

- Amer. Chem. Soc.*, **96**, 7853 (1974).
- (3) W. R. Ware, "Creation and Detection of the Excited State," Vol. 1A, A. Lamola, Ed., Marcel Dekker, New York, N.Y., 1971, pp 213-302.
- (4) (a) C. Lewis, W. R. Ware, L. J. Doemeny, and T. L. Nemzek, *Rev. Sci. Instrum.*, **44**, 107 (1973); (b) W. R. Ware, L. J. Doemeny, and T. L. Nemzek, *J. Phys. Chem.*, **77**, 2038 (1973).
- (5) W. R. Ware and C. Lewis, *J. Chem. Phys.*, **57**, 3546 (1972).
- (6) C. Lewis and W. R. Ware, *Mol. Photochem.*, **5**, 261 (1973).
- (7) W. R. Ware, "Fluorescence Techniques in Cell Biology," A. A. Thaer and M. Sernetz, Ed., Springer-Verlag, New York, N.Y., 1973.
- (8) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N.Y., 1970, pp 309-311.

Synthesis of Noble-Gas Dihalides by Laser Photolysis of Matrix-Isolated Halogens

Wilmont F. Howard, Jr., and Lester Andrews*

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. Received April 9, 1974

Abstract: Condensed inert gas-halogen mixtures have been subjected to argon-ion laser and mercury-arc photolysis, resulting in the photoproduction of KrF₂, XeF₂, XeCl₂, and XeClF. Raman-active vibrations have been measured for all four species, and infrared bands of XeCl₂ and XeClF have been identified. The limits of noble-gas reactivity under these conditions have been explored.

Since Bartlett¹ synthesized the first rare gas compound in 1962, researchers have reported dozens of new species containing "inert" gases. Shortly thereafter, the matrix-isolation technique was directed to the production of rare gas compounds; Turner and Pimentel^{2,3} observed the infrared spectra of matrix-isolated XeF₂ and KrF₂ produced by ultraviolet irradiation of condensed Ar:Xe:F₂ and Ar:Kr:F₂ mixtures. A more recent infrared investigation of the condensed products of a xenon-chlorine glow discharge by Nelson and Pimentel⁴ identified XeCl₂ and assigned a band at 313 cm⁻¹ to ν_3 . In one of the early Raman matrix-isolation studies, Boal and Ozin⁵ produced XeCl₂ using the same synthetic approach and identified ν_1 at 253 cm⁻¹.

Matrix-Raman studies of OF₂ and Cl₂O in this laboratory^{6,7} have shown that laser photodecomposition of the precursor gives rise to new chemical species, namely OF, ClO, and Cl-ClO, which were directly observed by laser Raman spectroscopy. The matrix moderates photodecomposition by the laser and allows the observation of Raman spectra of the precursor and photolysis product.

Accordingly, we attempted a study of inert gas dihalides using laser photolysis of matrix-isolated halogens in the inert gas matrix. For compounds of limited stability, like XeCl₂, and the new mixed halogen species XeClF, this was a particularly useful approach.

Experimental Section

The experimental techniques, equipment, and manometric procedures have been described in previous papers from this laboratory.^{8,9} Most experiments involved a 2% halogen-rare gas mixture; for one investigation, an Ar:Xe:F₂ ratio of 100:1:1 was used. Halogens were purified as follows: F₂ (Allied) was passed slowly through a stainless-steel U tube precooled with liquid N₂; Cl₂ (Matheson) was condensed with liquid N₂ and outgassed; OF₂, ClF, and ClF₃ (Ozark-Mahoning) were used without further purification. Rb³⁷Cl (99% enriched) was reacted with concentrated HNO₃ to produce ³⁷Cl₂. The gaseous product was passed through Drierite, condensed, and outgassed.

Prior to sample preparation of fluorine-containing species, the stainless-steel vacuum line and sample can were passivated overnight with 30-50 Torr of the appropriate compound. Sample deposition was 3 mmol/hr for the Raman experiments and varied from an initial rate of 1 mmol/hr to a final rate of 2 mmol/hr for infrared studies. Gases were deposited on a tilted copper wedge (Raman) or a CsI window (infrared) maintained at 16°K. In some

of the present experiments, the inert gas-halogen mixture was subjected to microwave discharge prior to deposition. The microwave discharge (Burdick Corp., Milton, Wis., Model MW 200, 2450 MHz, 375 W) was maintained through the flowing gas stream using a standard Evenson-Broida cavity on a quartz spray-on nozzle (2-mm orifice). The cavity was placed 6 in. from the copper block; the glow extended through the orifice to within 1 cm of the copper block.

