon and near 510 nm in neon. Nearly all the intensity appears in the first three bands. The bands are separated by about 500 cm^{-1} and the assignment is made to ν'_1 on the basis that the molecule is symmetrical and the transition is $^1\Pi_u \leftarrow X^1\Sigma_g^+$. A calculated value for ν''_1 of 672 cm^{-1} is obtained if all assumptions are correct. The analysis and even the assignment to SiCSi is very tentative. This is particularly true in light of the number of species known to be present in silicon carbide vapor (Drowart, 58).

$SiCl_2$

Milligan and Jacox (68c) have prepared $SiCl_2$ in argon at 14°K by the vacuum ultraviolet photolysis of SiH_2Cl_2 and SiD_2Cl_2.

A broad unstructured absorption at 315 nm with a half width of about 500 cm^{-1} is the only absorption appearing between 190 and 540 nm.

Infrared absorptions appear at 502 and 513 cm^{-1}. These correspond to the ν_1 and ν_3 stretching fundamentals, although it is not possible on the basis of the data to determine which is which. The absorptions appear as multiplets due to silicon and chlorine isotopic splittings. The bond angle is computed to be between 90 and 120°.

SiF_2

One electronic transition and all three vibrational modes of the species SiF_2 have been observed in several matrices at 4.2 and 14°K by Milligan (68d). Difluorosilane, SiH_2F_2, photolyzes readily with vacuum ultraviolet radiation, for example, the hydrogen 121.6 nm Lyman line, to yield directly SiF_2. The molecule has also been prepared and trapped via the reaction of SiF_4 with solid silicon at 1425°K (Bassler, 66a). Ratios of SiF_2 to SiF_4 in the final products are about 3:2, so that the latter system is far from spectroscopically clean. The SiF_4 infrared ν_3 absorption occurs in the same region as the absorptions of SiF_2 making observations more difficult.

In both neon and argon, ultraviolet absorptions corresponding to the gas phase $^1B_1 \leftarrow {}^1A_1$ transition at 4.40 μm^{-1} are observed (Khanna, 67). In argon, the absorption appears as a structureless feature 7.5 nm in half-width and centered at about 220 nm; while in neon, a progression of 8 distinct bands with an average separation of 253 cm^{-1} appears. This frequency corresponds to the upper-state bending mode of SiF_2. The bands can be correlated with the $(0, v'_2, 0)$, $(0,0,0)$ bands of the gas phase spectrum by assuming a matrix red shift of 130 cm^{-1}. The origin is not observed, and the first band at 4.44 μm is assigned to the $(0,2,0)$ level.

Infrared observations in an argon matrix yield the following frequencies for the vibrational modes: the bending mode, ν_2, appears at 343 cm^{-1}; the symmetric stretching fundamental, ν_1, at 843 cm^{-1}, and the asymmetric stretching vibration, ν_3, at 855 cm^{-1}. Warm-up behavior and isotopic substitutions are consistent with the assignments.

The use of a CO matrix has shown that H atom photodetachment is an important step in the photolysis process, whereas little or no F atom fragmentation occurs.

Numerous infrared bands not attributable to SiF_2 are observed. Some can be assigned to dimers or aggregates, others to unreacted precursors. Some, however, remain unexplained.

SrF_2

The infrared spectrum of SrF_2 in argon at 4.2°K shows a moderately strong doublet absorption with components at 447 and 450 cm^{-1}, and much weaker bands at 303 and 356 cm^{-1} (Snelson, 66). The latter bands are assigned to aggregates. The doublet nature is also retained in neon and krypton, appearing at 468, 471, 443 cm^{-1}, respectively. High resolution ^{86}Sr and ^{88}Sr isotope studies by Calder, et al. (69) of SrF_2 in krypton at 20°K have led to the assignment of the doublet components near 440 cm^{-1} to the two stretching fundamentals. The band at 443 cm^{-1} corresponds to ν_2 and the band at 441 cm^{-1} to ν_1. In addition, the bending mode, ν_2, is observed at 82 cm^{-1}. The observed isotope shifts lead to a calculated apex angle of 108°. Aggregate bands appear, in krypton, at 75 and 120 cm^{-1}.

TaO_2

The molecule TaO_2 has been observed in neon and argon matrices at 4.2 and 20°K following vaporization of tantalum oxide at 2270°K or via reaction of oxygen with tantalum metal at 2270°K (Weltner, 65a).

TaO_2 shows two absorptions in the visible part of the spectrum. In neon, a strong system of bands originates at 861 nm and a second, weaker series of bands appears at 616 nm. The former transition, designated A, consists of a progression of bands with a vibrational spacing of 285 cm^{-1}. The short wavelength portion of the system is overlapped by a second progression starting at 797 nm with the same vibrational frequency. The shift between the progressions is 927 cm^{-1}. In argon, much of the structure is lost and the bands appear broad. The principal progression frequency of 285 cm^{-1} corresponds to ν''_2, the upper state bending frequency. The system shows a long Franck-Condon envelope indicating a significant change in angle in the upper state. The second progression has been assigned as $(1,v''_2,0)$, $(0,0,0)$ giving a value for ν'_1 of 937 cm^{-1}. The second system, designated B, also shows a progression in v'_2 with a spacing of 281 cm^{-1}. Because it is significantly weaker, ν'_1 is not observed.

The ground state vibrational frequencies $\nu''_1 = 971$ and $\nu''_3 = 912$ cm^{-1} have been determined by infrared analysis of the same system. The assignments were made on the basis that the upper state frequency, $\nu'_1 = 937$ cm^{-1}, is normally smaller than the ground state frequency, ν''_1. This results in ν''_1 being greater than ν''_3, a situation, which in light triatomics almost never occurs. Thus, these assignments are tentative.

A molecular orbital scheme somewhat similar to Walsh's (53a,b) treatment for BAB molecules has been used to derive the term symbols for the ground state and the lowest allowed transitions. The ground state is suggested to be $^2B_1$ and the observed transitions may involve the upper states $^2A_1$ (2) and/or $^2A_2$.

<u>WO_2</u>

Vaporization of either yellow WO_3 or blue $WO_{2.96}$ at 1600°K or the reaction of oxygen with tungsten at 1900-2950°K yields several tungsten oxide species including WO_2 in sufficient yields for direct spectral observations in neon or argon matrices at 4.2 and 20°K (Weltner, 65b).

Two electronic transitions of WO_2 are observed in the visible. A strong system A, originating at 1.267 μm^{-1} and a weaker system, B, with an origin near 1.280 μm^{-1} both show long progressions in v'_2, of the upper state. The A system also shows a simultaneous progression in v'_1. The observed vibrational frequencies for the system A are $\nu'_1 = 972$ and $\nu'_2 = 300$ cm^{-1}, while the ν'_2 frequency of the B transition is 287 cm^{-1}. Isotope shifts with ^{18}O have been used to aid the analysis. The extended v'_2 progression leads to the conclusion that the upper state molecular angle differs significantly from that of the ground state. The transitions are assigned as $A(^3B_1) \quad X(^3A_1)$ and $B(^3B_2) \quad X(^3A_1)$,

Infrared observations on tungsten oxide deposits give several bands in the region 600-110 cm^{-1}. Of these, bands appearing at 928 and 992 cm^{-1} have been assigned to ν''_3 and ν''_1 respectively of the ground state WO_2 molecule. These assignments are consistent with the observed ^{18}O substituted isotope shifts. Most of the remaining bands have been assigned to higher oxides such as W_2O_4, W_3O_9, W_4O_{12}.

