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W.H. Parkinson, D.E. Freeman, and K. Yoshino

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
A 6.65 metre vacuum spectrograph operated at a wavelength resolution of 0.0006 nm has been used to study (a) The spectroscopy of rare gas molecules relevant to the development of intense vacuum ultraviolet radiation sources and lasers, and (b) Photoabsorption and predissociation processes in molecular nitrogen, which in the 80-100 nm region are important sources of upper atmospheric atomic nitrogen.

Absorption spectra of XeHe, XeNe, XeAr, XeKr, KrHe, KrNe, and KrAr →

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have been photographed and interpreted as arising from transitions from bound ground states to bound or free excited electronic states of these van der Waals molecules; bound excited states have been found for XeKr and XeAr. The emission spectrum of diatomic argon in the 100-150 nm region has been found to consist of four band systems all terminating on the ground electronic state; the only discrete band system, that emitted from the lowest excited state, has been analyzed rotationally and characterized spectroscopically as a triplet state for which the long range potential has been estimated. The absorption spectrum of atomic krypton in the 84-124 nm region has been obtained, and excited Rydberg states with principal quantum number as high as 60 have been assigned; the lowest two ionization energies have been accurately determined.

High resolution absorption spectra of dipole allowed transitions in molecular nitrogen, from the ground state to excited Rydberg and valence states have been rotationally analyzed. Some large anomalies in frequency spacings and relative intensities have been interpreted in terms of strong homogeneous perturbations rather than predissociations.

# HIGH RESOLUTION VACUUM ULTRAVIOLET SPECTROSCOPY OF SMALL MOLECULES

FINAL TECHNICAL REPORT

For the period October 1, 1979 to September 30, 1980

AFOSR-80-0018

## 1. STATEMENT OF WORK

In brief, a 6.65 metre vacuum spectrograph with extremely high resolution has been used to study (a) The spectroscopy of rare gas molecules that have potential use as lasers, and (b) Photoabsorption processes in $N_2$, which in the 80-100 nm region, are important sources of N $^2D$ in the upper atmosphere.

## 2. SUMMARY OF RESEARCH ACHIEVEMENTS

Significant research accomplishments in the spectroscopy of rare gas molecules and atoms relevant to the development of intense vacuum ultraviolet lasers and continuous radiation sources can be summarized under four headings:

(a) Vacuum Ultraviolet Absorption Spectra of Binary Rare Gas Mixtures and the Properties of Heteronuclear Rare Gas van der Waals Molecules. Vacuum ultraviolet absorption spectra of binary rare gas mixtures Xe/X (X = He, Ne, Ar, or Kr) and Kr/Y (Y = He, Ne, Ar, or Xe) near each of the first two resonance lines of Xe I and Kr I, respectively, have been photographed at high resolution by a 6.65 m spectrograph with a rare gas continuum as background source. The overall formation of spectral features near a resonance line is predominantly towards short wavelengths, and the degree to which discrete bands form near a resonance line generally increases with increasing atomic weight of X or Y. Partial interpretations of the absorption spectra are given in terms of transitions

within the heteronuclear rare gas van der Waals molecule XeX or KrY, from the bound ground electronic state ($\Omega = 0$) to bound or free excited electronic states ($\Omega = 0,1$). Bound excited electronic states are found for KrXe near the first resonance levels of Xe I and Kr I, and for KrXe and ArXe near the second resonance level of Xe I. A complete account is given in Ref. (1).

(b) Emission Spectrum of $Ar_2$ at Low Resolution in the Vacuum Ultraviolet Region. Emission spectra of the argon dimer have been studied in the vuv region. Liquid nitrogen cooled argon was excited with a rf (Tesla coil) discharge. Four band systems, I, II, III, and x, were observed in the 1000-1500 Å region and classified as transitions to the common ground state X $^1\Sigma_g^+$ ($0_g^+$) from the upper states A 4s $^3\Sigma_u^+$ ($1_u$), A 4s $^1\Sigma_u^+$ ($0_u^+$), B $5p\sigma(0_u^+)$ and x, respectively. Except for band system I, they consisted entirely of diffuse bands. A complete account is given in Ref. (3).