Raman spectra shifted 100-1200 cm⁻¹ from the laser source were recorded on a Spex Ramalog obtained by irradiation with the 4579, 4765, 4880, 4965, 5017, and 5145 Å argon ion and 3564 Å krypton ion laser lines using 50 to 150 mW of power at the sample unless otherwise specified.

Dielectric filters were employed to prevent unwanted plasma emission lines from appearing in the spectra, and band calibration was accomplished by superimposing emission lines on the spectrum during the running scan by replacing the dielectric filters with a neutral density filter. Infrared spectra were recorded on a Beckman IR-12, and calibrations were made relative to H₂O rotational lines present in the scans. Precision of band positions in infrared and Raman spectra is ± 1 cm⁻¹ or better (as listed). Slit widths were 500 μ for Raman surveys and varied from 3 cm⁻¹ at 300 cm⁻¹ to 1 cm⁻¹ at 800 cm⁻¹ during infrared scans.

Results

The experimental observations will be presented in turn for the several noble gas-halogen mixtures studied.

XeF₂ Raman. Laser irradiation of 2% F₂ in Xe yielded a Raman signal at 512.4 \pm 0.5 cm⁻¹, which is shown in Figure 1. This signal is in excellent agreement with the gas-phase assignment 514.5 cm⁻¹ to ν_1 of XeF₂ which is listed in Table I.¹⁰ Survey scans with blue (4579, 4765, and 4880 Å) excitation showed the XeF₂ band present immediately after sample exposure to the laser beam. Also, the signal intensity exhibited little change with prolonged irradiation from the beam. Green (5145 Å) excitation initially showed *no* signal in the spectrum, but 10 min of photolysis was sufficient to produce a weak band at the frequency shift appropriate to XeF₂. No signal was discernible for F₂, normally found about 890 cm⁻¹.

Streng and Streng¹¹ produced XeF₂ from sunlight irradiation of Xe:OF₂ mixtures, a reaction that was duplicated by laser photolysis of 2% OF₂ in Xe condensed at 16°K. The resultant XeF₂ band (512.5 \pm 1.0 cm⁻¹) was the strongest observed in this series of experiments and was even

noted with 3564-Å excitation, which normally yields very weak Raman signals. OF₂ is known to be an OF radical precursor,⁶ but there was no detectable OF signal at 1029 cm⁻¹. Other bands were observed in these spectra at 541 cm⁻¹, 463 (ν₂, OF₂), 915 (ν₁, OF₂),⁶ 423.0, and a weak band around 375 cm⁻¹. The XeF₂ band was roughly five times as strong as the other Raman bands.

A diluted Xe:F₂ sample (Ar:Xe:F₂ = 100:1:1) showed nearly identical behavior as the Xe:F₂ samples discussed above. Irradiation with 5145 Å produced no XeF₂ signal even after 30 min of photolysis. The higher energy Ar⁺ laser lines (4579–4880 Å) and the Kr⁺ 3564-Å beam all produced an XeF₂ signal showing a frequency shift of 512.2 ± 1.0 cm⁻¹. This band was roughly a factor of 10 weaker than the XeF₂ signal from the Xe matrix.

Attempts to make XeF₂ using other F atom sources, such as ClF and ClF₃, were unsuccessful. However, photolysis of Xe:ClF mixtures had unexpected, but not unwelcome, results, which will be discussed below.

XeCl₂ Raman. First attempts to synthesize XeCl₂ in a matrix involved passing a 2% Cl₂-Xe mixture through a microwave discharge.⁴ Initial survey scans with 5145- and 4880-Å excitation showed no signal other than the chlorine fundamental at 540 cm⁻¹. However, subsequent scans with the 4880-Å beam revealed a band at 254.6 ± 0.8 cm⁻¹ whose intensity grew with laser exposure time (see Figure 2). This band was assigned to ν₁ of XeCl₂ in agreement with earlier workers.⁵

Since microwave discharge produced less new signal than laser photolysis, several experiments were run without discharge in an attempt to produce XeCl₂ by laser photolysis of the condensed elements. Repeated scans with 5145-Å excitation (50 mW of power at the sample) produced no signal at 255 cm⁻¹, but 30 mW of 5017-Å light showed a measurable band after 15 min of photolysis. This signal continued to grow slowly for the duration of the photolysis (75 min), which is illustrated in Figure 2. This identifies the lowest energy laser beam capable of photoproducing XeCl₂. Excitation with 30 mW of 4880-Å light caused rapid growth of the XeCl₂ signal, which maximized with 35 min of irradiation and then decreased gradually as the laser beam caused product decomposition. Photolysis with 4765-Å light (25 mW) caused an intense signal due to XeCl₂ within 2 min, and this band remained at constant intensity, within experimental variations, for at least 30 min of scanning time. Lastly, 4579-Å photolysis (15 mW) yielded the XeCl₂ signal, which maximized in about 8 min, then rapidly decomposed, as is shown in Figure 2.