$XeCl_2$

Nelson and Pimentel (67a) report the preparation and isolation of the species $XeCl_2$ in sufficient quantities to record a complex infrared band assigned to ν_3 of the species. The band appears as a broad structured feature near 313 cm^{-1}. The observed absorption can be fitted closely with a calculated spectrum based on the available xenon and chlorine isotopes. The species is concluded to have a D_{oh} symmetry. No additional data on the molecule is available, therefore the identification should be regarded as tentative.

XeF_2

Photolysis of fluorine, xenon, argon mixtures at 20°K with the full light of an AH-4 medium pressure mercury lamp give sufficient XeF_2 for the observations of two of the three infrared fundamentals (Turner, 63a). A weak band at approximately 510 cm^{-1} assigned to ν_1 and an intense absorption at 547 cm^{-1} assigned to ν_3 are observed. At an F_2:Xe ratio of 5:1, evidence for the formation of XeF_4 is obtained.

$ZnBr_2$, $ZnCl_2$, ZnF_2, and ZnI_2

The infrared spectra of all the zinc halides have been investigated at 4.2 and 20°K in argon, krypton, and xenon matrices (McNamee, 62; Loewenschuss, 68). Each of the species, ZnF_2, $ZnCl_2$, $ZnBr_2$ and ZnI_2 can be vaporized directly from a Knudsen furnace, however, monomer yields appear to be greatest with a double furnace arrangement. Direct observations of ν_2 and ν_3 have been made.

Table III

Observed Infrared Frequencies for the Zinc Dihalides in Krypton (in cm^{-1})

	ν_2	ν_3
ZnF_2	151	758
$ZnCl_2$	103	508
$ZnBr_2$	73	404
ZnI_2	62	346

Bands attributable to dimers are also observed. The latter are found to depend significantly on the vaporization conditions. The bands assignable to monomers all show the multiplet structure expected from the natural isotopic abundance of Zn isotopes. In addition, splittings appropriate for ^{35}Cl, ^{37}Cl isotopes are observed. A band at 425 cm^{-1} for $ZnCl_2$ has been assigned to the ν_{12} vibration of the dimer (McNamee, 1962) assuming a D_{2h} symmetry for the species with two chlorine-bridge bonds between the zinc atoms.

Several other bands also appear in the spectra. These are in the range 450 cm^{-1} for ZnF_2 to 170 cm^{-1} for ZnI_2. Bands at 334 cm^{-1} and 297 cm^{-1} for $ZnCl_2$ have also been tentatively assigned to dimer frequencies, ν_9 and ν_{11} respectively.

All data are consistent with a linear structure for all the halides. Thermodynamic properties have been computed from the data (Loewenschuss, 68).

Part II

Tables of the Optical Properties of Matrix-Isolated Tri- and Polyatomic Molecules

Summarized in the following tables are the important optical features as observed in low temperature matrices. The data is as presented in the original references. Values are tabulated for one matrix only. Molecules are entered alphabetically by formula, with all triatomics presented first, followed by tetratomics, pentatomics, etc. The molecular formula is entered on the left.

Units are chosen, where possible, in accordance with the SI rules. Wavelengths are given in nanometers, nm, and frequencies in reciprocal micrometers, μm^{-1}. The latter is equal to 10^4 cm^{-1}. In exception to the SI rules, the wavenumber, cm^{-1}, has been retained for vibrational frequencies and the torr for pressures. The former is used because of its unanimous usage for this purpose and the latter because of instrumentation.

The states are listed in order of energy with the highest observed level first. The state description is given where known or proposed.

The origin energy, T_{00}, is the energy as determined from the position of the (0,0) band.

Under Observed Transitions, IR indicates infrared observations. For ultraviolet and/or visible results, the entry indicates whether the data is from absorption or emission or both. The spectral wavelength range of the transition is given when reported.

The fundamental vibrational frequencies are given under vibrational frequencies and are as observed in matrices. The matrix for which the values apply is identified under Remarks, if not otherwise obvious. The Herzberg (45) scheme for numbering vibrations is used. Polyatomic frequencies are identified when known.

Parentheses are used to designate uncertain, calculated or proposed data. The remaining table entries are self explanatory.

TRIATOMICS

Molecule	State	$T_{00}(\mu m^{-1})$	Observed Transition	Vibrational Frequencies(cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
Al_2O	X	0	IR	715	(238)	994	argon; ν_2 calc. overtone at $1867cm^{-1}$; ^{18}O	Ar	4.2	$Al + Al_2O_3$ 1465°K	Linevsky 64
BO_2	$B^2\Sigma_u^+$	2.14	B ← X				2 bands only	Ar	4.2	vaporization $ZnO_{(s)} + B_2O_3$ 1825°K	Sommer 63
	$A^2\Pi_u$	1.79	A ← X 400-565nm	930	465	2400	^{11}B				
	$X^2\Pi_g$	0	IR			1276	^{11}B; $^2\Pi_{1/2}$ may be frozen out; excess B_2O_3 masks low frequency region				
BaF_2	X	0	IR	390	(64)	413	krypton; polymer peak at $325cm^{-1}$ ν_2 calc.	Ne Ar Kr	4.2 20	vaporization 1475-2125°K	Calder 69 Snelson 66
$BeBr_2$	X	0	IR	(230)	207	993	neon; ν_2 not observed in argon polymer bands at 570 and 760 cm^{-1}; ν_1 calc.	Ne Ar	4.2	vaporization 975°K	Snelson 68
$BeCl_2$	X	0	IR	(390)	238	1122	neon; dimer bands at 870, $640cm^{-1}$; ν_1 calc.	Ne Ar Kr	4.2	vaporization 725-1275°K	Snelson 66,68
BeF_2	X	0	IR	(680)	330	1542	neon; aggregate bands at 790, 830 and 1250 cm^{-1}; ν_1 calc.	Ne Ar Kr	4.2	vaporization 875-1275°K	Snelson 66

Triatomics (continued)

Molecule	State	$T_{00}(\mu m^{-1})$	Observed Transition	Vibrational Frequencies (cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
BeI_2	X	0	IR	(160)		872	neon; ν_3 doublet ν_1 calc.	Ne Ar	4.2	vaporization 975°K	Snelson 68
C_3	$A^1\Pi_u$	2.46	A ↔ X 380-408nm	1125	305	(840)	neon; ν_3 tentative	CO_2 Ne N_2 SF_6 Ar O_2 Kr Xe	4.2 20	carbon vapor	Barger 62,64, 65 Brabson 65 Weltner 62b,64a 64b,66
	$a^3\Pi_u$	1.71	a → X				neon; excited via A ← X at 405 or 365nm				
	$X^1\Sigma_g^+$	0	IR	1235	(75)	2040	neon; average ν_2				
C_2H		0	IR		(1848)		no assignment; ^{13}C,D	Ar	14	vacuum UV photolysis of C_2H_2	Brabson 65 Milligan 67
CCO	?	(2.00)	? ← X (500nm)				broad, unstructured continuum	Ar N_2	4.2	1) C, from vacuum ultraviolet photolysis of N_3CN, + CO 2) vacuum ultraviolet photolysis of C_3O_2	Jacox 65b
	$X^3\Sigma$	0	IR	1978	381	1074		Ar	14		
CBr_2	X^1A_1	0	IR	595		641	numerous, other species present; ν_2 probably <200cm-1	Ar	15	Li + CBr_4	Andrews 68c
CClBr	X	0	IR	739		612	ν_2 not observed	Ar	15	1) Li+$CClBr_3$ 2) Li+CCl_3Br	Andrews 68c

Triatomics (continued)

