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March 1984

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PHOTOIONIZATION MASS SPECTROSCOPY OF Ne DIMERS

D. J. Trevor,^a J. E. Pollard,^b W. D. Brewer,^c S. H. Southworth,^d
C. M. Truesdale,^e D. A. Shirley and Y. T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Chemistry, University of California
Berkeley, California 94720 USA

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ABSTRACT

The photoionization efficiency curve of Ne₂ as a function of wavelength has been obtained between 560 Å and 620 Å with a synchrotron radiation photon source. Detailed considerations of the autoionization mechanisms and symmetry of the excited states of Ne₂ have led to the partial assignment of the excited electronic states of Ne₂ which are responsible for the structure observed in its photoionization efficiency curve, and demonstrated the importance of Rydberg states with a B²Π_g core. The lower bound to the dissociation energy of Ne₂⁺ was determined to be 1.24 ± 0.08 eV (28.6 ± 1.8 kcal/mole).

- a. Present address: Exxon Research and Engineering Company, Clinton Township, Route 22 East, Annandale, NJ 08801.
- b. Present address: The Aerospace Corporation, P. O. Box 92957, Los Angeles, CA 90009.
- c. Present address: Institut für Atome und Festkörperphysik, Freie Universität, Berlin, West Germany.
- d. Present address: National Bureau of Standards, Washington, DC 20234.
- e. Present address: Department of Applied Physics, Corning Glass Works, Corning, NY 14831.

I. INTRODUCTION

The electronic structure of the rare-gas dimers has been the subject of numerous theoretical and experimental studies in recent years. The understanding of ground, Rydberg and ionic states of these systems is very important for the elucidation of the detailed kinetics of rare gas halide and excimer laser systems. Lower bounds to the dissociation energies of the rare gas molecular ions (Rg_2^+) have been measured by various methods which include electron impact,¹ photon-induced associative ionization,² electron recombination fluorescence line-width measurements,³ and photoionization mass spectrometry.⁴⁻⁷ Semi-empirical⁸ and *ab initio*⁹ electronic structure calculations have also been performed with a variety of basis sets and formalisms. The study reported here is an extension of previous work in this laboratory on Ar_2 , Kr_2 ,⁵ and Xe_2 ,⁴ using a supersonic expansion as a source for producing van der Waals clusters in molecular beam photoionization mass spectrometric investigations. With an intense helium discharge photon source lower bounds were obtained for the dissociation energies of the diatomic rare-gas ions Ar_2^+ ,⁶ Kr_2^+ and Xe_2^+ .^{4,5} The first ionization potential of Ne_2 exceeds the energy range of intense laboratory ultraviolet sources. Consequently, a higher-energy continuum light source, synchrotron radiation, was used for this molecular beam study of the photoionization efficiency of Ne_2 .

Previous results on the homonuclear diatomic rare gas systems showed a trend of simplification in their spectra in going from Xe_2 to Ar_2 .⁵ Our previous attempt to assign the intense features in the simplest system studied, Ar_2 , left several possibilities for each. These features were

obviously groups of states located near the atomic resonance lines. With our laboratory apparatus the resolution was not sufficient to separate the overlapping or closely-spaced states. The photoionization studies of Ar_2 at much higher resolution by P. M. Dehmer^{6,7} still did not permit a complete assignment of the major features. The extension to Ne_2 was thought to have the following helpful advantages: with its expected larger dissociation energy and smaller mass, the density of states near threshold would be reduced, and its smaller spin-orbit splitting might substantially reduce the $\Omega = +1$ excitations, thus simplifying the analysis.

By far the most valuable of the previous experiments used in the analysis of these rare-gas spectra were the high resolution absorption spectra by Y. Tanaka and K. Yoshino¹⁰⁻¹³ and others.¹⁴⁻¹⁶ The most valuable theoretical treatment consisted of the estimates made by Mulliken in 1970 of the first few Rydberg states in Xe_2 .⁸

The present photoionization study of Ne_2 between 560 Å and 620 Å is the first measurement of photoionization efficiency of Ne_2 as a function of photon wavelength. These studies were carried out at the Stanford Synchrotron Radiation Laboratory (SSRL). The photoionization of Ne_2 produced in a supersonic expansion at 77K was observed to be dominated by autoionization near the threshold. Using considerations analogous to those used by Mulliken in his study of Xe_2 we have made partial assignment of the structure in the photoionization efficiency curve.

