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Lester Andrews

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LASER EXCITATION MATRIX-ISOLATION SPECTROSCOPY

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INTRODUCTION

Perhaps the most significant recent development in the field of matrix isolation spectroscopy has proven to be the laser-Raman matrix technique. The complementary use of both infrared absorption and Raman scattering spectroscopic methods provides more complete vibrational data for the large body of interesting molecular species which require matrix synthesis and stabilization. The laser-excitation technique offers several advantages over the infrared experiment: the possibility of laser photolysis to create new chemical species, the observation of resonance-Raman spectra which provides harmonic and anharmonic vibrational constants from overtone bands, and the possible observation of fluorescence from new chemical species. Specific experimental examples of complementary infrared and Raman studies, laser photolysis, resonance-Raman, and fluorescence spectra will be discussed.

In a recent review of infrared and Raman spectra of unique matrix-isolated molecules, this author discussed the complementary use of infrared and Raman techniques for investigating matrix-isolated species (1). As a matter of historical interest, the first laser-Raman spectrum of a matrix-isolated species at high dilution in an inert matrix was reported by Shirk and Claassen for SF_6 and CHCl_3 (2). Early laser-Raman matrix-isolation studies employing a variety of techniques to produce interesting chemical species have been described by Ozin (3). Nibler has also discussed some of the initial matrix-Raman experiments in his laboratory (4). This review will describe some of the previous studies in the author's laboratory and new results from the last two years of research. First, a few comments on the several experimental techniques will be presented.

EXPERIMENTAL

The details of infrared and Raman matrix isolation experiments have been described in several reviews (1,3,4) and manuscripts (5-7). Here, the sample deposition technique used for Raman studies will be discussed with particular attention to comparison with the infrared experiments.

Most laser-Raman matrix samples are deposited on tilted metal wedges from which the laser beam is scattered; OFHC copper, silver and aluminum are the most common block materials; near grazing angles of incidence of approximately 10° are commonly employed. Several major differences in infrared and Raman sample preparation are obvious. The infrared sample should be transparent to infrared radiation in general; deposition rates and window cleanliness are critical here; different deposition rates are sometimes required for producing transparent samples of different chemical systems. It is desirable to deposit transparent samples for infrared studies to maintain good signal-to-noise conditions and to allow examination of relatively thick samples which may be required for the observation of weak infrared bands. The Raman sample should be light in color for optimum light scattering. Obviously, dark samples will produce poor Raman scattering. It has been our experience that the most critical aspect of the Raman matrix experiment is sample deposition; visual monitoring of the sample during deposition is necessary for optimum sample preparation in these experiments. In general, less sample is required for the Raman experiment. Our Raman experiments require 4-6 hours of sample deposition (2 mmole/hour of gas deposited) whereas optimum infrared experiments require 18-24 hours. There is, of course, a practical limit to the laser penetration depth into the matrix sample, and laser beam heating of the sample surface will be more critical for thicker samples.

Laser power is an important parameter. Clearly, the minimum laser power for a good measurable signal is desirable, particularly for samples which may be photosensitive. We have observed the matrix isolated ozonide ion with 7 mW of 4880 Å excitation (this resonance Raman spectrum will be discussed in detail) (8), whereas approximately 700 mW of 4880 Å illumination was required to photoproduce OF and observe its Raman spectrum (9).

Frequencies can be measured more accurately in infrared than in the Raman experiments. Typical expanded scale, infrared slow-speed scans provide frequency accuracies of $\pm 0.5 \text{ cm}^{-1}$; with great care and in-place calibration, very sharp bands may be measured to $\pm 0.1 \text{ cm}^{-1}$. Accurate Raman frequency shift measurements require superposition of plasma emission lines on the actual scan. This can be conveniently done by reducing the amplification and replacing the laser transmitting "spike" dielectric filter with a neutral density filter. Ideally, a Raman shifted band should be measured relative to nearby fluorescence lines on high and low frequency sides. This careful measurement allows Raman shifts to be recorded with $\pm 0.5 \text{ cm}^{-1}$ accuracy. Five measurements of the OF fundamental in solid argon ranged from 1028.6 cm^{-1} to 1029.2 cm^{-1} (9); five measurements of O_2^- in the argon matrix isolated Li^+O_2^- species ranged from 1096.0 cm^{-1} to 1097.1 cm^{-1} (10).

Mercury arc photolysis has been widely used to photoproduce interesting new species for infrared spectral study. The Raman matrix technique conveniently provides a photolysis source, the laser excitation, for those molecules which undergo photolysis at the laser wavelength. The high power density of the laser beam makes photolysis practicable even for wavelengths

with low extinction coefficients. Laser photolysis of argon matrix isolated OF_2 has produced observable quantities of OF from photodecomposition of a small fraction the OF_2 precursor (9). In similar studies on Cl_2O in solid argon, Cl_2O Raman bands were observed along with the photolysis products ClO and ClClO (11). Raman studies of argon matrix isolated ozone showed a slow, continual photolysis of ozone as evidenced by growth of O_2 signal and decrease of O_3 signal (12). For appropriately selected precursor molecules, the matrix appears to moderate the photolysis process allowing Raman spectra of both precursor and photolysis product molecules to be obtained. Photochemical synthesis of XeCl_2 has been recently accomplished with blue laser light on xenon-chlorine mixtures (13). The wide range of excitation wavelengths found in the argon and krypton plasma lasers can be used to great advantage in photolysis of matrix isolated molecules.

The matrix also provides a suitable host medium for the observation of resonance Raman spectra. Photodecomposition of the matrix-isolated ozonide ion was moderated sufficiently to allow observation of resonance Raman spectra using argon ion excitation (8), whereas examination of polycrystalline material at these wavelengths produced decomposition (14). The matrix reaction technique also provides new species for resonance Raman study. The alkali metal-iodine matrix reaction produced a new species identified as M^+I_2^- which required red excitation for resonance enhancement (15). In the case of gas phase ClO_2 , laser excitation produced fluorescence (16); however, in an argon matrix host, quenching of fluorescence made possible the observation of the resonance Raman spectrum of ClO_2 and fluorescence at appropriately spaced frequencies (17). The resonance fluorescence spectrum has been

observed for gaseous NO_2 using 5145 and 4880 Å laser excitation (18). With these exciting wavelengths, argon matrix isolated NO_2 exhibits a resonance Raman spectrum of the ν_1 and ν_2 fundamentals and several overtone bands (19).

Laser-induced fluorescence studies of matrix-isolated species also provide a wealth of chemical information. Recent studies on C_2^- in solid argon indicate vibrational lifetimes in the ms range (20). In argon and krypton plasma laser investigations of matrix-isolated carbenes, fluorescence progressions in ν_1 and ν_2 of CCl_2 were observed (21). Sample dilution was a critical factor in these studies; reagent concentrations on the order of 0.1% were required to produce the best resolution of spectral features and to remove intermolecular perturbations.

We now turn our attention to a number of recent laser-excitation studies of matrix-isolated species.