Molecule	State	$T_{00}(\mu m^{-1})$	Observed Transition	Vibrational Frequencies(cm^{-1}) v_1	v_2	v_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
CCl_2	$A(^1A_1$ or $^1B_1)$	(1.78)	A ← X 440-560nm		305		16 bands, prog. in v_2	Ar N_2	14 15	1) C, from photolysis of $N_3CN + Cl_2$ 2) $Li+CCl_4$	Andrews 68b,e Milligan 67c
	X^1A_1	0	IR	720		746	most abundant species; CCl_4, CCl_3 and other impurities present				
CF_2	$A(^1A_1)$	3.74	A ← X 230-268nm		500		single prog. in v_1; 16 bands observed	Ar N_2 CO CO_2	4.2	1) discharge through C_4F_8 in Ar 2) photolysis of CF_2N_2 3) photolysis of F_2, N_3CN and argon or N_2 mixtures	Bass 62 Milligan 64c, 68a
	X^1A_1	0	IR	1222	668	1102	^{13}C; "impurities" present: $CF_2N_2CF_2$, C_2F_4, CF_4, CF_3, C_2F_6, $(CF_2N)_2$				
CHCl	A^1A''	(1.25)	A ← X 560-750nm		860		argon; several perturbations	Ar	14	C from N_3CN photolysis + HCl	Jacox 67b
	X^1A'	0	IR		1201	815					
CHF	A^1A''	1.73	A ← X 470-546nm		1010		argon; 0,0,0 not observed; progression $(0,v_2',0)$ matrix shift ~ $+30cm^{-1}$	Ar N_2	14	photolysis of CH_3F	Jacox 69a
	X^1A^1	0	IR		1405	1182	bands at 2918 or 3262 may be v_1 ^{13}C,D				

Triatomics (continued)

Molecule	State	$T_{00}(\mu m^{-1})$	Observed Transition	Vibrational Frequencies(cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
CH_2							indirect chemical evidence only				DeMore 58 Goldfarb 60a,b Jacox 63a Milligan 58, 62a,67d Moore 64,65 Robinson 60a
CHO	B^2A'	3.87	B ← X 210-260nm		1375	1035	hydrocarbon flame bands; origin not observed	CO	14	1) photolysis of HI, HBr or H_2S in CO 2) discharge through $CH_4/O_2/Ar$ mixtures 3) reaction of O atoms with C_2H_2	Ewing 60 McCarty 59b Milligan 64e, 69a Robinson 58b
	$A^2A''(\pi)$	(0.93)	A ← X 510-670nm		(800)						
	X^2A'	0	IR	2488	1090	1861	1937, 852 and 1800 cm^{-1} for DCO; ^{13}C,D				
CNN	?		? ← X 419-396nm			1355	2 bands	Kr Ar N_2		1) photolysis of N_3CN 2) photolysis of C_3O_2 in N_2 3) photolysis of CH_2N_2	Goldfarb 60b Milligan 65d, 66a Moll 66a Robinson 60a Schoen 66 Weltner 64b, 66
	$X^3\Sigma^-$	0	IR	2847	393	1241	^{13}C, ^{15}N	Ar	14		
COS		6.74	? ← X 115-145nm			(760)	krypton; Rydberg like; mode not assigned;	Ne Ar Kr CO N_2 CS_2 COS	2 80°	1) direct deposition 2) photolysis of S_2Cl_2 in CO	Roncin 69 J. Smith 68c Venderame 66
		5.96	? ← X		(495)		krypton				
		5.54	? ← X		511		argon; 15+ bands				
	$X^1\Sigma^+$	0	IR	2050	518	857	ν_3 argon; ν_1 and ν_2 pure solid				

Triatomics (continued)

Molecule	State	T_{0} (μm^{-1})	Observed Transition	Vibrational Frequencies (cm^{-1})			Remarks	Matrix	Temp. (°K)	Preperation	Reference
				ν_1	ν_2	ν_3					
CS_2		6.60	? ← X 135-152nm		(540)		neon; mode not assigned; 1st band; origin not clear; Rydberg series surpressed	Ar Kr Xe Ne N_2 CH_4	2 20	direct deposition	Bajema 70 Roncin 69
	($^1B_2$)	3.10	? ← X 290-330nm	560			argon; simultaneous progressions in v_1' and v_2' Renner-Teller splittings				
	($^3B_2$)or($^3A_2$)	1.82	? → X				two lifetime components τ_1 = 0.8msec; τ_2 = 2.6msec in argon				
	$X^1\Sigma_g^+$	0									
CaF_2	X	0	IR	485	163	554	krypton; dimer bands at 528cm^{-1}, 370 cm^{-1}; ^{40}Ca, ^{44}Ca	Ne Ar Kr	4.2 20	vaporization 1675 - 2175°K	Calder 69 Snelson 66
$CdBr_2$	$X^1\Sigma_g^+$	0	IR	(205)	62	319	dimer band at 270 cm^{-1}; polymers at 190 163 cm^{-1}; ν_1 calc.	Kr	4.2 20	vaporization	Loewenschuss 69
$CdCl_2$	$X^1\Sigma_g^+$	0	IR	(327)	89	420	krypton; ν_3 quartet; dimers at 371, 364 and 357 cm^{-1}; ν_1 calc.	Ar Kr Xe	4.2 20	vaporization	Loewenschuss 69 McNamee 62

Triatomics (continued)

Molecule	State	$T_{00}(\mu m^{-1})$	Observed Transition	Vibrational Frequencies(cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
CdF_2	$X^1\Sigma_g^+$	0	IR	(572)	123	662	polymer bands at 475, 384, and 377 cm^{-1}; ν_1 calc.	Kr	4.2 20	vaporization	Loewenschuss 69
CdI_2	$X^1\Sigma_g^+$	0	IR	(150)		270	dimer bands at 222, 217 cm^{-1}; polymers at 140, 127 cm^{-1}; ν_1 calc.	Kr	4.2 20	vaporization	Loewenschuss 69
Cl_3	X	0	IR	(273)		374	group of bands between 365-275 cm^{-1} ^{35}Cl, ^{37}Cl ν_1 calc. linear, slightly asymmetric	Kr	20	discharge thru Kr and Cl_2	Nelson 67b
ClCO	X	0	IR	1880	281	570	possible C-O triple bond ^{13}C	Ar	14	Cl sources HCl, Cl_2, Cl_2CO, $(ClCO)_2$	Jacox 65a
ClClO	X	0	IR	960		372	quartets; ^{18}O isotope shift smaller than expected	N_2	20	photolysis of Cl_2O in N_2	Rochkind 67b
ClO_2	$A(^2A_2)$	(2.30)	A ← X 300-430nm				diffuse	isopentane-methylcyclohexane	77	solutions	Arkell 67 Norman 55 Rochkind 67b
	X^2B_1	0	IR	940	448	1100	ν_1 and ν_2 appear as quartets	Ar	4.2	direct deposition	

Triatomics (continued)

Molecule	State	T_{00} (μm^{-1})	Observed Transition	Vibrational Frequencies (cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
ClOO	X	0	IR	1441	407	373	argon, O^{18}	N_2 O_2 Ar	4.2	1) photolysis of Cl_2 and O_2 mixtures 2) photolysis of OClO in Ar, N_2, O_2	Arkell 67 Rochkind 67b
$CoCl_2$	?	(4.58)	? ← X					Ar	4.2	vaporization	Clifton 69
	?	4.16	? ← X				broad band	Kr	14		DeKock 68 Jacox 69b
	?	(3.95)	? ← X					Xe			K. Thompson 68
	?	(3.64)	? ← X				shoulder				
	?	3.50	? ← X 286nm				single band				
	?	3.37	? ← X 290-320nm	233							
	?	(3.20)	? ← X								
	?	(3.08)	? ← X								
	X($^4\Phi_g$)	0	IR		95	493	most abundant species; linear				
$CrCl_2$	?	3.85	? ← X 260nm down				strong; continuous below 260nm; gas phase bands at 3.62 and 4.96 μm^{-1} not observed;	Ar	14	1) vaporization 2) reaction of Cl_2 with hot Cr 1035-1095°K	Jacox 69b
	?	3.26	? ← X				weak, unstructured				
	X	0	IR			490	most abundant species; linear				
FCO	A	(3.00)	A ← X 220-340nm				43 bands; 18 appear in progression(ν_1', 0,0) ^{13}C, ^{18}O	Co Ar	4.2 14 20	1) F +CO F from NF_2, OF_2, t-N_2F_2 2) photolysis of F_2CO and HFCO	Milligan 65b
	X^2A_1	0	IR	1855	626	1018					

