Emission spectra from the vacuum ultraviolet to the visible region have been obtained from the rare gas dimers of helium, neon, argon and krypton and from the xenon oxide excimer. Several new discrete and diffuse bands together with both structured and unstructured continua have been observed and some have been tentatively identified with specific electronic states of the molecule. Several of these spectra appear only under specific excitation conditions and were thus revealed in this research for the first time. Significant new results for helium and argon dimers have been obtained.
A study of the higher excited states of rare gas - oxide and sulfide excimer is underway.
RADIATION AND LASER POTENTIAL OF
HOMO- AND HETERO-NUCLEAR RARE-GAS DIATOMIC MOLECULES

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RESEARCH OBJECTIVES

This research involves a spectroscopic investigation of the electronic, vibrational and rotational levels of homo- and hetero-nuclear rare gas dimers and excimers of current interest for the development of middle and VUV lasers. The aim of the research is to obtain an unambiguous identification of the origin of the emission bands of rare gas dimers and rare gas halide and chalcogenide excimers and determine the energies of these excited states and derive accurate molecular constants and potential energy curves.
I. STATUS OF THE RESEARCH

The first three months of the current grant period (October 1, 1976 to December 30, 1976) were devoted to installing and aligning the VUV spectrographs and constructing appropriate light sources and gas handling systems. From January 1, 1977 on, we have been studying emission spectra from the dimers Ar$_2$, Ne$_2$ and He$_2$ in the 500-2000 Å region, principally with a 2 meter spectrograph. Emission spectra were taken under a variety of excitation conditions with both room temperature and liquid nitrogen cooled discharges. Excitation systems differing principally in current density and ratio of high to low frequency components were used to selectively excite high electronic states for study. Recently we have developed an efficient method for exciting rare gas oxide excimers utilizing an R.F. discharge in the megacycle frequency region. Since the data are not completely analyzed as yet, only a few of the most interesting results and interpretations are described below.

A. Argon Dimer: Ar$_2$

Dimer spectra in argon were excited principally in a Tesla coil discharge. Three series of band groups were observed and measured in the 1067-1222 Å region. One series appears between
1073-1125 Å. It consists of 17 band groups each of which consist of several sharp bands and associated dissociation continuum. This is the band series represented by the electronic transition $4s^2 3p^6 \frac{1}{2}^+ (0^+_g) \rightarrow 3p^6 \frac{1}{2}^+ (0^+_g)$, the lower state being the ground state of $\text{Ar}_2$. This transition represents the band system I classified from absorption spectra.

A second band series occurs in the 1067-1222 Å region. It consisted of 22 band groups but none of the individual group was resolved into a number of discrete bands even in the spectrum taken with higher order of the high resolution spectrograph. We classified this series as due to transition $4s \frac{1}{2}^+_u (0^+_u) \rightarrow 3p^6 \frac{1}{2}^+_g (0^+_g)$, which corresponds to the band system II of $\text{Ar}_2$ previously observed in absorption. The four well-resolved discrete bands observed in absorption in the 1068-1073 Å region of this band system are not observed in emission and instead this region is occupied by three diffuse structureless emission spectra. Serious inconsistencies observed between the emission and absorption spectra of this system can be reconciled by the suggestion that since this is a strong band system, individual emission bands will be easily absorbed by small amounts of argon dimer existing in its ground state in the discharge. The dissociation continuum, which appears in association with the individual band group, will not
easily be self absorbed and as a result we observe a series of short continua.

In the region between the two resonance lines of ArI at 1048 and 1066 Å, a number of emission bands and a large number of sharp absorption bands are observed simultaneously. We believe, in this stage of the work, that these all belong to band system III produced by transition $4s^+ \leftrightarrow 3p^6 \, 1^+_\Sigma^+ (0^+_g)$, again the lower state is the ground state. Since this band system is the strongest of the three, the absorption spectra dominate and this accounts for the observation of many sharp absorption and apparent emission bands.