A ³⁷Cl₂ sample (99% enriched) was prepared and laser photolyzed in a Xe matrix. Only two bands were noted in the Raman spectrum: the ³⁷Cl₂ molecular vibration at

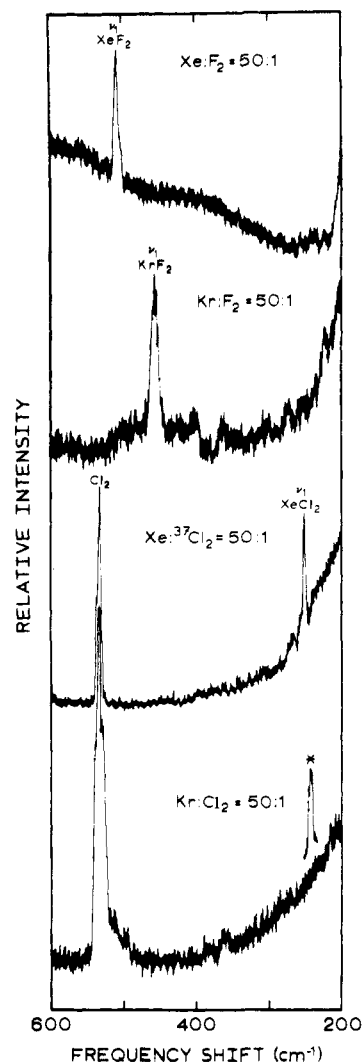


Figure 1. Raman spectra of laser-irradiated noble-gas halogen mixtures at 16°K: 30–50 mW of 4880 Å at the sample; 50 cm⁻¹/min scan speed; 1 × 10⁻⁹ A range for Xe/F₂, 0.1 × 10⁻⁹ A range for others; 3 sec rise time. Band marked with an asterisk was produced by microwave discharge, not by laser photolysis.

527.9 ± 0.6 cm⁻¹, and the Xe³⁷Cl₂ band at 247.7 ± 0.5 cm⁻¹. Both signals exhibited isotopic shifts consistent with ³⁷Cl substitution.

XeCl₂ Infrared. As in the Raman studies, a 2% Cl₂:Xe mixture was used for this work. After 6–8 hr of deposition, the sample was irradiated with light from a mercury-arc lamp passed through both a water filter and Corning filters

Table I. Comparison of Gas-Phase, Solid, and Matrix-Isolated Frequencies for Rare Gas Dihalide Frequencies

Halide	Gas-phase frequency, cm ⁻¹	Solid frequency, cm ⁻¹	Matrix-isolated frequency, cm ⁻¹	Assignment
KrF ₂	449 ^a	462.3 ^a	452.4 ^b	ν ₁ (R)
	232.6 ^a		236 ^c	ν ₂ (ir)
	588 ^a		580 ^c	ν ₃ (ir)
XeF ₂	514.5 ^d	497 ^e	512.4 ^b	ν ₁ (R)
	213.2 ^c			ν ₂ (ir)
	555 ^e		547 ^e	ν ₃ (ir)
XeCl ₂ ^g			547 ^f	ν ₁ (R) Xe ³⁸ Cl ₂
			253, ^h 255.0, ⁱ 254.6 ^b	ν ₁ (R) Xe ^{35,37} Cl ₂
			251.5 ⁱ	ν ₁ (R) Xe ^{35,37} Cl ₂
			248.0, ⁱ 247.7 ^b	ν ₁ (R) Xe ³⁷ Cl ₂
XeClF ^g			313, ^j 313 ^b	ν ₃ (ir)
			316 (ir), 315.5 (R) ^b	ν ₁
			480.6 (ir), 479.5 (R) ^b	ν ₃

^a Reference 12. ^b This work. ^c Reference 2. ^d Reference 10. ^e J. G. Malm, H. Selig, J. J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 199 (1965). ^f Reference 3. ^g ν₂ of XeCl₂ and XeClF are unknown. ^h Reference 5. ⁱ Reference 19. ^j Reference 4.