RAMAN STUDIES OF ALKALI-METAL ATOM MATRIX REACTION PRODUCTS

Matrix Reactions with O₂

Alkali metal atom-oxygen molecule matrix reactions have been extensively studied by this author and his coworkers using infrared and Raman techniques. The primary reaction yields the superoxide species which will be discussed in

detail. Two secondary reactions yield the peroxide species

and the disuperoxide species

In the first study of M-O₂ matrix reactions, this author reported a new chemical species, lithium superoxide Li⁺O₂⁻, with ionic bonding between Li⁺ and O₂⁻, and an isocles triangular structure (22). These conclusions were based upon the near agreement between the O-O mode for LiO₂ and the O₂⁻ fundamental and the observation of sharp triplet bands in the reaction of ¹⁶O₂/¹⁶O¹⁸O/¹⁸O₂ with ⁷Li atoms at high dilution in argon and a vibrational analysis involving six isotopic LiO₂ molecules. Figure 1 contrasts the infrared spectrum in this critical experiment with the Raman spectrum of a similar argon matrix sample (10).

First, examine the O₂⁻ region near 1100 cm⁻¹. The 1096.1 cm⁻¹ Raman band observed at 1096.6 cm⁻¹ in the infrared is due to ⁷Li⁺¹⁶O₂⁻; the 1065.7 cm⁻¹ Raman band recorded at 1066.5 cm⁻¹ in the IR is due to ⁷Li⁺¹⁶O¹⁸O⁻; the 1034.6 cm⁻¹ Raman signal measured at 1035.2 cm⁻¹ in the infrared is due to ⁷Li⁺¹⁸O₂⁻. The large 61 cm⁻¹ oxygen isotopic shift indicates the pure

oxygen character of this vibration, which is identified as ν_1 , the intraionic $(O \leftrightarrow O)^-$ mode. The central feature reveals the molecular structure. In both infrared and Raman experiments, the single 16-18 isotopic band was sharp, just as sharp as the 16-16 and 18-18 isotopic bands. This indicates that the 16-18 isotope produces a single molecular arrangement M_{18}^{16} with equivalent oxygen atoms, in contrast to two possible M-16-18, M-18-16 arrangements which would be expected to produce a split central band as was observed for $H^{16}O^{18}O$ and $H^{18}O^{16}O$ (23). In the infrared experiments, this band was very sharp, 1.0 cm^{-1} half-width. It appears that 0.2 cm^{-1} is a reasonable upper limit on the inequivalence of the O atoms in $Li^+O_2^-$ in the $Li^{+16}O^{18}O^-$ isotopic band.

Second, in the Li-O stretching region, two intense resolved triplet bands were observed in the infrared, a single **broader**, weaker feature was observed in the Raman spectrum. The large lithium isotopic shift and smaller oxygen isotopic shift indicate that the band near 700 cm^{-1} is the symmetric interionic mode ν_2 , $Li^+ \longleftrightarrow O_2^-$, and the smaller lithium isotopic shift and larger oxygen isotopic shift show that the band near 500 cm^{-1} is ν_3 , the antisymmetric interionic mode. The G-matrix elements for these normal modes weight the participation of Li and O atoms differently (22).

Comparison of band intensities in Figure 1 also reflects on the bonding in the $Li^+O_2^-$ species. The infrared spectrum shows a weak intraionic mode, ν_1 , and very intense interionic modes, ν_2 and ν_3 , as would be expected for an ionic model. The Raman spectrum contains a very intense intraionic mode ν_1 , a moderately intense symmetric interionic mode ν_2 and the antisymmetric interionic mode ν_3 is absent. The ionic model for LiO_2 is supported by the complementary Raman spectrum.

The heavier alkali metals Na, K, Rb, and Cs react with oxygen to produce the superoxide $M^+O_2^-$ species (24,25,26). Raman spectra for the Na, K, Rb, and Cs atom- O_2 reactions show a strong band near 1110 cm^{-1} for the O_2^- vibration (27,28). The infrared spectra are typified by Cs atom cocondensation spectra with four isotopic oxygen samples (26). The very sharp, weak infrared band at 1115.6 cm^{-1} has a strong Raman counterpart at 1114 cm^{-1} . Isotopic substitution shows that this is the $\nu_1 O_2^-$ intraionic fundamental in a $Cs^+O_2^-$ species with two equivalent oxygen atoms. The very intense bands near 230 cm^{-1} and weak bands at 260 cm^{-1} are the interionic ν_2 and ν_3 modes, respectively, of $Cs^+O_2^-$.

The $Cs^+O_2^-$ vibrational data are contrasted in Table I with frequencies for the other $M^+O_2^-$ molecules. Note the increase in ν_1 with increasing cation size. This trend has been rationalized (10) as follows: increasing the cation polarizability increases the induced dipole moment on the cation which is opposite in sense to the ion dipole; accordingly, a small amount of antibonding electron density is removed from O_2^- increasing the fundamental frequency in the direction of the O_2 value (1552 cm^{-1}). Also, note the larger decrease in ν_2 and smaller decline in ν_3 with increasing alkali atomic weight which is required by the G-matrix elements for these normal modes.

The peroxide species, $M^+O_2^{2-}M^+$, has been observed for the five alkali metals. Intense antisymmetric Li-O stretching bands at 796 and 446 cm^{-1} for the ^7Li species showed isotopic splittings appropriate for a species containing two equivalent lithium atoms and two equivalent oxygen atoms. A rhombus structure with an O-O bond was suggested for the $M^+O_2^{2-}M^+$ molecule (22). In the heavier species, the sodium frequency counterparts were observed at 525 and 254 cm^{-1} (24), and the upper band only was observed for

TABLE I

Fundamental Frequencies (cm^{-1}) Assigned to the ν_1 Intraionic and ν_2 and ν_3 Interionic Modes of the C_{2v} Alkali Metal Superoxide Molecules in Solid Argon at 15 K

<u>Molecule</u>	<u>ν_1</u>	<u>ν_2</u>	<u>ν_3</u>
$^6\text{LiO}_2$	1097.4	743.8	507.3
$^7\text{LiO}_2$	1096.9	698.8	492.4
NaO_2	1094	390.7	332.8
KO_2	1108	307.5	---
RbO_2	1111.3	255.0	282.5
CsO_2	1115.6	236.5	268.6

the K, Rb, and Cs species at 433, 389, and 357 cm^{-1} (25,26).

The disuperoxide species, M^+O_4^- , have been observed for the heaviest alkali metals. The small lithium ion apparently is not large enough to stabilize the large O_4^- anion. The new MO_4 species was first observed in K and Rb studies which produced extraordinarily intense, very sharp, bands at 993.4 and 991.7 cm^{-1} , respectively (25). The cesium counterpart at 1002.5 cm^{-1} illustrates the isotopic behavior of the new species; the intense new band shifted to 946.5 cm^{-1} in the $^{18}\text{O}_2$ reaction. The stoichiometry of the new species is revealed by the mixed isotopic reactions; the $^{16}\text{O}_2 + ^{18}\text{O}_2$ sample produced a symmetric triplet at 1002.0, 970.2, and 946.5 cm^{-1} , which indicates the presence of two equivalent O_2 molecules in the new species. A well-resolved sextet was produced in the scrambled oxygen isotopic experiment. The explicit interpretation of the sextet indicates a species with equivalent O_2 units with equivalent O atoms in each unit. Accordingly, a D_{2d} structure was first proposed by this author for the O_2KO_2 species (25). Subsequently, Jacox and Milligan pointed out the existence of the O_4^- ion in ion-molecule reactions and suggested the O_4^- arrangement (29). Possible O_4^- anion arrangements and M^+ cation positions have been explored by CNINDO calculations; "puckered five-membered ring" M^+O_4^- structure was suggested in which the two O_2 parts of O_4^- are equivalent but the inequivalence in atomic positions for each O_2 unit, which would be small spectroscopically, was not resolved in the infrared spectrum (26). The O_4^- anion was suggested to contain two "superoxide" bonds and a weak intermolecular bond between the two O_2 units. A very strong Raman band near 300 cm^{-1} for the K^+O_4^- , Rb^+O_4^- , and Cs^+O_4^- species was assigned to this symmetric intermolecular mode $(\text{O}_2 \leftrightarrow \text{O}_2)^-$; interpretation of this low-frequency

Raman band requires a very weak oxygen bond which is provided by the O_4^- anion in the $M^+O_4^-$ species (28). The presence of the cation certainly influences the geometry of the O_4^- anion in the $M^+O_4^-$ ion-pair.