In addition to the three band systems stated above, we also observed 15 emission bands which appeared in the 1110-1157 Å region. When argon was mixed with other rare gases such as helium or neon the bands appear slightly enhanced. The bands appear stronger when argon pressure is low, ~1 torr, and they are excited much more strongly by pulsed transformer discharge rather than by a Tesla coil discharge. The individual bands are quite diffuse yet show a degradation toward short wavelength. The origin of these is unknown at this time. By analogy with Mulliken's potential curves for Xe$_2$, these bands could be produced by transitions from one or more of the 5dII ($0^+_u$, 1$^+_u$) states to the ground state. In addition to these band spectra, we also observe the well known emission continua
called "first continuum" with a peak at 1070 Å and "second continuum" with a peak at 1270 Å. By buffering argon with helium or neon we find that band system II vanishes simultaneously with the second continuum. Both may be restored by increasing the argon concentration. This strongly suggests that the second continuum arises from the same electronic transition responsible for band system II and that the peak of the second continuum is due to transitions from the lowest upper vibration level \( v' = 0 \) to the purely repulsive part of the ground state potential. The origin of the first continuum is as yet unknown. The spectrum near the resonance line at 1066.6 Å within about ±9 Å is a mixture of a) broadened resonance line, b) a small part of band systems I and II and c) a true continuum. It is difficult, however, to find energy levels which will produce a pure continuum in this region in combination with the ground state.

B. Neon Dimer: \( \text{Ne}_2 \)

The \( \text{Ne}_2 \) spectrum was studied under a variety of excitation conditions in the 600-1000 Å region. Band system I, which corresponds in electronic assignment to band system II of \( \text{Ar}_2 \), was observed in emission. Approximately seven band groups were identified in the 744-754 Å region. Each individual group consists of two or three sharp bands and associated dissociation
continua. These band groups are produced by the transition
$3s^1\Sigma_u^+ (0_u^+) \rightarrow 2p^6^1\Sigma_u (0_g^+)$. No band groups, which correspond
to band system I of Ar$_2$, were observed in neon. An additional
band group, which corresponds to Ar$_2$ band group observed in
the 1110-1157 Å region, was observed in the region 759-775 Å.
the suggestion made for the origin of the similar group in
Ar$_2$ probably applies also to neon.

C. Helium Dimer: He$_2$

The He$_2$ spectrum is well known in the 500-1100 Å region,
however, we have found that the character of the spectrum is
highly dependent on the type of excitation. With low current,
high frequency excitation from a Tesla coil the intensity
ratio of the two known prominent peaks at 674 and 818 Å of the
helium continuum is reversed from that normally observed so
that in our work the 674 Å peak becomes the stronger. In
addition, the two strong Hopfield bands at 648 and 662 Å do
not appear but are replaced by three bands at 645, 651 and
659 Å. It is thus possible to study these new bands for the
first time. These new bands appear to terminate on the ground
state as do the Hopfield bands. Further study of these bands
and others in neon and helium is continuing.

Analysis of the bulk of the above results is still under-
way but already a few important new results have been obtained.
One of these is a determination of the $^1\Sigma_u^+$ to $^3\Sigma_u^+$ state separation in $\text{Ar}_2$. A paper reporting this result is being written. In addition, a method of studying the helium bands at 645, 651 and 659 Å in He has been developed. These bands apparently originate on states different from those of the Hopfield bands. Further work on these bands is in progress.

D. Krypton Dimer: $\text{Kr}_2$

The emission spectrum of the krypton dimer in the VUV region is not well known except for two continua, one peaking at about 1236 Å (first continuum) and the other at 1500 Å (second continuum).

In this work $\text{Kr}_2$ is excited by a transformer or a Tesla coil discharge in the pressure range 1-300 torr. The following is a summary of our recent results in $\text{Kr}_2$.