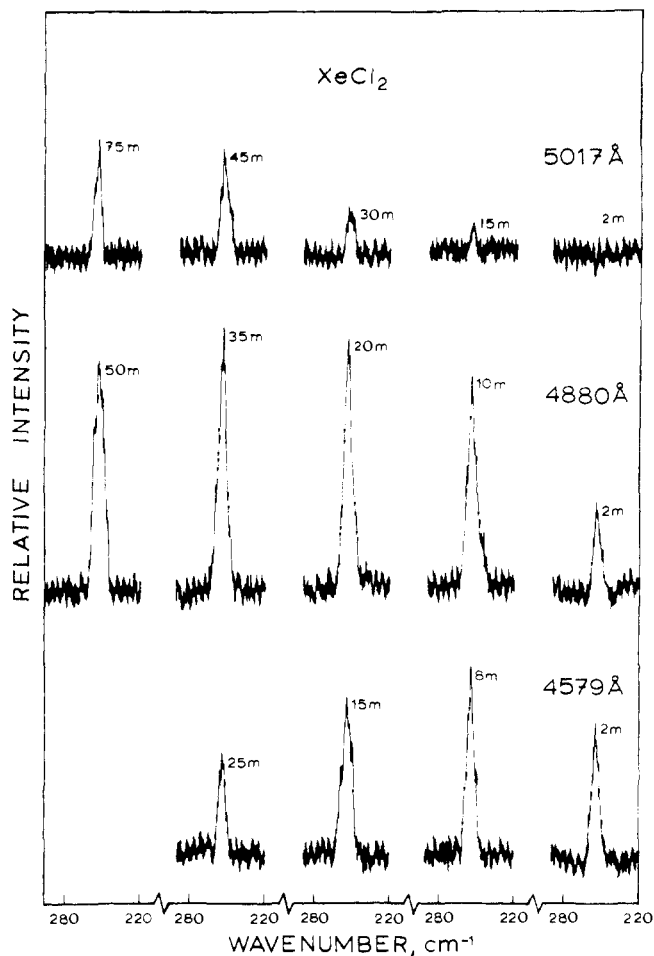


Figure 2. Time dependence of XeCl_2 Raman signal growth using different laser lines for photolysis and Raman scattering. Laser power at the sample: 5017 Å, 30 mW; 4880 Å, 30 mW; 4579 Å, 15 mW. Scan speed: 20 $\text{cm}^{-1}/\text{min}$. Range: 0.1×10^{-9} Å. Rise time: 3 sec.

No. 4303 and 306, effectively stopping radiation below 4000 and above 5650 Å. Thirty minutes of photolysis produced a symmetric band centered at 313 cm^{-1} (0.08 o.d., 4 cm^{-1} half-width); this signal was maximized (0.18 o.d.) after 105 min of photolysis, the last 15 min without the Corning filters; further photolysis slowly eliminated the band. The band is probably due to ν_3 of XeCl_2 , in agreement with Nelson and Pimentel;⁴ a second experiment under the same conditions successfully reproduced the 313- cm^{-1} feature.

XeCIF Raman. The spectrum resulting from 4765-Å laser irradiation of 2% CIF in Xe is shown in Figure 3. Bands appearing in the scan are identified as follows: ^{35}CIF at 751 cm^{-1} , Cl_2 at 541 cm^{-1} , two new bands at $479.5 \pm 0.5 \text{ cm}^{-1}$ and $315.5 \pm 0.5 \text{ cm}^{-1}$, and a weak XeCl_2 signal at about 255 cm^{-1} . Note that no XeF_2 was produced by laser photolysis of CIF in solid Xe. Full growth of the new bands was accomplished in less than 5 min with 4579- and 4765-Å laser excitation, with very little tendency for signal decay. Band growth with 4880-Å light was much slower; nearly 30 min of photolysis was needed before maximum band intensity was attained.

A mixed $\text{Cl}_2\text{-F}_2$ sample ($\text{Xe}:\text{Cl}_2:\text{F}_2 = 100:1:1$) was subjected to laser photolysis, and the resulting Raman spectrum may be seen in Figure 3. As in previous Xe-F_2 runs, no signal due to F_2 was observed, but bands attributable to molecular Cl_2 , ν_1 of XeF_2 and XeCl_2 , and the new 316- cm^{-1} signal were noted after irradiation with any of the blue laser lines.