Triatomics (continued)

Molecule	State	T_{00} (μm^{-1})	Observed Transition	Vibrational Frequencies (cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
FNC, BrNC, ClNC							see text				Milligan 67b
$FeCl_2$	?	(4.76)	? ← X				Jacox 69 reports 4.16 superimposed on increasing continuum only; band maxima	Ar	4.2 14	1)vaporization 2)reaction of Cl_2 with hot Fe (1085°K)	DeKock 68 Jacox 69b K. Thompson 68
	?	(4.41)	? ← X								
	?	(4.16)	? ← X 240nm								
	?	(3.98)	? ← X 250 down								
	?	(3.75)	? ← X								
	$X^5\Delta_g$	0	IR		88	493	most abundant species; linear; strong N_2 shift of ν_3 to 447 cm^{-1}				
GeF_2	X^1A_1	0	IR	685	(263)	655	neon; strongest component; from gas phase; bands at 800 cm^{-1} due to GeF_4; bands at 600cm^{-1} and 670cm^{-1} due to dimers or polymers	Ne Ar	4.2	vaporization at 425°K	Hastie 68
HCN	X	0	IR	3303	720	2093	argon; dimer bands at 3301, 3202, 2114 2090, 797, 792, and 732cm^{-1}; greatest isolation in N_2	Ar N_2 CO	4.2 20	1)direct deposition 2)photolysis of diazomethane	Becker 56 C. King 68 Moore 65
H_2O	X	0	IR	3619	1590	3733	argon; free or nearly free rotation; complex bands; D	Ne Ar Kr Xe N_2 CO_2	4.2 to 27	direct deposition	Catalano 59 Glasel 60 Harvey 68 Hopkins 68 Jacox 61 Redington 62,63 D. Robinson 63

Triatomics (continued)

Molecule	State	T_{00}(μm^{-1})	Observed Transition	Vibrational Frequencies(cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
HCl_2	X	0	IR	(260)		696	ν_1 from (ν_1 + ν_2) at 956cm^{-1}; proposed $D_{\infty h}$	Ar	14	Discharge thru $HCl/Cl_2/Ar$ mixtures	Noble 68a
HNC	X($^1\Sigma^+$)	0	IR	3620	477	2029	presence of N_2 in neighboring site perturbs the normal modes. values shift to 535,2032, and 3583 in Ar when significant amounts of N_2 are present	Ar N_2	4.2 14	1) vacuum UV photolysis of HCN 2) photolysis of CH_3N_3	Milligan 63c, 67b
HNF	A^2A'	2.03	$^2A' \leftarrow {}^2A''$ 390-500nm		1033		progression in v_2	Ar	14	reaction of F atoms with NH; F from photolysis of N_2F_2 or F_2; NH from HN_3	Jacox 67a
	X^2A''	0	IR		1432	1000	D, ^{15}N				
HNO	A^1A''	1.31	A ← X 575-760nm		1422	982	argon progression in $v_2' + v_3'$	Ar N_2O CO_2	4.2 14 20	1) discharge thru $N_2H_4/O_2/H_2O/Ar$ 2) photolysis of CH_3NO_2 or CH_3ONO 3) discharge thru $Ar/H_2/NO$ 4) photolysis of HN_3 in CO_2 or N_2O	H. Brown 58 Harvey 59 McCarty 59b Milligan 62c Robinson 57a, 58a,b,d
	X^1A'	0	IR	(3592)	1570	1110	argon angle ~110° disagreement regarding ν_1				
HNSi	X	0	IR	3583	523	1198	linear; possible singlet ground state; D	Ar	4.2	photolysis of SiH_3N_3	Ogilvie 66

Triatomics (continued)

Molecule	State	T_{00}(μm^{-1})	Observed Transition	Vibrational Frequencies(cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
HOBr	X	0	IR	3590	1164	626	natural isotopes; O^{18}, D; estimated angle 110°	Ar	4.2	photolysis of $Ar/HBr/O_3$	Schwager 67
HOCl	X	0	IR	3581	1239	729	natural isotopic species, O^{18}, D	Ar	4.2	photolysis of $Ar/HCl/O_3$ mixtures	Schwager 67
HOF	X	0	IR	3483	1393	884	N_2; complex bands in argon; D ^{18}O	N_2 Ar	14 20	photolysis of $F_2/H_2O/N_2$ or Ar mixtures	Noble 68b
HOO	X^2A''	0	IR	3414	1389	1101	argon; oxygens nonequivalent	Ar	4.2	H, from photolysis of HI or HBr + O_2	Milligan 63b, 64a
$HgBr_2$	$X^1\Sigma_g^+$	0	IR	(219)	73	294	dimer band at 286 cm^{-1}; polymer at 261cm^{-1}; ν_1 calc.	Kr	4.2 20	vaporization	Loewenschuss 69
$HgCl_2$	$X^1\Sigma_g^+$	0	IR	(348)	107	407	krypton; ν_3 triplet; unidentified band at 412 cm^{-1}; dimer at 402cm^{-1}; ν_1 calc.	Ar Kr Xe	4.2 20	vaporization	Leowenschuss 69 McNamee 62
HgF_2	$X^1\Sigma_g^+$	0	IR	(588)	172	642	ν_3 doublet; dimer bands at 586cm^{-1} other bands at 660, 384cm^{-1}; ν_1 calc.	Kr	4.2 20	vaporization	Loewenschuss 69

Triatomics (continued)

Molecule	State	T_{00} (μm^{-1})	Observed Transition	Vibrational Frequencies (cm^{-1})			Remarks	Matrix	Temp. (°K)	Preparation	Reference
				ν_1	ν_2	ν_3					
HgI_2	$X^1\Sigma_g^+$	0	IR	(158)	63	238	other bands at 229, 220, 234cm^{-1}; ν_1 calc.	Kr	4.2 20	vaporization	Loewenschuss 69
KrF_2	X	0			236	580	aggregate bands at 575 and 245cm^{-1}; bond strengths similar to XeF_2	Ar	20	photolysis of F_2/Kr/Ar mixtures	Turner 63a,b
Li_2O	X	0	IR	(685)	112	987	probably linear; ^{6}Li; ν_1 calc.	Kr	20	vaporization 1640°K	Seshadri 66 White 63b
LiON	X	0	IR	1352	333	650	molecular arrangement proposed LiON; ν_3 strongest band	Ar	15 4.2	codeposition of Li and NO	Andrews 66a,b
LiO_2	X	0	IR	(340)	231	685	best fit for C_{2v}; ν_1 calc.; angle = 170°	Kr	20	vaporization	Seshadri 66 White 63b
MgF_2		0	IR	478	242	837	krypton; ^{24}Mg, ^{25}Mg, ^{26}Mg; bands at 450 and 480cm^{-1} assigned to polymers; angle 158°	Ne Ar Kr	4.2 20	vaporization 1500-1575°K	Calder 69 Mann 67 Snelson 66