1. With the Tesla coil discharge, a long train of wavy structure was observed for the first time. It consisted of about 19 broad peaks and occupies the region 1250-1405 Å. It is very similar to band system II of $\text{Ar}_2$ in the following respects: a) it has a diffuse appearance and no discrete bands were observed; b) its location with respect to the KrI resonance line, 1236 Å, and the second continuum, 1500 Å; c) the number of diffuse peaks (-19) observed; d) energy
separation of consecutive peaks. Because of these similarities we concluded that the wavy structure belongs to band system II of Kr₂.

2. By using krypton mixed with helium or neon in the ratio 1:10-30, band system II was almost completely eliminated from the spectrum whereas system I remained strong. In the case of Ar₂, intensity of the second continuum varied in parallel to that of band system II; for example, when the band system disappeared completely, the second continuum also vanished. This relation does not hold in Kr₂ as strictly as in Ar₂, although the second continuum greatly weakened, it was still observable when band system II had disappeared. The observed evidence, however, still indicates, again as in Ar₂, that the second continuum belongs to band system II and both of these are the product of the electronic transition 5s \( \frac{1\Sigma_u^+}{0_u^+} \rightarrow \frac{1\Sigma_g^+}{0_g} \), the lower state being the ground state.

3. We failed to observe band system III, 5s' \( 0_u^+ \rightarrow \frac{1\Sigma_g^+}{0_g} \), in emission and instead they appeared in absorption mixed with several of structureless emission bands which have not been previously observed in absorption (see J. Chem. Phys. 59, 5160 (1973)). The emission bands could be interpreted as produced by a free-free transition proposed for the 600 Å bands of He₂ by Mies and Smith (see J. Chem. Phys. 45, 994 (1966)).
4. Five narrow but diffuse emission bands were observed at the immediate short wavelength side of the second resonance line, 1165 Å, of KrI. The observed wavelengths agree well with those of the absorption bands previously observed (see J. Chem. Phys. 29, 5160 (1973)). The origin of these is yet to be explained.

5. Ten diffuse bands, all degraded toward short wavelengths, were observed in the 1323-1363 Å region. These can be produced strongly when one torr of krypton is excited by transformer pulsed discharge. With respect to a) the mode of excitation; b) general appearance and c) location relative to those of the first resonance line of KrI and the second continuum, the observed bands are very similar to the diffuse bands of Ar₂ mentioned earlier in this report. A quick survey was carried out on the Xenon dimer and it showed about ten diffuse emission bands in the 1585-1648 Å region which are very similar to the above Kr₂ diffuse bands. Presently, we are trying to identify the origin of these bands which should be common in Ar₂, Kr₂, Xe₂ and probably Ne₂ (see Scientific Pap. I.P.C.R. 35, 447 (1939)).

E. Rare Gas - Oxide and Chalcogenide Excimers

Recently we began a study of the higher excited states of excimers such as ArO, KrO and XeS. Although the visible bands
of these molecules have recently received considerable attention, little is known of their higher states, particularly those originating from the first excited state of the rare gas coupled to ground state oxygen or sulfur atoms. We have recently developed an efficient excitation scheme for these states involving an electroless, radio frequency discharge in the 1-10 megahertz region. Preliminary spectra from Xenon doped with O₂ reveal a new uv band near 2350 Å in addition to the well known "green bands" and the 3000 Å continuum. The 2350 Å band appears to be correlated with the states deriving from Xe* + O(^3P). We are planning a systematic study of this band at high resolution in NeO, ArO, KrO, XeO and XeS.
Publications

1. The Vacuum uv Absorption Spectrum of $O_2$ from its Metastable States $b \frac{1}{2}^+_g$ and $a \frac{1}{2}^+_g$. D.H. Katayama, S. Ogawa, M. Ogawa and Y. Tanaka, J. Chem. Phys. 67, 2132 (1977).


Papers in Preparation

1. Emission Spectra of Rare Gas Dimers in the VUV: I Ar$_2$.
   To be submitted to J. Chem. Phys.
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