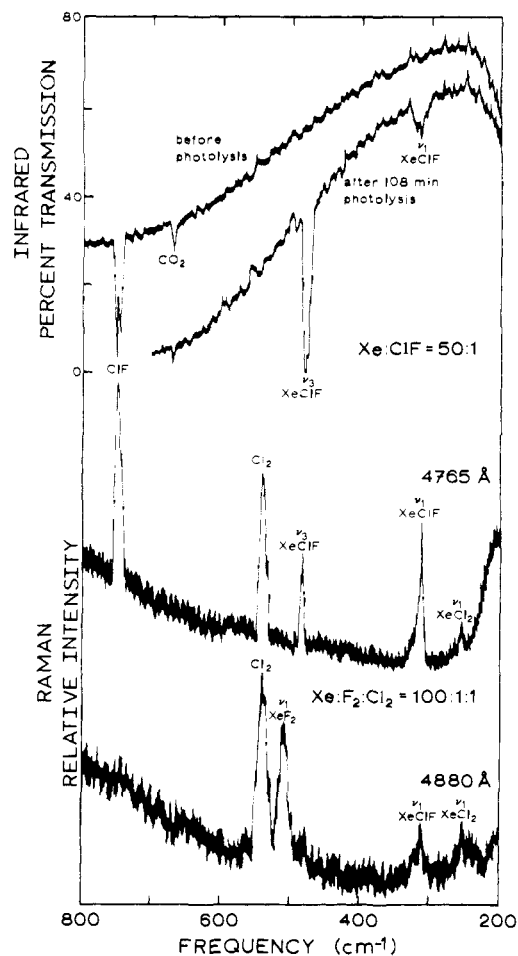


Figure 3. Infrared and Raman spectra of photolyzed Xe/CIF samples with Raman spectrum of $\text{Xe/F}_2/\text{Cl}_2$ shown for comparison. The infrared study utilized blue mercury-arc photolysis; Raman studies employed 30–40 mW of laser power at the sample.

XeCIF Infrared. Six to eight hours of slow deposition of 2% CIF in Xe without irradiation was followed by several Hg-arc photolysis periods as deposition was concluded. As before, Corning filters No. 4303 and 306 were employed to eliminate the hard uv light. Figure 3 shows the appropriate spectrum before and after photolysis, with the following assignments: ^{35}CIF and ^{37}CIF at 751.9 (1.3 o.d.) and 745.0 cm^{-1} (0.46 o.d.), respectively. New bands appeared at 480.6 cm^{-1} (completely absorbing), with an unresolved shoulder, and at 316 cm^{-1} (0.10 o.d.), which are in agreement with the new Raman signals. Other than a small band from CO_2 impurity, there were no other signals between 200 and 800 cm^{-1} .

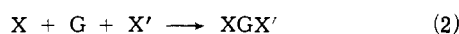
KrF₂ Raman. Laser photolysis of Kr:F_2 (50:1) mixtures resulted in the growth of an intense Raman band shifted $452.4 \pm 0.6 \text{ cm}^{-1}$ from the exciting line. The spectrum is illustrated in Figure 1. This feature is assigned to ν_1 of KrF_2 , since the gas-phase mode has been reported¹² at 449 cm^{-1} . No signal was noted in repeated spectra using the 5145-Å laser beam, but 30 min of 4965-Å laser illumination caused the appearance of a moderately intense KrF_2 signal. The other blue laser lines (4579, 4765, and 4880 Å) produced an immediate strong KrF_2 band in the Raman survey scans. As with XeF_2 , this band showed no sign of laser-induced deterioration. A very weak signal at $890 \pm 2 \text{ cm}^{-1}$ was attributed to molecular F_2 .

Other Species. Several experiments were run in an attempt to photosynthesize the species XeBr_2 , KrCl_2 , and KrCIF . No trace of a new xenon compound was found after

1 hr of laser photolysis of a condensed 2% Br-Xe mixture.^{13a} The Raman spectrum of a Kr:Cl₂ (=50:1) sample is shown in Figure 1; no new bands were produced by laser irradiation. However, when a Kr:Cl₂ sample was passed through the microwave discharge immediately prior to deposition, the Raman spectrum revealed two signals, one at 539 cm⁻¹ due to chlorine and a new band at 242 cm⁻¹. The latter signal (denoted by an asterisk and inset in Figure 1) was degenerated by exposure to the laser beam, and normal laser photolysis of Kr-Cl₂ samples untreated with the discharge failed to recreate the band. Photoproduction of KrClF from 2% ClF-Kr mixtures was attempted; apart from the ClF (764 ± 2 cm⁻¹) and Cl₂ (impurity) signals, no Raman bands were observed in the region 150–1000 cm⁻¹. The infrared ClF signal appeared at 763.6 (completely absorbing) and 756.5 cm⁻¹ (0.97 o.d.) due to Cl isotopic splitting, and aggregate bands were observed at 754, 747, and 740 cm⁻¹; no new infrared bands were produced upon photolysis by blue mercury arc light. Repeated laser-Raman scans of Ar:F₂ and Ar:Cl₂ samples, with and without microwave discharge, showed no trace of new features.