Matrix Reactions with Ozone

Extensive infrared and Raman studies of matrix-isolated isotopic ozone molecules have been conducted by Andrews and Spiker (12). Here isotopic ozones ($^{16}O_3$, $^{18}O_3$, and $^{16,18}O_3$) were synthesized by tesla coil discharge of O_2 gas in a pyrex finger immersed in liquid nitrogen. Oxygen was outgassed from the blue, liquid ozone sample by evacuating the sample at 77 K. Argon/ozone samples were prepared using standard (careful!) manometric techniques in a stainless steel vacuum system.

Matrix reactions of alkali metal atoms and ozone have also been studied using infrared and Raman methods. The infrared spectra (30) were characterized by very intense bands near 800 cm^{-1} depending upon the alkali atom and the weaker bands near 600 cm^{-1} for the heavier alkali metal reactions. The intense 800 cm^{-1} bands were assigned to ν_3 and the weak 600 cm^{-1} bands were attributed to ν_2 of O_3^- in the $M^+O_3^-$ species, produced by charge-transfer reaction (4).

The cesium atom-ozone reaction produced intense ν_3 bands at 802 and 757 cm^{-1} for $Cs^{+16}O_3^-$ and $Cs^{+18}O_3^-$, respectively, and weaker ν_2 bands at 600 and 567 for the same respective isotopic species. In addition, oxygen atom abstraction was evidenced by observation of Cs_2O at 457 cm^{-1} and CsO at 322 cm^{-1} (30).

Sample preparation for Raman scattering experiments was closely monitored using white light; formation of the $M^+O_3^-$ species was evidenced by the appearance of the orange ozonide color (8). Great care must be taken to prevent excess alkali metal which produces darker, and, thus, poorer scattering samples. Figure 2 illustrates the Raman spectra of Na- O_3 matrix reactions (8). A very intense Raman band was observed at 1011 cm^{-1} with a site splitting at 1024 cm^{-1} in the $Na^{+16}O_3^-$ spectrum. Large oxygen-18 shifts are indicated by the $Na^{+18}O_3^-$ spectrum; the intense band and site splitting shifted to 956 and 970 cm^{-1} , respectively. The $Na^{+16,18}O_3^-$ Raman spectrum shows five well-resolved components, the broader central component contains both 16-18-16 and 18-16-18 isotopic species. A five-component multiplet with the same relative intensities has been observed for ν_1 of matrix-isolated 55% oxygen-18 enriched ozone (12). As was the case for ν_3 of O_3 and O_3^- in the infrared spectra (30), ν_1 of O_3 and O_3^- produced similar isotopic bands in the Raman spectra.

The weak band at 599 cm^{-1} in the $Na^{+16}O_3^-$ Raman spectrum has an ozone-18 counterpart at 567 cm^{-1} ; individual isotopic components were not resolved in the $^{16,18}O_3$ reaction. These features are in good agreement with the infrared assignments to ν_2 of O_3^- in the cesium species (30); accordingly, the weak Raman bands were assigned to ν_2 of O_3^- in the sodium ozonide molecule (8).

The very intense fundamental Raman bands for the ozonide species and the deep orange sample color prompted a search for overtones of the ν_1 fundamental. An electronic absorption band with vibrational fine structure in the $5100\text{-}3700\text{ \AA}$ region has been observed by Jacox and Milligan (31) and this author (32) for O_3^- in the $M^+O_3^-$ species. Accordingly, $4880\text{ \AA}$ laser excitation of matrix-isolated $Cs^+O_3^-$ yielded

a regular progression of fundamental and overtone bands at 1018, 2028, 3024, and 4014 cm^{-1} with regularly decreasing intensities. The $\text{Cs}^{+18}\text{O}_3^-$ species produced a progression out to $5\nu_1$; bands were observed at 962, 1915, 2859, 3795, and 4724 cm^{-1} (8). The regularly decreasing intensity pattern for an overtone progression is characteristic of the resonance Raman effect.

Figure 3 contrasts the use of six different laser exciting lines on the Raman spectrum of Na^+O_3^- . The 6471 Å line produced a weak fundamental at 1011 cm^{-1} on a steep fluorescence background. 5682 Å excitation gave an intense fundamental at 1011 cm^{-1} and a weak first overtone at 2013 cm^{-1} . The 5309 Å line produced an intense fundamental at 1012 cm^{-1} , a first overtone at 2013 cm^{-1} and a weak second overtone at 3001 cm^{-1} . 5145 Å excitation yielded the intense 1011 cm^{-1} fundamental, intense first and second overtones at 2013 and 3002 cm^{-1} and a weak third overtone at 3977 cm^{-1} ; the 4880 Å line produced the intense fundamental and two intense overtones at the same frequencies. Figure 3 concludes with the 4579 Å exciting line which gave the intense fundamental and two moderately intense overtones (8). Clearly, the overtone intensity is enhanced as the excitation wavelength approaches the electronic absorption band maximum. This increase in overtone intensity relative to fundamental intensity as the exciting wavelength enters the electronic band is characteristic of resonance Raman spectra.

Analysis of the overtone progressions for the $\text{Cs}^{+16}\text{O}_3^-$ species produced the vibrational constants $\omega_1 = 1028.2 \pm 1.0\text{ cm}^{-1}$ and $x_{11} = 4.95 \pm 0.25\text{ cm}^{-1}$. The harmonic and anharmonic vibrational constants provide a measure of the heat of atomization, $\text{O}_3^- \rightarrow 2\text{O} + \text{O}^-$, of the ozonide ion using a linear

Birge-Spooner extrapolation to the dissociation limit. The spectroscopic heat of atomization, 153 ± 3 kcal/mole, agrees well with the thermodynamic value, and it provides an independent check on the electron affinity of ozone (8).

The present Raman spectra for the $M^+O_3^-$ species demonstrate the usefulness of the matrix reaction technique to produce and stabilize observable quantities of unstable species for laser examination. The ozonide Raman fundamentals near 1010 cm^{-1} in the matrix isolation study agree with He-Ne observations on polycrystalline ozonides (14) and very recent resonance Raman studies of O_3^- produced by γ -radiolysis of $KClO_3$ crystals (33). The matrix host moderates the photodecomposition of the $M^+O_3^-$ molecule, quenches fluorescence and allows the resonance Raman spectrum of O_3^- to be observed using argon ion excitation.

Alkali Metal-Fluorine Reaction Products

Fluorine was the first halogen molecule to be studied in alkali metal matrix reactions owing to the presence of a 475 cm^{-1} Raman band in sodium- OF_2 studies which showed no oxygen-18 shift (34). Matrix samples prepared by codepositing Na atoms with argon containing 1% F_2 exhibited a strong Raman band at 475 cm^{-1} and a weaker band at 892 cm^{-1} due to F_2 using $4880\text{ \AA}$ laser excitation (35,36). The 475 cm^{-1} scattering species was photosensitive; the signal had a half-life of approximately 10 min. Matrix reactions of Li, K, Rb, and Cs with F_2 were performed and the new Raman bands observed near 460 cm^{-1} are listed in Table II.