(c) Rotational Analysis of the Emission Spectrum of $Ar_2$ at High Resolution in the Vacuum Ultraviolet Region. The emission spectrum of $Ar_2$ excited by a Tesla discharge has been photographed at high resolution in the region 1073.5-1081.5 Å by a 6.65 meter spectrograph. Experimental conditions were chosen to produce only the band system emitted in the transition from the lowest excited state to the ground state. Rotational analyses of several bands indicate that the coupling scheme in the lowest excited state is closer to Hund-Mulliken case b than to case c, so that the excited state symmetry may be assigned approximately as $^3\Sigma_u^+$ rather than $1_u$, $0_u^-$. Rotational constants obtained for seven high-lying emitting levels with consecutively decreasing vibrational quantum numbers range

from 0.073 to 0.105 $cm^{-1}$. An attempt has been made to use spectroscopic results to depict the shapes and positions of the long range portions of the potential curves of the first two excited states ($^3\Sigma_u^+$ and $^1\Sigma_u^+$) of $Ar_2$ relative to each other and to that of the ground state X $^1\Sigma_g^+$. A complete account is given in Ref. (4).

(d) Absorption Spectrum of Atomic Krypton in the Vacuum Ultraviolet Region. The absorption spectrum of atomic krypton in the wavelength region 840-1240 Å has been investigated with a 6.65 m vacuum spectrograph. The expected five ns and nd Rydberg series have been observed. The series have been extended as far as n = 60 for $nd(3/2)_1^o$ and n = 59 for $nd'(3/2)_1^o$. The ionization energies obtained are 112914.6 ± 0.1 $cm^{-1}$ and 118284.6 ± 0.2 $cm^{-1}$ for $^2P^o_{3/2}$ and $^2P^o_{1/2}$ states of Kr II, respectively. Strong interactions have been observed as perturbation and autoionization. A complete account is given in Ref. (5).

Significant research accomplishments in elucidating the nature and mutual interactions among the excited states of molecular nitrogen formed by photoabsorption in the 80-100 nm region can be summarized under two headings:

(a) The Influence of Homogeneous Perturbation between the Rydberg Level $c_4'(0)\ ^1\Sigma_u^+$ and the Valence Level $b'(1)\ ^1\Sigma_u^+$ on the Photoabsorption Spectrum of $N_2$ near 95.8 nm. The first member of the $^1\Sigma_u^+$ Rydberg series of $N_2$, $c_4' - X$, has been studied in absorption using a 6.65 m vacuum spectrograph. Rotational analyses of the (0,0) band of the $c_4' - X$ as well as the (1,0) band of the $b' - X$ are given. Mutual perturbation between $c_4'(0)$

and b'(1) levels has been studied as a homogeneous interaction. The results were compared with the previous work in absorption and in emission, and confirmed the identity of Worley's c state and Gaydon's p' state as the $c_4'(0)\ ^1\Sigma_u^+$ state. A complete account is given in Ref. (2).

(b) High Resolution Vacuum Ultraviolet Absorption Spectrum of $N_2$, $c_4'\ ^1\Sigma_u^+ \leftarrow X\ ^1\Sigma_g^+$ Bands. Absorption spectra of the $c_4'\ ^1\Sigma_u^+ \leftarrow X\ ^1\Sigma_g^+$ Rydberg bands of $N_2$ in the 885 to 995 Å region are photographed at high resolution by a 6.65 m vacuum spectrograph. Rotational analyses of the $c_4'(v) \leftarrow X(0)$ and $c_4'(v) \leftarrow X(1)$ bands with v = 1-4 are given, together with a preliminary discussion of the homogeneous perturbations $c_4'\ ^1\Sigma_u^+ \times b'\ ^1\Sigma_u^+$. Some abnormal frequency shifts and distributions of rotational line intensities previously observed in emission bands having $c_4'$ upper levels are attributed to the effects of perturbations rather than predissociations. A complete account is given in Ref. (6).