Triatomics (continued)

Molecule	State	$T_{00}(\mu m^{-1})$	Observed Transition	Vibrational Frequencies(cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
$MnCl_2$	?	5.00	? ← X				all bands broad,	Ar	4.2	1)vaporization	DeKock 68
	?	4.57	? ← X 250nm down				unstructured shoulder		14	2)reaction of Cl_2 with hot Mn surface 995-1085°K	Jacox 69b K. Thompson 68
	?	4.39	? ← X 228nm								
	$X^6\Sigma_g^+$	0	IR		83	477	most abundant species				
N_3	X	0	IR			(2150)	other bands at 962 and 737cm^{-1}; ^{15}N; identification uncertain; Peyron *et al.* propose an $\overline{N}$-N_2 complex	N_2	20	1)discharge thru nitrogen 2)photolysis of HN_3	Becker 57 Harvey 59 Milligan 56 Peyron 59a,b
NCN	$B^3\Sigma_u^-$	3.31	B ← X 340-300nm	1040			argon; photolysis with λ = 2500A	N_2 CO Ar	14 20	photolysis of N_3CN	Comeford 66 Milligan 65c,d 66c,69c Mall 66a Schoen 66
	$^1\Delta_g$	3.00	$^1\Delta$ ← X 335nm				mean lifetime 500 μsec in N_2				
	$^3\Pi_u$	2.99	Π ← X 300.....	1140			argon; structureless				
	$X^3\Sigma_g^-$	0	IR	1197	423	1475	$(\nu_1 + \nu_3)$ = 2672 ^{13}C, ^{15}N				

Triatomics (continued)

Molecule	State	$T_{00}(\mu m^{-1})$	Observed Transition	Vibrational Frequencies(cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
NCO	$B^2\Pi$	3.16	B ← X 400-450nm	2295		1036	neon (R_2); ~40 bands	Ne Ar N_2 CO	4.2 14	1)$CH_4/Ar/N_2/O_2$ discharge 2)vacuum UV photolysis HNCO 3)vacuum UV photolysis HN_3 in CO 4)C (from N_3CN) + NO 5)O (N_2O) + CN (from HCN)	McCarty 59b Milligan 67c Robinson 58b
	$A^2\Sigma^+$	2.28	A ← X 240-320nm	2325	687	1270	neon (Q); 5 bands				
	$X^2\Pi_1$	0	IR	1922	487	1275	considerable spin splitting ($A=956cm^{-1}$) transitions from $^2\Pi_{3/2}$ only at 14° K and below; large Renner splitting				
NH_2	$A^2A_1(\pi)$	1.02	A ← X 344-790nm	3350	680		T_e & ν_2' extrapolated; alternate bands; originates in $0''_o$. Π and B vibronic sub bands; ν_1' average value $b \sim 3cm^{-1}$	Ar Kr N_2	4.2 14	1)discharge thru N_2H_4/Ar 2)vacuum UV photolysis of NH_3 3)photolysis of HN_3	Keyser 60 Milligan 65e Robinson 57a, 58a,b,c, 59,62c
	X^2B_1	0	IR		1499	3220	possible free rotation in matrix				

Triatomics (continued)

Molecule	State	$T_{00}(\mu m^{-1})$	Observed Transition	Vibrational Frequencies(cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
N_2O	F	9.20	$F \leftarrow X$				observed only in argon	solid	1.5	direct deposition	DeMore 59a
	E	9.01	$E \leftarrow X$				Ne	Ne Ar	63		Granier-Mayence 53
	D	8.33	$D \leftarrow X$				Ne, continuous	Kr			Romand 52
	C	7.34	$C \leftarrow X$				Ne, continuous	N_2			Sibleyras 68
	B	(6.20)	$B \leftarrow X$		(590)		progression in v'_2; average spacing; origin not observed;				
	$A(^1\Sigma^+)$	(4.00)	$A \leftarrow X$				structureless $b=3600cm^{-1}$				
	$X^1\Sigma^+$	0	IR				in nitrogen; all transitions strongly blue shifted				
NO_2	B		$B \leftrightarrow X$ 300-470nm				N_2; diffuse	N_2 Ar	1.5 4.2	direct deposition	Bass 56 Becker 56
	$A(^2B_1)$	1.12	$\leftarrow X$ 340-700nm		(620)		argon; blue shifted from gas by 55-70cm^{-1}	O_2 CO_2 H_2	20		Broida 57b,58c DeMore 59a Fateley 59
	X^2A_1	0	IR	(1320)	750	1611	argon; numerous dimer bands	N_2O			Harvey 58 Peyron 59a Robinson 57a

Triatomics (continued)

Molecule	State	T_{00} (μm^{-1})	Observed Transition	Vibrational Frequencies (cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
$NiCl_2$	?	4.15	? ← X				very weak	Ar	4.2 14	1) vaporization, 675-800°K 2) reaction of Cl_2 with hot Ni surface at <1375°K	DeKock 68 Gruen 68 Jacox 69b Milligan 65a K. Thompson 68
	?	3.69	? ← X 265-290nm	283			extended progression				
	?	3.35	? ← X 290-325nm	249			extended progression				
	?	3.05	? ← X 330-370nm	256			extended progression				
	?	2.13	? ↔ X 440-470nm	350			3 parallel progressions				
	?	2.12	? ← X 470-500nm				featureless				
	?	2.02	? ← X 480-500nm				band separation $114 cm^{-1}$ (4 bands)				
	?	1.95	? → X 510-530nm								
	?	1.72	? → X								
	$X^3\Pi_g$	0	IR	360	85	521	most abundant species				
NiF_2	$X(^3\Pi)$	0	IR	(606)		780	most abundant species; peaks near 715 may be due to dimers; ν_1 calc.	Ar	14	vaporization 1075-1175°K	Milligan 65a
O_3	B	(1.90)	B ← X 400-670nm				first observed band	N_2 O_2 CO_2	4.2 20	1) direct deposition 2) discharge through O_2	Bass 58 DeMore 58 Harvey 58 Moll 66b
	X^1A_1	0	IR	1120	705	1050	O_2; overtones at 3060, 2800, 2150, 2110, and $2060 cm^{-1}$				
OCl_2	X	0	IR	631	296	671	pure solid ν_1 = 636 in argon; bent; ^{18}O	N_2 Ar pure sol.	20 77	direct deposition	Rochkind 65

Triatomics (continued)

Molecule	State	T_{00} (μm^{-1})	Observed Transition	Vibrational Frequencies (cm^{-1})			Remarks	Matrix	Temp. (°K)	Preparation	Reference
				ν_1	ν_2	ν_3					
OF_2	X	0	IR	812	461	926	nitrogen; ν_3 doublet; ν_2 from gas phase	N_2 Ar O_2	4.2 20	1) photolysis of F_2 and O_2 mixtures 2) direct deposition	Arkell 65a,b Spratley 66a,b
OOF	X	0	IR	1495	585	376	resembles O_2F_2; angle ~110°; ^{18}O	N_2 O_2 Ar	4.2 20	photolysis of OF_2/O_2 matrix or F_2/O_2 matrix mixtures	Arkell 65b Noble 66 Spratley 66b
PH_2	A^2A_1	1.82	A ← X 436-522nm	(2320)	930		origin not observed; ν_1 estimated;	Ar	4.2	discharge thru PH_3 argon mixtures	McCarty 59b
	X^2B_1	0					5 bands $(0,v_2',0)$, $(0,0,0)$				
SO_2	D	(4.23)	D ← X					Ne Ar Kr Xe CH_4 CD_4 SF_6 C_4F_4 N_2 O_2	4.2 to 110	direct deposition	Allavena 69 Conway 69 B. Meyer 68 Phillips 69a,b
	C	(4.15)	C ← X								
	A^1B_1	2.96	A ← X 280-310nm	(720)	(220)		Kr; origin not observed; 17 bands; frequency differences from first observed bands				
	a^3B_1	2.56	a → X 390-470nm				SF_6; lifetime 13.5 msec at 4.2°K in SF_6				
	X^1A_1	0	IR	1150	519	1351	Kr; ^{34}S; ^{18}O; Zeeman effect				