Discussion

Laser photoproduction of rare gas dihalides from the condensed halogen-rare gas mixtures is a novel, but not unexpected, means of preparation of these species. The lighter halogen convergence limits are listed in Table II, and it is obvious that blue light will dissociate these compounds (the absorption continuum of F₂ extends to nearly 5000 Å). Thus, the high-photon-density blue laser beams should easily separate molecular halogens into two atoms. The atoms are in such close proximity to the matrix host that it becomes a simple process to combine with a rare gas atom in an adjacent matrix site. The overall reaction may be shown as



where X denotes a halogen, G the rare gas, and X and X' may or may not be the same species. The halogen molecules listed in Table II are expected to undergo blue laser dissociation, and the atoms might react with the appropriate rare gas under ideal conditions.

New bands were observed in infrared experiments at 480.6 and 316 cm⁻¹ following blue light photolysis of Xe:ClF samples and at 479.5 and 315.5 cm⁻¹ in similar Raman experiments using 4765-Å irradiation. Following the above mechanism, these new bands are assigned to the heretofore unreported XeClF species. The intense infrared band and weaker Raman signal are probably more antisymmetric in character; they are assigned to ν_3 . The more intense Raman band and weaker infrared band are probably more of a symmetric type mode and are denoted as ν_1 .

Bondybey and Pimentel^{13b} have passed mixtures of argon, xenon, and ClF through a glow discharge⁴ and condensed the effluent gases at 20°K. The infrared spectrum contained strong bands at 543 and 311 cm⁻¹ due respectively to XeF₂ and XeCl₂, a new band at 480 cm⁻¹, and a new shoulder on the high frequency side of the 311-cm⁻¹ XeCl₂ band. These workers concluded that the 480-cm⁻¹ band is due to the Xe-F stretch of XeClF and that the Xe-Cl stretch is near 315 cm⁻¹. These independent results support the present assignments to XeClF produced by mercury arc and laser photolysis.

Comparison of the stretching frequencies for XeF₂, XeClF, and XeCl₂ listed in Table I shows a consistency which supports the assignments to XeClF and XeCl₂. The

Table II. Dissociation or Convergence Limits for the Lighter Halogen Molecules^a

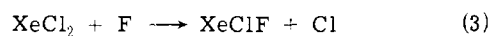
Halogen	Dissociation, cm ⁻¹ (Å)
F ₂	35,400 ^b -20,000 (2825-5000)
ClF	21,508 (4650)
Cl ₂	20,893 (4786)
Br ₂	19,585 (5106)

^a G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, Van Nostrand, Princeton, N. J., 1950. ^b Continuum maximum.

average XeF₂ matrix frequency ($\nu_1 + \nu_3$) ($\frac{1}{2}$) is 530 cm⁻¹ and the average XeCl₂ frequency is 284 cm⁻¹. The higher normal mode for XeClF at 480 cm⁻¹ falls *below* the XeF₂ average, whereas the lower vibration of XeClF is approximately the same *above* the XeCl₂ average. This comparison is based upon the assumption that the XeClF bond properties are analogous to XeF₂ and XeCl₂.

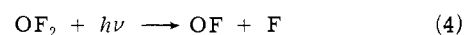
The mobility of F atoms in a rigid matrix was demonstrated in the Ar:Xe:F₂ (= 100:1:1) experiment. There is a statistical chance of 1 in (100 × 100)/12 = 833 that a Xe atom and a F₂ molecule will occupy adjacent matrix sites in the closest packed solid-argon lattice, thus allowing immediate XeF₂ formation upon photodissociation of F₂. If this were the only means of forming XeF₂, there would not be sufficient fluoride produced to give a respectable Raman signal. In actual practice, the XeF₂ Raman band was 10% as strong as the signal produced from undiluted Xe:F₂ runs. This is significantly stronger than would be predicted on statistical grounds and points out the ability of F atoms to migrate through the matrix and react according to reaction 2.

In the Xe:Cl₂:F₂ experiment, the results (see Figure 2) suggest that not all the dissociated F atoms react immediately with Xe, but some diffuse through the matrix, producing XeClF according to reaction 3. Reaction 3 is upheld by



the relative stabilities of the two rare gas compounds; XeClF is the stronger of the pair, and is much more resistant to laser photodecomposition. Also, there was no evidence for ClF formation, as the blue laser beam would retard, if not prevent, the combination of F and Cl atoms.