TABLE II

Fundamental Frequencies (cm^{-1}) Assigned to the ν_1 Intraionic ($\text{X} \leftrightarrow \text{X}$)⁻
Mode of the M^+X_2^- Species Observed in Matrix Raman Spectra

	F_2^-	Cl_2^-	I_2^-
Li^+	452	246	115
Na^+	475	225	114
K^+	464	264	113
Rb^+	462	260	116
Cs^+	459	259	115

Figure 4 contrasts Raman spectra of fluorine-chlorine and sodium matrix reaction products. The top spectrum shows the 475 cm^{-1} band from the reaction with F_2 and the bottom spectrum, to be described fully in the next section, exhibits Cl_2 signal at 538 cm^{-1} , a weak band at 275 cm^{-1} and a strong signal at 225 cm^{-1} , the latter of which is due to Cl_2^- in the Na^+Cl_2^- species. The middle trace shows the Raman spectrum of a mixed $\text{F}_2\text{-Cl}_2$ reaction; only two dominant product signals were noted and these appeared at 475 and 225 cm^{-1} , the same positions observed in the F_2 and Cl_2 runs, respectively. This indicates that the scattering species contains two halogens, and therefore, the formula must be M^+X_2^- .

It is proposed that F_2^- was formed as an intermediate in reaction (5) which goes completely in some cases, but the M^+F_2^- "collision complex" is stabilized by the matrix in sufficient quantities for laser Raman detection.

Photodecomposition of M^+F_2^- probably proceeds to the more thermodynamically stable MF and F products.

The Raman signals for the M^+F_2^- species are assigned to the intraionic $(\text{F-F})^-$ vibration. Their appearance at approximately half of the F_2 fundamental is in qualitative agreement with molecular orbital theory for diatomic molecules which predicts a one-half bond order for F_2^- . The alkali metal shift on the F_2^- wavenumbers arises from interaction between the interionic $\text{M}^+\longleftrightarrow\text{F}_2^-$ vibration and the $(\text{F}\longleftrightarrow\text{F})^-$ mode; the former, is of course, very sensitive to the alkali mass. The M^+O_2^- species provide a guide as to the expected positions of the interionic modes; a cross-over occurs between Li and Na with the F_2^- mode. Interionic modes for ${}^6\text{Li}^+-\text{F}_2^-$ and Na^+-F_2^- have been

identified at 708 and 454 cm^{-1} in infrared studies (36). Interaction between the higher-frequency lithium-stretching and $(\text{F-F})^-$ stretching modes forces the latter to a lower frequency, whereas the heavier sodium interionic mode shifts below the F_2^- mode and forces F_2^- to a higher frequency. Increasing the mass to K, Rb, and Cs removes the interaction, and the F_2^- mode appears near 460 cm^{-1} .

An optical absorption study of alkali metal atom-halogen molecule reaction products is in progress (37). A very strong absorption at 310 nm was produced in the Na- F_2 reaction; this band was photobleached by a tungsten lamp. The 310 nm optical band is believed due to F_2^- ; its appearance to the long wavelength of F_2 at 284.5 nm (38) is noted.

Alkali Metal-Chlorine Reaction Products

Matrix reactions of chlorine and alkali metal atoms produced extraordinarily intense Raman signals in the 225-260 cm^{-1} shifted region. Owing to the orange color of these matrix samples, resonance enhancement of the intensity was suspected and intense overtone series were noted with argon ion laser lines (39,40).

Figure 5 contrasts the Raman spectra of the five alkali metal products of reaction (6). Note the very intense fundamentals, ranging from 264 cm^{-1}

for K^+Cl_2^- to 225 cm^{-1} for Na^+Cl_2^- which show a clear alkali metal trend as listed in Table II. These signals are assigned to the intraionic $(\text{Cl-Cl})^-$ mode, and the alkali metal dependence is believed to be due to interaction

with the interionic $M^+ \leftrightarrow Cl_2^-$ stretching mode which is predicted higher in the $Na^+Cl_2^-$ case, forcing the $(Cl-Cl)^-$ mode down to 225 cm^{-1} , and in the $K^+Cl_2^-$ species, the interionic mode is predicted at 200 cm^{-1} forcing the $(Cl-Cl)^-$ vibration up to 264 cm^{-1} .

Figure 6 shows the extensive overtone series observed for the $Cs^+Cl_2^-$ species using $4579\text{ \AA}$ laser excitation. Notice the resolution of natural chlorine isotopes in the overtones; the observed 9/6 intensity ratio for the upper two bands in each member of the progression for the (35-35) and (37-35) isotopic species confirms the presence of two equivalent chlorine atoms. The fundamental and first three overtones for the (37-37) isotopic species were observed using a $^{37}Cl_2$ sample (40).

Standard wavenumber plots of the overtone data produce an excellent straight-line fit and the vibrational constants $\omega_e = 262.1 \pm 0.3\text{ cm}^{-1}$ and $\omega_e x_e = 1.55 \pm 0.07\text{ cm}^{-1}$ for Cl_2^- in the $Cs^+Cl_2^-$ species. It is also of interest that the upper limit to the $(Cl-Cl)^-$ dissociation energy calculated from the harmonic and anharmonic vibrational constants, 31.8 kcal/mole , is in very good agreement with the $28.8 \pm 2.5\text{ kcal/mole}$ thermochemical value (40).

The optical absorption of Cl_2^- in the $Cs^+Cl_2^-$ species produced a band at 350 nm (37). Figure 7 contrasts the Raman spectra of this species using 514.5 , 488.0 , 476.5 , and 457.9 nm excitation. As the laser wavelength approached the absorption band maximum, intensity enhancement of the fundamental and overtone series was noted (40).

The intense Raman signal at 275 cm^{-1} in the $Na-Cl_2$ reaction spectrum of Figure 5 is due to ν_1 of Cl_3^- in the $Na^+Cl_3^-$ species. $NaCl$ molecules, also produced in the cocondensation reaction and identified by an intense infrared band at 335 cm^{-1} (40), react with Cl_2 to produce $Na^+Cl_3^-$, reaction (7).

This assignment has been confirmed by salt-molecule matrix reactions where NaCl and Cl₂ have been codeposited in solid argon (41).

Alkali Metal-Iodine Reaction Products

Matrix reactions of alkali metal atoms and iodine provide a particularly interesting chemical system for laser-Raman study. Using the potassium-iodine reaction products for the purpose of discussion, a very strong resonance Raman progression beginning at 113 cm⁻¹ with five overtones decreasing in intensity was observed using 6471 Å excitation. The 5682 and 5309 Å lines produced only a weak fundamental, and no signal was detected with 5145 Å excitation. However, when the 4880, 4579, and 3507 Å laser lines were used, an increasingly strong fundamental was observed near 112±2 cm⁻¹ (15).