Triatomics (continued)

Molecule	State	$T_{00}(\mu m^{-1})$	Observed Transition	Vibrational Frequencies(cm^{-1})			Remarks	Matrix	Temp. (°K)	Preparation	Reference
				ν_1	ν_2	ν_3					
S_2O	A	2.90	A ← X	(720)	(286)	415	xenon; new origin, previous gas phase origin in error (see Herzberg 67) ν_1 estimated; ν_2 reevaluation of gas phase	Ar Kr Xe	20 77	$SOCl_2$/matrix gas + Ag_2S at 433°K	Blukis 64 Phillips 69a
	X^1A'	0	IR	1165	388	679	pure solid at 77°K				
ScF_2		(3.14)	(? ← X)	(580)			neon; tentative may be due to ScF_3	Ne	4.2	vaporization of ScF_3 1875°K	McLeod 66
	X	0	IR	(661)		(709)	not positively identified				
SeO_2	B	3.10	B ← X 240-322nm 310-520nm	(620)	(310)	com	complex absorption, possibly 2 transitions or 2 progressions in $(v_1', 0, 0)$ and $(v_1', 1, 0)$; resonance fluorescence	Ar Kr Xe SF_6 CH_4 C_4F_8	20	vaporization 409°K	Voigt 70
	?	>2.20	? ← X 320-410nm				weak absorption; may involve state C				
	C	2.20	C ← X 425-613nm				C is triplet state τ = <0.2 msec in Xe; 2.5 msec in SF_6; 2.0 msec in C_4F_8; excited at 365nm				
	X	0			365						
Si_3	$A(^3\Sigma_u^-)$	2.15	A ← X	310			7 bands; tentative	Ne	4.2	vaporization of silicon 2175-2675°K	Weltner 64c
	$X(^3\Sigma_g^-)$	0									

Triatomics (continued)

Molecule	State	$T_{00}(\mu m^{-1})$	Observed Transition	Vibrational Frequencies(cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
SiCC	$A^1\Pi_u$	2.01	$A^1\Pi_u \leftrightarrow X^1\Sigma^+$ 400-497nm 500-550nm	1461	230	1015	possible positive X'_{13} adsorption; fluorescence; little r_e change;	Ne Ar	4.2 20	vaporization 2775-3125°K	Weltner 64c
	$X^1\Sigma_g^+$	0	IR	1742	300	853	from fluorescence data ν_3 gas phase, 853cm-1				
SiCSi	$A^1\Pi_u$	1.89	A ← X 450-500nm	500			identification tentative;	Ne Ar	4.2 20	vaporization silicon carbide 2775-3125°K	Weltner 64c
	$X^1\Sigma_g^+$	0		(672)			calculated				
$SiCl_2$		0	IR	502		513	assignments tentative; may be reverse	Ar	14	vacuum UV photolysis of SiH_3Cl_2	Milligan 68c
SiF_2	A^1B_1	4.40	A ← X 213-226nm		253		neon	Ne Ar CO N_2	4.2 14 20	1)vacuum UV photolysis of SiH_2F_2 2)reaction of SiF_4 with Si at 1425°K	Bassler 66a Milligan 68d
	X^1A_1	0	IR	843	343	855	argon				
SrF_2	$X(^1A_1)$	0	IR	(441)	82	(443)	krypton apex angle 108° bands near 303 and $256cm^{-1}$ assigned to aggregates; ^{86}Sr, ^{88}Sr	Ne Ar Kr	4.2 20	vaporization 1625°K	Calder 69 Snelson 66
TaO_2	$B(^2A)$	1.62	B ← X 558-616nm		281		weak	Ne Ar	4.2 20	1)vaporization 2)reaction with hot tantalum (2270°K)	Weltner 65a
	$A(^2A)$	1.16	A ← X	937	285		progression in v_2'; also see $(1,v_2'0)$, (0,0,0)				
	$X(^2B_1)$	0	IR	(971)		(912)	assignment based on a decrease from $\nu'_1 \leftarrow \nu''_1$				

Triatomics (continued)

Molecule	State	$T_{00}(\mu m^{-1})$	Observed Transition	Vibrational Frequencies (cm^{-1}) ν_1	ν_2	ν_3	Remarks	Matrix	Temp. (°K)	Preparation	Reference
WO_2	$B(^3B_2)$	1.28	B ← X		287		neon	Ne Ar	4.2 20	1)vaporization WO_3 or $WO_{2.96}$ 1600°K 2)reaction of O_2 with tungsten at 1900-2950°K	Weltner 65b
	$A(^3B_1)$	1.27	A ← X	972	300		neon; ^{18}O; extended progression in ν'_2				
	$X(^3A_1)$	0	IR	992		928	neon; ^{18}O; numerous IR absorptions between 600-1000cm^{-1} assigned to higher oxides				
$XeCl_2$	X	0	IR			313	complex absorption due to Xe isotopes	Xe	20	Xe + Cl_2 through microwave discharge	Nelson 67a
XeF_2	X	0	IR	(510)		547	high F_2:Xe ratios give XeF_4	Ar	20	photolysis of F_2 in Xe	Turner 63a
$ZnBr_2$	$X^1\Sigma_g^+$	0	IR		73	404	most abundant species in Kr; band at 326 assigned to dimers	Ar Kr Xe	4.2 20	vaporization	Loewenschuss 68 McNamee 62
$ZnCl_2$	$X^1\Sigma_g^+$	0	IR		103	508	most abundant species in Kr; bands at 425, 334 and 297 assigned to dimers	Ar Kr Xe	4.2 20	vaporization	Loewenschuss 68 McNamee 62
ZnF_2	$X^1\Sigma_g^+$	0	IR		151	758	most abundant species in Kr; band at 665 assigned to dimer	Ar Kr Xe	4.2 20	vaporization	Loewenschuss 68 McNamee 62
ZnI_2	$X^1\Sigma_g^+$	0	IR		62	346	most abundant species in Kr; band at 272 assigned to dimer	Ar Kr	4.2 20	vaporization	Loewenschuss 68 McNamee 62

Tetratomics

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies(cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
AlF_3	X	0	IR	300 (ν_2) 965 (ν_3) 270 (ν_4)		Ne Ar Kr	4.2	vaporization of AlF_3(s) at 1150-1875°K	Snelson 67b
$(BO)_2$	X	0	IR	1921 (ν_3)	multiplet	Ar	4.2	vaporization of B_2O_3 + B 1450-1500°K	Sommer 63
CBr_3	X	0	IR	582 (ν_1) 773 (ν_3)	ν_2 and ν_4 not observed	Ar	15	reaction of Li atoms with CBr_4	Andrews 68c
CCl_3	X	0	IR	674 (ν_1) 898 (ν_3)	ν_2 and ν_4 not observed	Ar	15	reaction of Li atoms with CCl_4	Andrews 67d 68a,e
CF_3	X	0	IR	1087 (ν_1) 703 (ν_2) 1251 (ν_3) 512 (ν_4)	^{13}C; other bands observed	Ar	14 20	photolysis of CF_2N_2/ and $\underline{t}N_2F_2$	Comeford 66 Milligan 66b, 68a
CF_2N	$A(^2A_1)$	2.76	$^2A_1 \leftarrow {}^2B_2$		fine structure	N_2 Ar	14	photolysis of FCN and t-N_2F_2	Jacox 68a
CF_2O	Π*	4.4	n→Π*		$(FCO)_2$ also produced; continuous absorption	CO	4.2	photolysis of OF_2, N_2F_2 or $\underline{t}N_2F_2$ in CO matrix	Milligan 65b
	X	0	IR	585 620 1913 1941					