Another case that demonstrated some F atom mobility in solid xenon was the formation of XeF₂ and XeF₄ (based on the agreement between the 541-cm⁻¹ matrix and 543-cm⁻¹ solid XeF₄ Raman bands) during laser photolysis of frozen Xe:OF₂ samples. Irradiation of OF₂ with 2480–4950 Å light causes the following decompositions.¹⁴



In an earlier study, Andrews⁶ demonstrated that reactions 4 and 5 occur in an argon matrix by monitoring the growth of OF, F₂, and O₂ Raman signals. Thus, after XeF₂ is formed *via* reactions 1 and 2, diffusing F atoms may add to this molecule, producing XeF₄. The ratio of XeF₂:XeF₄ band intensities was about 5:1, furthering the argument for F atom migration, even in the rigid Xe matrix. Since the yield of XeF₂ was greatest with the OF₂ reagent, these results imply that OF₂ photolysis *via* reaction 4 occurs more readily than F₂ dissociation. The 423-cm⁻¹ Raman signal was unique to the Xe:OF₂ system; it could be due to a FXeOF species but this possibility must be considered tentative.

It is noteworthy that no XeF₂ was produced in the Xe:ClF experiment, which indicates immediate reaction of F and Cl with an adjacent Xe atom. Appreciable diffusion of

F atoms from their site of photoproduction surely would have produced XeF₂. The absence of XeF₂ in the Xe:ClF experiments supports the mechanism set forth in reactions 1 and 2.

The behavior and position of the XeF₂ Raman band was entirely as expected. XeF₂ is stable with respect to photolysis, with no absorptions above 2300 Å,¹⁵ and the species produced in the matrix was not adversely affected by the laser. Further, the ν_1 frequency shift of matrix-isolated XeF₂ is closer to the gas-phase value than the solid-phase frequency (see Table I). Experience has shown this to be the case for most matrix-isolated species with covalent bonding.

The absence of a F₂ Raman signal in the Xe:F₂ experiments is not unusual; this band is very weak under the best of circumstances, and Xe matrices tend to scatter the exciting line. Thus an already poor signal is further diminished. The same argument applies to condensed Kr:F₂ samples, although a weak F₂ band was observed.

Laser photoproduction of KrF₂ was straightforward, but proceeded more slowly than XeF₂ formation. This is consistent with the infrared work³ where hours of mercury-arc photolysis were required for KrF₂ synthesis whereas only minutes were needed for XeF₂. Irradiation of Kr:F₂ samples with the 4965-Å laser line produced a viable KrF₂ Raman signal after 30 min, but 75 min of photolysis with 5017-Å light yielded no trace of the difluoride. Thus, the low-energy limit for F₂ dissociation in Kr falls at about 20,000 cm⁻¹. As with XeF₂, the KrF₂ Raman band showed no sign of laser decomposition, and actually continued to increase slowly in intensity for the duration of the survey scans, consistent with the stability of KrF₂.

Before this work, the XeCl₂ species had been observed only as a glow discharge product of xenon and chlorine. There is some controversy in the literature as to the identification of microwave discharge products as ions or radicals; see, for example, the HCl₂ vs. HCl₂⁻ case.^{16,17} Owing to the proximity of the XeCl₂ Raman signal at 255 cm⁻¹ to the Cl₂⁻ fundamental¹⁸ at 246 cm⁻¹, we decided to seek other synthetic approaches to XeCl₂.

In the present Xe:Cl₂ blue laser studies, the ³⁵Cl₂ band at 254.6 ± 0.5 cm⁻¹ shifted to 247.7 ± 0.5 cm⁻¹ with the ³⁷Cl₂ reagent; the calculated shift for a pure chlorine vibration is 247.6 cm⁻¹. German and Beattie¹⁹ have also produced the new signal with 4880-Å photolysis of Xe:Cl₂ samples; these workers observed a well-resolved triplet with components at 255.0, 251.5, and 248.0 cm⁻¹ with a 9:6:1 relative intensity ratio. This triplet specifically indicates a mode involving *two* (equivalent) chlorine atoms. This rules out the only other species that could be synthesized from photolytically produced chlorine atoms, namely Cl₃ radical. Clearly, ions such as Cl₂⁻ cannot be created in Raman-observable quantities by 4880-Å light owing to the much higher ionization energies of Cl, Cl₂, and Xe. Accordingly, the only species consistent with the isotopic frequency shift and intensity data which can be produced with the available energy is XeCl₂; the intense Raman band is clearly ν_1 , the symmetric Xe-Cl stretch. The same rationale applies to the blue light production of the 313-cm⁻¹ infrared band, which confirms the Nelson and Pimentel⁴ ν_3 assignment to XeCl₂.