The triiodide ion absorbs strongly at 294 and 364 nm in the near ultraviolet (42), and Raman spectra of I₃⁻ in solution have been observed using blue and ultraviolet laser lines (43). However, I₃⁻ has no absorption in the red visible region. It was proposed that the red-enhanced-intensity scattering species was I₂⁻ produced by reaction (8). Reactions (9) and (10)

suggest a mechanism to produce I₃⁻ which is responsible for the matrix Raman signals stimulated by blue and uv laser lines. The I₂⁻ fundamentals

were a several cm^{-1} function of M^+ , which arises from the $\text{M}^+ \longleftrightarrow \text{I}_2^-$ stretching interaction with the $(\text{I-I})^-$ mode. The $\text{M}^+ \text{I}_2^-$ Raman wavenumbers are also listed in Table II.

In optical absorption work in progress, the sodium-iodine matrix reaction produced strong bands at 380 nm for $\text{Na}^+ \text{I}_3^-$ and 695 nm for $\text{Na}^+ \text{I}_2^-$ (37) which supports the resonance Raman observation of I_2^- in the matrix reaction product $\text{M}^+ \text{I}_2^-$ (15).

LASER PHOTOLYSIS RAMAN STUDIES

The OF and ClO Free Radicals

The oxygen fluoride free radical was first observed by Arkell and co-workers (44) following the mercury-arc photolysis of argon-OF₂ samples at 4 K. The matrix reactions of OF₂ and Li, Na, K, and Mg atoms were studied by Andrews and Raymond. The intense, sharp OF fundamental was observed at $1028.6 \pm 0.3 \text{ cm}^{-1}$, independent of the metal reagent; metal fluoride molecules were observed for all reagent metals (45).

The sodium-OF₂ matrix reaction was examined using the Raman matrix technique; a weak band at 1028 cm^{-1} was observed; however, it was noticed that the 1028 cm^{-1} band grew during the laser illumination period (34). The Raman spectrum of argon matrix-isolated OF₂ without alkali metal atoms is illustrated in Figure 8 (a); the sharp OF₂ fundamental bands ν_2 and ν_3 are noted at 464 and 825 cm^{-1} along with the Fermi doublet ν_1 , $2\nu_2$ at 920, 931 cm^{-1} (9). These frequencies are within one cm^{-1} of the infrared matrix assignments. Figure 8(a) also shows the laser photolytic production of the OF species. Note in the first trace, no signal was detected at 1029 cm^{-1} after 8 min of exposure to 700 mW of 4880 Å excitation; however, after 25 min of laser illumination on the same spot of sample, a small signal appeared at 1029 cm^{-1} which grew to a strong signal after two hours of laser photolysis. Clearly, the 1029 cm^{-1} signal increased as a function of laser illumination time. In addition to the OF photolysis product, O₂ and F₂ were also observed at 1552 and 892 cm^{-1} , respectively. Accurate measurements of the OF fundamental frequency using argon emission lines superimposed on the actual scan yielded $1028.9 \pm 0.5 \text{ cm}^{-1}$, which is in excellent agreement with the infrared observations.

Figure 8(b) illustrates the Raman spectrum of an Ar/OF₂ = 100/1 sample deposited for four hours with simultaneous 4880 Å photolysis for the last three hours (9). Note the strong signals at 1029 cm⁻¹ and 892 cm⁻¹ for photolysis products of OF₂ and the strong signals for unphotolysed OF₂. The matrix apparently moderates the laser photodecomposition of OF₂ such that excellent Raman spectra of precursor and photolysis products can be obtained.

The advantage of laser photolysis is demonstrated for OF₂. The electronic transition for OF₂ photodecomposition increases in intensity with decreasing wavelength; the extinction coefficient is 75×10^{-5} at 2100 Å (46). Accordingly, the OF species was first observed by Arkell and co-workers following mercury arc photolysis of matrix isolated OF₂ (44). However, the OF₂ absorption tails out into the visible region with an extinction coefficient of 0.14×10^{-5} at 4880 Å. The high power density of the laser beam compensates for the low extinction coefficient at 4880 Å such that photolysis products of OF₂ are produced by laser illumination, and they can be identified by Raman spectra.

A similar laser-Raman study of Cl₂O was done by Chi and Andrews (47). Figure 9 contrasts the 4880 Å excited Raman spectrum of 1% Cl₂O in argon with the infrared spectrum of a similar sample subjected to 10 m of mercury arc photolysis. First, the stretching modes of Cl₂O were observed in both spectra and, in addition, ν_2 was detected in the Raman spectrum. Rochkind and Pimentel previously identified the 962 and 375 cm⁻¹ infrared bands with a new photoisomer Cl-C1O (48). The Raman study confirmed their observation and added the Cl-Cl-O bending mode assignment of 239 cm⁻¹. Perhaps of most interest is the direct Raman observation of the elusive ClO free radical

fundamental at 850 cm^{-1} which is in agreement with hot band spacings in the electronic spectrum (49).

Noble Gas Dihalides

The matrix isolation technique was employed in early infrared studies of XeF_2 and KrF_2 by Turner and Pimentel (50). Xenon dichloride was first identified by a 313 cm^{-1} infrared absorption arising from the condensed discharge products of xenon and chlorine (51); Raman studies on similar systems produced a 253 cm^{-1} band for ν_1 of XeCl_2 (52). Owing to the appearance of this latter band in the Cl_2^- region, discussed in the previous section, and the possibility of trapping ions from discharge sources, photolytic methods of synthesizing XeCl_2 were sought. Howard and Andrews (53) and, independently, Beattie and German (54), found that 4880 Å laser irradiation of frozen samples of chlorine in xenon produced a strong Raman signal at 254 cm^{-1} . The observation of a 9/6/1 triplet (54) required two equivalent chlorine atoms in the scattering species and the energy available in blue light is sufficient to dissociate (and not ionize) molecular chlorine (53) which confirmed the identification of XeCl_2 .

In a detailed wavelength study of laser photosynthesis of XeCl_2 , Howard and Andrews found that production of the 254 cm^{-1} Raman signal was not possible with 5145 Å light, was slow with 5017 Å , rapid with 4880 Å , and very rapid with 4765 Å laser lines. The dissociation limit of Cl_2 at 4786 Å identifies the mechanism as the reaction of a photolytically produced pair of chlorine atoms with a xenon atom in the matrix cage (53).

In order to confirm this mechanism, xenon-fluorine and krypton-fluorine matrix samples were exposed to blue laser examination. XeF_2 was produced immediately, as identified by a strong Raman band at 512 cm^{-1} ; KrF_2 was synthesized more slowly, but a strong Raman band at 452 cm^{-1} was observed. Figure 10 contrasts the $4880\text{ \AA}$ laser synthesis of XeF_2 , KrF_2 , and XeCl_2 for Raman study. A similar laser photolysis experiment with krypton and chlorine failed to produce a new signal; however, microwave discharge of krypton and chlorine produced an extremely unstable signal at 242 cm^{-1} which was tentatively assigned to isolated Cl_3^- (53).

The mixed compound XeClF was reported by Howard and Andrews (53) using blue photolysis of ClF in solid xenon. Figure 11 contrasts the infrared and Raman spectra of XeClF . Note the strong 480 cm^{-1} and weak 316 cm^{-1} infrared bands and the appearance of these same signals in the $4765\text{ \AA}$ excited Raman spectrum. The 480 cm^{-1} infrared band was observed independently by Bondeybey and Pimentel following the condensation of excited xenon atoms with ClF diluted in argon (55). These compounds mark the limit of noble gas reactivity as attempts to prepare KrCl_2 and XeBr_2 met with no success (53).