## 3. PUBLICATIONS

(1) "Vacuum Ultraviolet Absorption Spectra of Binary Rare Gas Mixtures and the Properties of Heteronuclear Rare Gas van der Waals Molecules," D.E. Freeman, K. Yoshino and Y. Tanaka, J. Chem. Phys. 67, 3462 (1977).

(2) "High Resolution VUV Absorption Spectrum of $N_2$, Homogeneous Perturbation between $c_4'(0)\ ^1\Sigma_u^+$ and $b'(1)\ ^1\Sigma_u^+$ Levels," K. Yoshino and Y. Tanaka, J. Mol. Spectros. 66, 219 (1977).

(3) "Emission Spectrum of Rare Gas Dimers in the Vacuum UV Region. I. $Ar_2$," Y. Tanaka, W.C. Walker and K. Yoshino, J. Chem. Phys. 70, 380 (1979).

(4) "Emission Spectrum of Rare Gas Dimers in the Vacuum UV Region. II. Rotational Analysis of Band System I of $Ar_2$," D.E. Freeman, K. Yoshino and Y. Tanaka, J. Chem. Phys. 71, 1780 (1979).

(5) "Absorption Spectrum of Krypton in the Vacuum UV Region," K. Yoshino and Y. Tanaka, J. Opt. Soc. Am. 69, 159 (1979).

(6) "High Resolution VUV Absorption Spectrum of $N_2$, $c_4' \, ^1\Sigma_u \leftarrow X \, ^1\Sigma_g^+$ Bands," K. Yoshino, D.E. Freeman and Y. Tanaka, J. Mol. Spectros. 75, 153 (1979).

(7) "High Resolution VUV Absorption Spectrum of $N_2$, $c_5' \, ^1\Sigma_u^+ \leftarrow X \, ^1\Sigma_g^+$ Bands," K. Yoshino and D.E. Freeman (in preparation).

4. INTERACTIONS (COUPLING ACTIVITIES)

The following spoken presentations of research have been given:

June 1977, Molecular Structure and Spectroscopy Symposium, Ohio State University, "Absorption spectrum of $N_2$ in the VUV region. The $c' \, ^1\Sigma_u^+ - X \, ^1\Sigma_g^+$ system."

June 1977, Zeeman-Laboratorium der Universiteit van Amsterdam, "High resolution VUV spectroscopy of small molecules."

October 1977, AFOSR/AFGL Chemical Dynamics Conference, Hanscom AFB, "High resolution spectroscopy of small molecules."

April 1979, Physics Dept., University of Massachusetts at Amherst, "High resolution spectrum of $N_2$ in the VUV region."

May 1979, Osaka City University, Japan, "High resolution spectroscopy in the VUV region."

May 1979, Tsukuba University, Japan, "High resolution spectra of rare gas dimers."

June 1979, Molecular Structure and Spectroscopy Symposium, Ohio State University, "The emission spectrum of $Ar_2$ in the VUV region."

August 1979, Herzberg International Conference on van der Waals Molecules, Université Laval, Quebec, Canada, "Electronic spectra of rare gas dimers."

October 1979, AFOSR/FJSRL Molecular Dynamics Conference, USAF Academy, Colorado Springs, Colorado, "High resolution VUV spectra of small molecules."

November 1979, University of Maryland, "High resolution spectra of rare gas dimers."

December 1979, National Research Council, Ottawa, Canada, "Emission spectra of rare gas dimers in the VUV region."

June 1980, Molecular Structure and Spectroscopy Symposium, Ohio State University, "Absorption Spectra of rare gases in the VUV region."

September 1980, Eidgenossiche Technische Hochschule, Zurich, Switzerland, "High resolution VUV spectrum of $N_2$."

October 1980, AFOSR/AFGL Molecular Dynamics Conference, Hanscom AFB, "High resolution VUV spectrum of $N_2$."


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