Infrared and Raman surveys of irradiated Kr:ClF and Kr:Cl₂ samples were void of signals below 500 cm⁻¹. The band marked with an asterisk in Figure 1 evolved from a Kr:Cl₂ microwave discharge experiment; it could not be produced with discharge of Ar:Cl₂ mixtures. Identical experiments in the infrared by Nelson and Pimentel²⁰ showed

a structured band at 373 cm⁻¹ which was assigned to ν_3 of Cl₃. However, very recent studies of the sodium-chlorine matrix reaction have produced this infrared band which was assigned to ν_3 of Cl₃⁻ in the Na⁺Cl₃⁻ species; a 275-cm⁻¹ Raman band in similar samples was attributed to ν_1 of this molecular anion.²¹ Accordingly, the 242-cm⁻¹ Raman band produced by the krypton-chlorine glow discharge is probably due to the same species observed by Nelson and Pimentel,²⁰ which we now believe is the isolated trichloride anion. The 242-cm⁻¹ Raman band is tentatively assigned to ν_1 of isolated Cl₃⁻. Its instability to blue laser light is probably due to photodetachment of the anion electron or photodissociation to Cl₂ and Cl⁻.

Both irradiation and microwave discharge of Xe:Br₂ mixtures caused no change in the Raman spectrum, which showed an intense band at 297 cm⁻¹ assigned to bromine. Due to the instability and extreme reactivity of BrF, no attempt was made to photoproduce XeBrF, although this compound might be marginally stable in a cryogenic matrix.

Conclusions

In a series of Raman and infrared matrix studies, we have succeeded in photoproducing the rare gas compounds KrF₂, XeF₂, and XeCl₂ and a new species XeClF. In the Raman experiments, the noble-gas halides were produced by the laser exciting line dissociating the halogen into atoms which subsequently reacted with the matrix host. We have confirmed the extensive mobility of F atoms in argon matrices and have shown that the compounds listed above mark the limit of noble-gas dihalide formation by photolysis at cryogenic temperatures. These boundaries were reached when several attempts to produce ArF₂, KrClF, KrCl₂, and XeBr₂ by *in situ* photolysis or microwave discharge prior to condensation met with no success.

Acknowledgment. The authors gratefully acknowledge financial support for this research by the National Science Foundation under Grant GP-38420X. We thank Dr. W. B. Fox for the F₂, ClF, and ClF₃ samples and Drs. A. German and I. Beattie for permission to quote their data before publication.

References and Notes

- (1) N. Bartlett, *Proc. Chem. Soc., London*, 218 (1962).
- (2) J. J. Turner and G. C. Pimentel, *Science*, **180**, 974 (1963).
- (3) J. J. Turner and G. C. Pimentel, "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, pp 101-105.
- (4) L. Y. Nelson and G. C. Pimentel, *Inorg. Chem.*, **6**, 1758 (1967).
- (5) D. Boal and G. A. Ozin, *Spectrosc. Lett.*, **4**, 43 (1971).
- (6) L. Andrews, *J. Chem. Phys.*, **57**, 51 (1972).
- (7) F. K. Chi and L. Andrews, *J. Phys. Chem.*, **77**, 3062 (1973).
- (8) L. Andrews, *J. Chem. Phys.*, **48**, 972 (1968).
- (9) D. A. Hatzenbuehler and L. Andrews, *J. Chem. Phys.*, **56**, 3398 (1972).
- (10) P. Tsao, C. C. Cobb, and H. H. Claassen, *J. Chem. Phys.*, **54**, 5247 (1971).
- (11) L. V. Streng and A. G. Streng, *Inorg. Chem.*, **4**, 1370 (1965).
- (12) H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, *J. Chem. Phys.*, **42**, 1229 (1965).
- (13) (a) ¹²⁹XeBr₂ has been produced by β decay of ¹²⁹Br₂⁻, but this can hardly be considered chemical synthesis. See G. J. Perlow and H. Yoshida, *J. Chem. Phys.*, **49**, 1474 (1968). (b) V. E. Bondybey, Ph.D. Thesis, University of California, Berkeley, Calif., 1971, and G. C. Pimentel, personal communication, 1974.
- (14) A. Glissman and H.-J. Schumacher, *Z. Phys. Chem., Abt. B*, **24**, 328 (1934).
- (15) E. G. Wilson, J. Jortner, and S. A. Rice, *J. Amer. Chem. Soc.*, **85**, 813 (1963).
- (16) P. N. Noble and G. C. Pimentel, *J. Chem. Phys.*, **49**, 3165 (1968).
- (17) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **53**, 2034 (1970).
- (18) W. F. Howard, Jr., and L. Andrews, *J. Amer. Chem. Soc.*, **95**, 2056 (1973).
- (19) A. German and I. Beattie, unpublished results.
- (20) L. Y. Nelson and G. C. Pimentel, *J. Chem. Phys.*, **47**, 3671 (1967).
- (21) W. F. Howard, Jr., and L. Andrews, *Inorg. Chem.*, to be published.