LASER EXCITATION STUDIES OF MOLECULAR HALOGENS

As supporting studies for the previously discussed matrix reactions of molecular halogens, a systematic laser excitation investigation of halogen molecules in matrices was undertaken in the Raman and fluorescence spectral regions.

Molecular fluorine at concentrations of 1 or 2% in solid argon produced a moderate 892 cm^{-1} Raman signal using blue laser excitation, which is in agreement with the gas phase value and near the solid value (35,36). No fluorescence attributable to molecular fluorine was detected; however, a system of bands between $14,000$ and $19,000\text{ cm}^{-1}$ with a 580 cm^{-1} spacing was observed with blue laser excitation of fluorine in argon, krypton, xenon, and nitrogen. This fluorescence is believed to be due to a metal fluoride arising from the reaction of fluorine with the vacuum system (56).

Raman and fluorescence spectra of matrix-isolated Cl_2 depended upon concentration. Using 1 or 2% Cl_2 in argon, a Raman band was observed at 538 cm^{-1} (39) and a broad series of fluorescence bands appeared between $11,000$ and $15,000\text{ cm}^{-1}$ with a beginning spacing of approximately 520 cm^{-1} when samples of $\text{Ar}/\text{Cl}_2 = 300/1$ and more dilute were studied, a 550 cm^{-1} Raman band and a sharp fluorescence series of 9/6/1 triplets between $11,000$ and $15,000\text{ cm}^{-1}$ were observed using 5145, 4880, 4579, and $3507\text{ \AA}$ laser lines. The latter sharp triplet fluorescence and 550 cm^{-1} Raman band have been assigned to matrix isolated Cl_2 and the series of broad fluorescence bands and 538 cm^{-1} Raman signal have been attributed to aggregated chlorine. Agreement of the latter Raman band with the solid chlorine value was noted (57).

Laser excitation spectra of bromine in matrices followed the same pattern. For concentrations of 1%, a Raman fundamental at 295 cm^{-1} and overtones at 586, 882, and 1176 cm^{-1} were observed for aggregated bromine using 4579 Å excitation (58) along with a broad series of fluorescence bands. More dilute samples ($\text{Ar}/\text{Br}_2 = 500/1$) gave resonance Raman bands of matrix isolated Br_2 at 316, 629, 940, and 1249 cm^{-1} and a fluorescence system from 10,500 to $13,500\text{ cm}^{-1}$ which showed a beginning spacing of 313 cm^{-1} and gave $\omega_e = 317.5\text{ cm}^{-1}$ and $\omega_{eXe} = 1.1\text{ cm}^{-1}$ for Br_2 (57).

Molecular iodine proved even more difficult to matrix isolate, as the Raman spectra of Figure 12 indicate. At $\text{Ar}/\text{I}_2 = 400/1$ a strong resonance Raman progression with a 180 cm^{-1} fundamental dominates the spectrum. However, at $\text{Ar}/\text{I}_2 = 2500/1$, a strong resonance Raman series beginning at 212 cm^{-1} is the only feature present. The agreement of these iodine fundamentals with the solid and gas phase values, respectively, denote the matrix-isolated scattering species as aggregated iodine and monomeric iodine (58).

It was found, as expected, that the more polarizable halogen molecules were more difficult to isolate as the diatomic molecule. Perhaps surprising was the fact that an iodine concentration of 1 part per 2500 matrix gas was required to eliminate the resonance Raman spectrum of aggregated iodine molecules.

In the fluorescence region, a relatively broad and strong fluorescence band with maxima at about $16,600$ and $15,700\text{ cm}^{-1}$ was observed with yellow, green, and blue laser lines (59). Since this broad fluorescence was observed under conditions where all of the resonance Raman signal was due

to monomeric iodine, the broad bands are believed due to I_2 fluorescence broadened by matrix solvent effects.

Of special interest were two series of sharp fluorescence bands between 14,475-13,112 and 13,080-12,100 cm^{-1} which appeared in almost all matrix studies of iodine. The two series had beginning spacings of 178 and 152 cm^{-1} which increased out the fluorescence series showing a positive anharmonicity which can be explained by a new linear species of iodine. While the present information does not provide a basis for definitive identification of this linear iodine species, possibilities include transition metal diiodides such as FeI_2 (60).

It is also possible to do meaningful quantitative intensity studies on matrix-isolated molecules. Grzybowski and Andrews (59) performed a laser excitation investigation of TiI_4 at approximately 0.1% concentration in solid argon aimed at resonance Raman observation of TiI_4 and found instead progressions in monomeric I_2 out to $\underline{\nu} = 25$. Owing to the previously discussed strong tendency of I_2 molecules to aggregate, the laser-induced decomposition of matrix-isolated TiI_4 produced twice the concentration of isolated I_2 that could be obtained with the element. High intensity resonance Raman overtone progressions out to $\underline{\nu} = 3, 14, 23, 24, 25, 17$, and 3 have been observed with 457.9 nm, 476.5 nm, 488.0 nm, 514.5 nm, 530.9 nm, 568.2 nm, and 647.1 nm excitation, respectively, for monomeric iodine isolated in an argon matrix. The intensity ratios, $R_{\underline{\nu}}$ (overtone/fundamental), were determined and plotted versus the laser excitation energy which formed excitation profiles for the overtones. ^{resonance Raman excitation profiles} Figure 13 illustrates a plot of the $\underline{\nu}$ for the first seven overtones of I_2 in solid argon. The two maxima strongly suggest that the resonance Raman intensity enhancement is due to a resonance coupling of the exciting

radiation with not only the $^3\Pi_{ou} \leftarrow ^1\Sigma_g^+$ transition, but also with the $^1\Pi_{1u} \leftarrow ^1\Sigma_g^+$ transition. The dashed curves in Figure 13 represent the intensity ratio curves for the two cases of exact resonance which extrapolate to the two electronic transition energies. Appropriate wavenumbers of the deconvoluted peaks as determined from the MCD spectra of matrix-isolated iodine are $19,700\text{ cm}^{-1}$ and $18,600\text{ cm}^{-1}$ for the singlet-singlet and singlet-triplet transitions, respectively (61).

RESONANCE RAMAN SPECTRA OF NO₂ and ClO₂

Resonance Raman spectra have been discussed in previous sections for the anions O₃⁻, Cl₂⁻, and I₂⁻, produced in alkali metal matrix reactions, and the Br₂ and I₂ molecules. The visible absorbing molecules NO₂ and ClO₂ have received extensive gas-phase laser excitation study (16, 18, and references therein), and their laser examination in matrices provides additional means to characterize the role of the matrix in laser-excitation studies. Furthermore, it was heretofore impossible to obtain Raman spectra of NO₂ and ClO₂ because of their intense visible absorption and fluorescence, and the explosive nature of ClO₂. It was believed that matrix isolation might circumvent these difficulties.

Tevault and Andrews recorded Raman spectra of NO₂ and N₂O₄ using 4880 Å excitation of a sample of Ar/NO₂ = 100/1 deposited at 16 K (19). The most intense feature in the spectrum was the 262 cm⁻¹ ν₃ band of N₂O₄; the ν₁ and ν₂ bands of N₂O₄ appeared as weak signals at 1383 and 813 cm⁻¹. "Isolated" NO₂ produced equally strong ν₁ and ν₂ signals at 1325 and 752 cm⁻¹, respectively. Upon warming the deposited sample to 40 K and re-cooling to 16 K, the NO₂ signals were markedly reduced and the N₂O₄ signals increased threefold.