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies(cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
CH_2F	X	0	IR	996 1163 (C-F)	argon; assignments tentative	Ar N_2	14	photolysis of CH_3F	Jacox 69a
CH_2N	X	0	IR	1338	uncertain	Ar	14	photolysis of HCN	Milligan 67b
CH_2O	A'A"	2.82	A→X 360-540nm		progression in v_2", v_4" and v_6"	Xe Kr SF_6 N_2	4 to 200	direct deposition	Harvey 62 J. Smith 69
	a^3A"	2.44	a→X 410-460nm		τ = 1.1 sec in Kr				
	X^1A_1	0	IR	2796 (ν_1) 1742 (ν_2) 1498 (ν_3) 2862 (ν_4) 1245 (ν_5) 1168 (ν_6)	argon; ν_1, ν_2, ν_4, ν_6 triplets	pure solid			
CH_3	?	6.65	?←X		D; planar	N_2 Ar CO	14	photolysis of CH_4 and reaction of CH_2X with Li atoms	Andrews 66b, 67b Milligan 67d
	X	0	IR	611 (ν_2) 730 (ν_2) 1383 (ν_3)	ν_3 not observed				
CO_3	X	0	IR	568 593 972 1073 1880 2045 3105 3922	probably planar C_{2v} with one carbonyl bond	4.2 50 77		1) photolysis of CO_2 2) photolysis of O_3/CO_2 mixtures 3) condensation of discharged CO_2	Moll 66
$(ClO)_2$	X	0	IR	951	multiplet	N_2	20	photolysis of Cl_2O	Alcock 68 Rochkind 67b

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies(cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
FNCN	X	0	IR	873 2068	^{13}C, ^{15}N	Ar	14	photolysis of $N_2CN{:}F_2$	Milligan 68b
$(HBr)_2$	X	0	(IR)	2433 2469 2500		Ar	83 103	from liquid solutions	Atwood 67
$(HCl)_2$		0	IR	232	argon, D	Ne Ar Kr Xe	4.2 20 103	deposition of HCl	Katz 67b Keyser 66b
HNCO	X	0	IR	460 (OCN) 1098 (OC) 1241 (OH bend) 2294 (C-N) 3506 (O-H)	N_2 D	N_2 Ar	14	vaporization of cyanuric acid	Jacox 64b
HNCS	X	0	IR	3505 (ν_1) 1979 (ν_2) 988 (ν_3) 577 (ν_4) 461 (ν_5)	D	Ar	20	direct deposition	Durig 67
HNF_2	X	0	IR	877 1425 1313	Decrease with prolonged photolysis	Ar	14	photolysis of $HN_3/F_2/Ar$	Jacox 67a
HN_3	X	0	IR	3324 (ν_1) 2150 (ν_2) 1273 (ν_3) 1168 (ν_4) 527 (ν_5) 588 (ν_6)	dimer		20	direct deposition	Pimentel 66

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies(cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
H_2O_2	X	0	IR	3417 (ν_1) 3578 (ν_5) 1292 (ν_6)	tentative overtone at 2750 several other unassigned bands	N_2	4.2	direct deposition	Catalano 63b
Li_2F_2	X	0	IR	($^7Li_2F_2$) 641 (B_{3u}) 553 (B_{2u}) 287 (B_{1u})	^6Li	Ne	20	vaporization of Li at 1175-1475° K; direct deposition F_2	Snelson 67a
NH_3	$A(^1A_2'')$	5.25	A ← X		fine structure; dimers; D	Ar N_2 CO_2	4.2 20 53	direct deposition	Dressler 60 Jacox 63b Milligan 61a Pimental 62a
	X	0	IR	3332 (ν_1) 970 (ν_2) 3440 (ν_3) 1632 (ν_4)	N_2				
$(NO)_2$	X	0	IR	1776 1865	argon; cis; trans	Ar NO	4.2	deposition of NO	Fateley 59
NO_3	?	1.60	? ← X 629nm		weak; diffuse bands; band maxima	N_2	20	1) NO_2 + O 2) photolysis of N_2O_5 3) discharge thru NO_2/O_2 mixtures	DeMore 59a
	?	1.50	? ← X 666nm						
	X	0							
N_2H_2	X	0	IR	1279 3074 1286 (ν_5) 1481 (ν_2)	ν_3 preferred; cis; ν_1 or ν_4; cis; trans trans	N_2	20	photolysis of HN_3	Rosengren 65

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies(cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
O_2F_2	X	0	IR	624 612 462 368		N_2 Ar O_2	20	photolysis of F_2 and O_2	Spratley 66a, b
$SiCl_3$	?	4.08	$? \leftarrow X$		unstructured	N_2 Ar CO	14	photolysis of $HSiCl_3$	Jacox 68b
	?	3.03	$? \leftarrow X$						
	X	0	IR	470 (ν_1) 582 (ν_3)	argon; ^{29}Si; ^{30}Si				
$(SiC)_2$	($^3\Sigma^-$)	1.54	$? \leftarrow X$			Ne Ar	4.2 20	vaporization of SiC(s) at 2600°K	Weltner 64c
	X	0	IR	595(Si=Si st) 657(C=Si st) 994(C=C st) 1967(C=C st)	argon; additional unassigned bands				
SiF_3	X	0	IR	832 (ν_1) 406 (ν_2) 954 (ν_3) 290 (ν_4)	argon; non planar; ^{29}Si, ^{30}Si	Ar N_2 CO	14	photolysis of $SiHF_3$	Milligan 68e
WO_3	A	3.46	$A \leftarrow X$	894 (A'_1)	neon; tentative	Ne	4.2	1)vaporization of WO_3 or $WO_{2.96}$ at 1600°K 2)reaction of O_2 with tungsten at 1900-2950°K	Weltner 65b
	X	0	IR	1040(E')					

PENTATOMICS

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies(cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
B_2O_3	X	0	IR	2128 (ν_1) 733 (ν_2) 536 (ν_3) 172 (ν_4) 260 (ν_4) 476 (ν_5) 2128 (ν_6) 1242 (ν_7) 471 (ν_8) 493 (ν_9)	$^{10}B_2O_3$; ^{11}B	Ar	4.2	vaporization 1400°K	Sommer 63 Weltner 62a
CBr_3Li	X	0	IR	462 (C-Br st) 377 (Li st)	^6Li	Ar	15	reaction of CBr_4 with Li atoms	Andrews 68d
CCl_3Li	X	0	IR	521 (C-Cl st) 429 (Li st)	^6Li	Ar	15	reaction of CCl_4 with Li atoms	Andrews 68d
$CHCl_3$	X	0	IR	2500	D; bands widened in matrix	Ar CS_2 CCl_4	20 77	deposition of vapor mixtures of $CHCl_3$ and $(C_2H_5)_3N$	Denariez 65 S. King 68 W. Thompson 60
CH_2CO	X	0	IR	3043 (ν_1) 2133 (ν_2) 1374 (ν_3) 1131 (ν_4) 3140 (ν_5) 971 (ν_6) 440 (ν_7) 616 (ν_8) 529 (ν_9)	D	Ar	20	photolysis of acetone	Moore 63

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies(cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
CH_2N_2	X	0	IR	3069 (ν_1) 2096 (ν_2) 1407 (ν_3) 1168 (ν_4) 3182 (ν_5) 1105 (ν_6) 420 (ν_7) 542 (ν_8) 427 (ν_9)	D, N^{15}	N_2 Ar	20		Moore 64a
CH_3Cl	X	0	IR		chlorine isotopic splitting patterns are determined	Ar	20	direct deposition	S. King 68
CH_3F		0	IR	1041 1463 2866 2972 3022	correlate with gas phase	Ar N_2	14	direct deposition	Jacox 69a
CH_3Li	X	0	IR	2780 (ν_1) 1158 (ν_2) 530 (ν_3) 2820 (ν_4) 1387 (ν_5) 409 (ν_6)	^{6}Li, D	Ar	15	reaction of CH_3X with Li atoms	Andrews 67b,c Tan 68
CH_4	X	0	IR	3037 (ν_3) 1306 (ν_4)	multiplets D	Ar Kr Xe	2 40	direct deposition	Cabana 63 Frayer 68
C_3O_2	X	0	IR	2282 (ν_3) 1594 (ν_4) 536 (ν_6)	linear symmetric; overtones	Ar	4.2 20	direct deposition	Ames 63 W. Smith 66

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies (cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
NF_2CN	X	0	IR	576 619 840 888 1021	^{13}C, ^{15}N	Ar	14	photolysis of $N_3CN:F_2$	Milligan 68b
N_2O_3	X	0	IR	788 1303 1596	solid	CO_2 solid	4.2	1) heating NO_2 2) $NO + NO_2$	Fateley 59
N_3CN	B	4.75	B ← X		broad band	Ar N_2 CO CO_2	14	direct deposition	Milligan 65d, 66c
	X	0	IR	444, 450 865, 923 1263, 2101 2151, 2163 2208, 2249	no definite assignments				
SiH_2Cl_2		0	IR	2210 948 877 584 523		Ar	14	direct deposition	Milligan 68c
SiH_2F_2		0	IR	980 972 863 714		Ar N_2	14	direct deposition	Milligan 68d, 68e

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies(cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
SiH_3Cl		0	IR	2198 945 663 544		Ar	14	impurity	Milligan 68c
SiH_3F		0	IR	890		Ar N_2	14	impurity	Milligan 68d, 68e
XeF_4	X	0	IR	290 (ν_2) 568 (ν_6)		Ar	20	photolysis of F_2/Xe/Ar mixtures	Turner 63a

OTHERS

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies(cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
CH_3LiBr	X	0	IR	730	Li, Na, K, Br, I	Ar	15	reaction of CH_3X with M atoms	Tan 68
CH_3OH	X	0	IR	3660 (OH st)	polymers	N_2	20	direct deposition	Van Thiel 57a
C_2Br_4	X	0	IR	595.0 (ν_1) 640.5 (ν_3)		Ar	15		Andrews 68c
$(HCN)_2$	X	0	IR	732 792 797 2090 2114 3202 3301	closely correlated to monomer peaks; D	Ar CO N_2	4.2 20	direct deposition	C. King 68
N_2H_4	X	0	IR	3390 (ν_1) 1312 (ν_4) 1087 (ν_5) 832 (ν_6) 394 (ν_7) 3356 (ν_8) 3297 (ν_9) 1265 (ν_{11}) 982 (ν_{12})	N_2	N_2 Ar	4.2	direct deposition	Catalano 63a
N_2O_4	X	0	IR	740 755 1258 (ν_1) 1738 (ν_9) 1767	argon; possible isomers	Ar CO_2	4.2	deposition of NO_2	DeMore 59a Fateley 59

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies(cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
$NbCl_5$	X	0	IR	444 (ν_3) 126 (ν_4) 396 (ν_5) 159 (ν_6) 99 (ν_7)	N_2	N_2 C_6H_{12}	5 to 10	vaporization	Werder 67
$CH_2(CN)_2$	X	0	IR	2264 (ν_2) 887 (ν_4) 573 (ν_5) 2272 (ν_9) 974 (ν_{11})	overtones	Ar	20	direct deposition	Ames 63
N_2O_5	X	0	IR	719 737 1248 1316 1700 1752	CO_2	CO_2 N_2	4.2 20	direct deposition deposition	DeMore 59a Fateley 59
Al_2F_6			IR	995 (ν_8) 340 (ν_9) 660 (ν_{13}) 805 (ν_{16}) 575 (ν_{17}) 300 (ν_{18})		Ne Ar Kr	4.2	vaporization of AlF_3(s) at 1150-1875°K	Snelson 67b
$(BF_3)_2$	X	0	IR	662 674 1410 1460 1515	correlated to monomer bands	Ar Kr	20 50		Bassler 66b

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies(cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
$(CH_3)_3N$	X	0	IR	1475 (ν_3)	D; C_{3v}	Ar	20	direct deposition	Goldfarb 67a
				1470 (ν_4)					
				1187 (ν_5)					
				823 (ν_6)					
				365 (ν_7)					
				1456 (ν_{15})					
				1440 (ν_{16})					
				1405 (ν_{17})					
				1098 (ν_{18})					
				1037 (ν_{19})					
				823 (ν_{20})					
				421 (ν_{21})					
				259 (ν_{22})					
$(CH_3)_2SiH_3N$	X	0	IR	2872(C-Hst)	multiplet	Ar	20	direct deposition	Goldfarb 67b
				2196(Si-Hst)	multiplet				
				1472(CH_3def)	multiplet				
				1295(CH_3rock)	multiplet				
				1187(C-Nst)					
				900(C-Nst)					
				990(Si-Nst)					
				965(SiH_3def)	multiplet				
				695(SiH_3rock)	multiplet; pyramidal				
$CH_3(SiH_3)_2N$		0	IR		planar	Ar	20	direct deposition	Goldfarb 67b
				2891(C-H st)	multiplet				
				2179(Si-Hst)	multiplet				
				1470(CH_3def)	multiplet				
				1200(CH_3rock)	multiplet				
				1091(C-N st)					
				986(Si-Nst)					
				923(SiH_3def)	multiplet				
				716(SiH_3rock)	multiplet				

Molecule	State	T_{00} (μm^{-1})	Observed Transitions	Vibrational Frequencies(cm^{-1})	Remarks	Matrix	Temp. (°K)	Preparation	Reference
$(SiH_3)_3N$	X	0	IR	2174 (ν_1) 2155 (ν_2, ν_{14}) 942 (ν_3) 921 (ν_4) 767 (ν_5) 454 (ν_7) 2193 (ν_{12}) 2186 (ν_{13}) 966 (ν_{15}) 955 (ν_{16}) 934 (ν_{17}) 734 (ν_{18}) 693 (ν_{19})	C_{3v}; overtones	Ar	20	direct deposition	Goldfarb 67a
$Fe(C_5H_5)_2$	F	5.00	F←X		strong; allowed, no structure.	Ar Kr Xe N_2 CH_4	20 —	vaporization 300°K	J. Smith 68a A. Armstrong 67
	E	4.05	E←X	400	cyclopentadienyl ring; perturbation at v' = 4.				
	D	3.50	D←X	250	iron ring vibration; charge transfer.	EPA	77		
	C	2.90	C←X	450	cyclopentadienyl ring.				
	B	2.50	B←X		3d-3d transition no structure.				
	A	2.00	A→X		τ = 1.25 sec. excited via C-X no structure.				
	X	0			all bands broad at 77°K				
$Eu(C_5H_5)_3$					complex hypersensitive line groups		4.2 77	frozen solution in 2-methyl-tetrahydro-furan	Pappalardo 68

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