In the overtone region, 2ν₂, ν₁ + ν₂ and 2ν₁ were observed for ¹⁴NO₂ and ¹⁵NO₂ with lower intensities than the fundamentals; 3ν₂ was also detected for ¹⁴NO₂. The resonance Raman spectrum of nitrogen dioxide is somewhat unusual in that two strong symmetric fundamentals, ν₁ and ν₂, and overtones of each were observed along with the combination band ν₁ + ν₂. No fluorescence was observed in the laser excitation study of matrix-isolated NO₂ (19).

Laser excitation studies of ClO_2 in argon, krypton, xenon, and nitrogen matrices were done with the 4579, 4765, 4880, and 5145 Å argon ion lines (17). The most energetic line, which reaches the electronic absorption of ClO_2 , produced the richest spectrum which is illustrated in Figure 14. The intense resonance Raman progression in the ν_1 fundamental of ClO_2 is noted with decreasing intensities out to 6 ν_1 along with four series of fluorescence bands labelled a, b, c, and d, which increase in intensity and then decrease in the series. The first a band at 290 cm^{-1} is in excellent agreement with the excited state bending frequency ν_2' . The a fluorescence series follows the quenching of one quantum of ν_2' and gives a progression in ν_1'' . The a series members were designated $(\underline{\nu}_1, 0)$ where $\underline{\nu}_1$ is the ν_1 quantum number. The b series is shifted from a by one quantum of ν_2'' and its identification follows as $(\underline{\nu}_1, 1)$. Likewise, it can be seen that the c and d series involve fluorescence progressions in $\underline{\nu}_1$ with higher combinations of $\underline{\nu}_2$ which were designated $(\underline{\nu}_1, 2)$ and $(\underline{\nu}_1, 3)$, respectively.

In the ClO_2 studies where both resonance Raman and fluorescence progressions were observed, the matrix quenches fluorescence and allows the resonance Raman spectrum to be observed (17), which is in marked contrast to the gas phase studies (16).

FLUORESCENCE STUDIES

While searching unsuccessfully for the Raman spectrum of CCl_3 , three groups of workers found a broad progression of fluorescence bands arising from CCl_2 also present in the matrix samples (62,63,64). However, Tevault and Andrews, using the alkali metal matrix reaction to synthesize CCl_2 by reactions (11) and (12), found that dilution of the samples to one part

reagent per thousand parts matrix gas reduced the series of broad bands and enhanced several series of sharp bands (64). The fluorescence spectra of CCl_2 at two sample dilutions using 4880 Å excitation are contrasted in Figure 15, which also shows a $^{13}\text{CCl}_2$ spectrum. The sharp fluorescence bands are due to combination progressions of ν_1'' and ν_2'' of CCl_2 . The values of ν_1'' for CCl_2 and $^{13}\text{CCl}_2$ deduced from the fluorescence spectra are in excellent agreement with infrared measurements of these fundamentals (65). Upon annealing the deposited sample, the sharp series was replaced by the broad series which was attributed to CCl_2 aggregated with another molecule present in the sample (64).

Similar work with dilute samples of CFC1 synthesized by the high yield matrix reaction of alkali metal atoms with CFC1_3 produced 120 resolved bands between 25,000 and 15,000 cm^{-1} using 3507 and 3564 Å krypton plasma laser excitation. These bands were interpreted as progressions in ν_2'' of CFC1 with combinations of ν_1'' and ν_3'' emanating from three adjacent vibrational levels in the excited state (66). Again, agreement with the infrared stretching fundamentals (67) was noted. The CFC1 fluorescence spectrum

produced by the 3640 Å line from a high-pressure mercury arc in these alkali metal studies was similar to the ultraviolet laser-induced spectrum, but as might be expected, two orders of magnitude weaker.

In an alkali metal reaction study with the CCl_2Br_2 precursor, the fluorescence spectrum of CClBr was excited using the 5682 Å krypton ion laser line (68). Several progressions in ν_2'' were observed with combination progressions involving ν_1'' and ν_3'' , the latter of which matched the direct infrared measurements (69).

Yellow laser excitation of alkali metal- CBr_4 samples produced a fluorescence from 11,5000-15,000 cm^{-1} which consisted of 17 sharp bands spaced 196 cm^{-1} apart and a weaker series of ten bands with the same spacing but shifted approximately 136 cm^{-1} lower in energy than the major progression. The two fluorescence series, illustrated in Figure 16, were assigned to progressions in ν_2'' of CBr_2 with the weaker series arising from a lower vibronic level by one quantum which provides a measure of ν_2' for CBr_2 of approximately 136 cm^{-1} (68).

In a particularly interesting vibronic study of matrix isolated PbS, Teichman and Nixon (70) observed fluorescence from three different excited electronic states in the visible region using 5682, 5145, 4880, and 4579 Å laser excitation. The three fluorescence progressions, identified as $B \rightarrow X$, $A \rightarrow X$, and $\underline{a} \rightarrow X$ by comparison to gas phase studies, exhibited average band spacings of 407 cm^{-1} in close agreement with the 423 cm^{-1} matrix infrared and Raman value for the PbS fundamental.

Excitation with the 4579 Å line reached the $\underline{\nu}' = 0$ level of the B state and about $\underline{\nu}' = 12$ and $\underline{\nu}' = 30$ in the A and $\underline{a}$ states. The relative intensities of the $\underline{a}$ and B emissions were much greater than the A emission.

On the other hand, 4880 and 5145 Å excitation produced a more intense A emission than a emission; however, a strong a emission was observed with 5682 Å excitation. The inference from these observations is that the a and B states are strongly coupled, conceivably by a mechanism involving the matrix, but that coupling between the a or B and A states is weak (70).

Finally, it is appropriate to conclude this review with fluorescence studies of C_2^- which have shown that vibrational lifetime measurements can be made on matrix-isolated molecules (20). The absorption spectrum of C_2^- in solid argon has been observed following hydrogen resonance photolysis of C_2H_2 during deposition (71,72). Since the 0-0 transition of C_2^- in solid argon, $19,193\text{ cm}^{-1}$, is near the $19,430\text{ cm}^{-1}$ argon ion laser line, an intense fluorescence spectrum of C_2^- was observed (73). Fluorescence progressions including 0-0, 0-1, and 0-2 bands were observed in N_2 and Ar matrices, but of most interest, a second progression containing 1-3, 1-2, 1-1, and 1-0 bands was observed in argon. The 1-0 feature on the blue side of the $19,430\text{ cm}^{-1}$ exciting line indicates that emission arises from the $\underline{v}' = 1$ level, apparently reached by secondary excitation of a substantial $\underline{v}'' = 1$ level population. It was concluded that vibrational relaxation for C_2^- in solid argon is slow in both ground and excited electronic states (73).

By using an elegant optical double-resonance technique, Allamandola and Nibler have determined vibrational half-lives of 0.2 and 1.2 ms for the $\underline{v}'' = 1$ and $\underline{v}'' = 2$ states of argon matrix-isolated C_2^- , respectively (20). The method employs a pumping laser to populate the 1'' and 2'' states by absorption to 1' and fluorescence to the 1'' and 2'' levels. A tunable probe laser was used to selectively excite 1'' to 0' and the 0' $\rightarrow$ 0'' fluorescence

markedly increased. By turning off the pumping laser, the decay of the $0' \rightarrow 0''$ fluorescence gives a measure of the rate of depletion of the $1''$ level. These successful studies indicate an exciting future for vibrational lifetime measurements of matrix-isolated molecules and the study of vibrational energy transfer phenomena in matrices.

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FIGURE CAPTIONS

- Fig. 1. Infrared and Raman spectra of lithium superoxide, Li^+O_2^- using lithium-7 and 30% $^{18}\text{O}_2$, 50% $^{16}\text{O}^{18}\text{O}$, 20% $^{16}\text{O}_2$ at concentrations of $\text{Ar}/\text{O}_2 = 100$. Raman spectrum recorded using 200 mW of 4880 Å excitation and long wavelength pass dielectric filter in 1000 cm^{-1} region.
- Fig. 2. Raman spectrum of argon matrix-isolated sodium ozonide using 200 mW of 5145 Å excitation. (Reprinted from Ref.(8), by courtesy of the American Institute of Physics).
- Fig. 3. Raman spectra of argon matrix-isolated sodium ozonide using different exciting wavelengths. $\text{Ar}/\text{O}_3 = 100$. (Reprinted from Ref.(8), by courtesy of the American Institute of Physics).
- Fig. 4. Raman spectra of F_2 and Cl_2 matrix reactions with Na atoms. Parameters: $\text{Ar}/\text{F}_2 = 50/1$, 45 mW of 4880 Å excitation, 0.1×10^{-9} Å range; $\text{Ar}/\text{F}_2/\text{Cl}_2 = 400/3/1$, 250 mW of 5145 Å excitation, 0.1×10^{-9} Å range; $\text{Ar}/\text{Cl}_2 = 100/1$, 150 mW of 4880 Å excitation, 0.3×10^{-9} Å range. All scan speeds $20\text{ cm}^{-1}/\text{min}$. (Reprinted from Ref.(36), by courtesy of the American Chemical Society).
- Fig. 5. Raman spectra of alkali metal-chlorine matrix reaction products. P denotes the Cl_2 precursor signal. Parameters: 0.3×10^{-9} Å range, 3 sec rise time, $20\text{ cm}^{-1}/\text{min}$ scan speed. Li, Na, K used 150 mW of 4880 Å excitation, Rb used 75 mW of 4765 Å and Cs used 600 mW of 4579 Å excitation. (Reprinted from Ref.(40), by courtesy of the American Chemical Society).

Fig. Cap. contd.

- Fig. 6. Resonance Raman spectrum of argon matrix-isolated Cs^+Cl_2^- at 16 K. Note resolution of $^{35}\text{Cl}_2^-$ and $^{35}\text{Cl}^{37}\text{Cl}^-$ splittings in overtones. Parameters: 75 mW of 4579 Å excitation, 20 $\text{cm}^{-1}/\text{min}$ scan speed, (A) 0.3×10^{-9} Å range, 3 sec rise time, (B) 0.1×10^{-9} Å range, 10 sec rise time. (Reprinted from Ref.(40), by courtesy of the American Chemical Society).
- Fig. 7. Resonance Raman spectra of Cs^+Cl_2^- as a function of laser excitation wavelength. 5145 and 4880 Å, 150 mW; 4765 Å, 100 mW; 4579 Å, 75 mW at sample. (Reprinted from Ref.(40), by courtesy of the American Chemical Society).
- Fig. 8. Raman spectra from 300-1100 cm^{-1} for oxygen difluoride in solid argon at 16 K using 4880 Å excitation, $\text{Ar}/\text{OF}_2 = 100$. Spectrum(a) initial spectrum recorded, arrows denote region of spectrum scanned after indicated time of exposure to the 4880 Å laser line. Spectrum (b) sample deposited for four hours with simultaneous 4880 Å photolysis for the last three hours, initial spectrum recorded. (Reprinted from Ref.(9), by courtesy of the American Institute of Physics).
- Fig. 9. Infrared and Raman spectra of Cl_2O and its photolysis products. $\text{Ar}/\text{Cl}_2\text{O} = 100$. Infrared spectrum recorded after 10 min of ultraviolet photolysis. Raman spectrum recorded with 300 mW of 4880 Å excitation.
- Fig. 10. Raman spectra produced by laser excitation of noble-gas halogen mixtures at 16 K. 30-50 mW of 4880 Å light at the sample. 1×10^{-9} Å range for $\text{Xe}:\text{F}_2$ and 0.1×10^{-9} Å range for others. continued...

Fig. Cap. contd.

Fig. 10. Inset 242 cm^{-1} band marked with an asterisk in Kr:Cl₂ spectrum contd.

was produced by microwave discharge, not by laser photolysis.

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Fig. 11. Infrared and Raman spectra of photolysed Xe:ClF samples with Raman spectrum of Xe:F₂:Cl₂ shown for comparison. The infrared study used blue mercury-arc photolysis; Raman studies employed 30-40 mW of laser power at the sample. (Reprinted from Ref. (53), by courtesy of the American Chemical Society).

Fig. 12. Resonance Raman spectra of iodine as a function of concentration in argon matrices. 5145 Å excitation and $50\text{ cm}^{-1}/\text{min}$ scan speed for all spectra. Ar/I₂ = 2500 and 1000, 125-150 mW laser power and $0.1 \times 10^{-9}\text{ Å}$ range. Ar/I₂ = 400/1 (low region) 15 mW, $0.1 \times 10^{-9}\text{ Å}$ range; (high region) 150 mW $0.3 \times 10^{-9}\text{ Å}$ range. (Reprinted from Ref. (58), by courtesy of D. Reidel Publishing Co.).

Fig. 13. Resonance Raman excitation profiles for the first seven overtones of argon matrix isolated monomeric I₂. The broken curves represent intensity ratio curves for the two cases of exact resonance. (Reprinted from Ref. (59), by courtesy of D. Reidel Publishing Co.).

Fig. 14. Laser excitation spectrum of argon matrix-isolated chlorine dioxide, Ar/ClO₂ = 150, using 200 mW of 4579 Å light. Resonance Raman progression in ν_1 of ClO₂ labelled $n\nu_1$. Fluorescence bands labelled a, b, c, and d. (Reprinted from Ref. (17), by courtesy Academic Press, Inc.).

Fig. Cap. contd.

Fig. 15. High-resolution fluorescence spectra of samples produced by the co-deposition of alkali metal atoms and CCl_4 diluted in argon using 4880 Å laser excitation. Top spectrum shows broad bands common to more concentrated samples. The two bottom spectra contrast dilute carbon isotopic samples. Dashed lines show that sharp bands in the concentrated sample coincide with bands in the middle spectrum and indicate the isotopic shifts of the a and d progressions. Broken line shows the coincidence of the isotopic broad band spectra which were also observed in the $^{13}\text{CCl}_4$ experiment. (Reprinted from Ref. (21), by courtesy of Academic Press, Inc.).

Fig. 16. Fluorescence spectrum of CBr_2 produced by 5682 Å excitation of a matrix prepared by codepositing Na atoms with an $\text{Ar/CBr}_4 = 1000/1$ gas mixture on a copper wedge at 12 K. (Reprinted from Ref. (68), by courtesy of the American Chemical Society).

XBL 753-734

Figure 1

XBL 753 - 5985

Figure 2

-45

XBL 754-6122

Figure 3

Figure 4

-47-

Figure 5

Figure 6

-49-

Figure 7

Figure 8

XBL 753-733

Figure 9

Figure 10

-53-

Figure 11

Figure 12

XBL 753-732

Figure 13

Figure 14

Figure 15

Figure 16

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