II. EXPERIMENTAL

The apparatus used in these experiments consisted of a differentially pumped supersonic molecular beam source, a quadrupole mass spectrometer, a photon intensity monitor, and an ultrathin (1500 Å) aluminum/silicon window separating the molecular beam apparatus from the synchrotron light source. A schematic of the apparatus is shown in Fig. 1.

The experiments were performed on Beam line I-2 (8°) at SSRL. This branch line has been described in detail elsewhere.¹⁷ Briefly it consists of a system of 3 mirrors arranged to focus the radiation from the stored electron beam onto the entrance slit of a 1 m Seya-Namioka monochromator with a 1200 lines/mm grating blazed at 540 Å, and an additional mirror to refocus the monochromator output beam into the experimental chamber. The photon intensity available for these experiments was approximately 4×10^7 photons (sec)⁻¹ (mA)⁻¹ (Å)⁻¹ at 584 Å as measured with a calibrated NBS photodiode, using a photon wavelength resolution of 2.5 Å FWHM and a stored electron beam current of 42 mA under dedicated operation. The measured photon intensity as a function of wavelength after passing through a 1500 Å thick Al/Si window is shown in Fig. 2. This aluminum window was needed to protect the ultrahigh vacuum of the beam line from possible contamination by the background gas in the ionization chamber. This window isolation system was also equipped with an interlocked fast-closing gate valve to protect against vacuum failure, and has been described in detail.¹⁸ The monochromatic photon beam was focused to an image approximately 1 mm x 3 mm in the interaction region.

The supersonic molecular beam was produced by expanding neon through a 20 μm -diameter nozzle. The nozzle assembly which was designed to be operated at cryogenic temperature was incorporated into the inner dewar of a modified liquid He cryopump. The neon gas passed through two cryotrap to remove any condensable impurity before reaching the nozzle. For these experiments both the inner and outer dewars were kept at liquid nitrogen temperature. The temperature of the nozzle was monitored by a thermocouple and/or a carbon resistance thermometer. The expanded gas was skimmed by a 660 μm -diameter skimmer located 8 mm downstream from the nozzle, separating the beam source chamber from the interaction region. The source chamber was pumped by a 500 liter/sec turbomolecular pump.

The collimated molecular beam intersected the focused monochromatic photon beam 27 mm from the nozzle in the center of the extraction lenses for the quadrupole mass spectrometer. The interaction region was pumped by a second 500 liter/sec turbomolecular pump. After passing through the interaction region most of the beam molecules were pumped away by a 270 liter/sec turbomolecular pump connected to the beam catcher. The interaction chamber ion gauge reading (uncorrected), when the beam was running with 2000 torr of Ne behind a 20 μm -diameter nozzle at 77 K was 1.5×10^{-6} torr. This low background pressure was necessary in order to avoid interfering chemi-ionization and collisional ionization processes involving electronically excited Ne atoms. The estimated number density of the beam in the interaction region was $10^{11} - 10^{12} \text{ cm}^{-3}$ with only a very small fraction of beam gas existing as diatomic Ne_2 .

The ions created in the center of the interaction region were extracted by a 200 V cm^{-1} field. A pair of cylinder lenses was used to focus the ions at the entrance of the quadrupole mass filter (Extranuclear Laboratories) located in a separate chamber which was differentially pumped by a 200 liter/sec noble ion pump. In addition to the conventional resolution control, the ion kinetic energy along the quadrupole field was adjusted in order to obtain the maximum transmission for the desired resolution. The mass selected ions were accelerated to 3.5 keV and detected by a Spiraltron electron multiplier and pulse-counting electronics.

After intersecting the molecular beam the photon beam impinged upon either a calibrated NBS Al_2O_3 photodiode or a sodium salicylate coated quartz disc from which fluorescence was monitored by an RCA 8850 photomultiplier tube. The fluorescence efficiency of sodium salicylate has been shown to be a constant over the wavelength regions of interest,¹⁹ in contrast to the photoyield of the Al_2O_3 diode. Thus, the sodium salicylate monitor was chosen for the majority of these measurements. The output current of the RCA photomultiplier tube was amplified by a Keithly 417 picoammeter and processed by a 10 kHz voltage to frequency converter. This frequency was then registered concurrently with the ion signal.

The monochromator wavelength stepping motor, ion scaler, and photon scaler were microprocessor controlled. A photoionization efficiency spectrum was measured by recording simultaneously the ion and photon signals as functions of decreasing wavelength. The photon signal, after a constant correction for scattered light and photomultiplier dark current, was used to calculate the photoionization efficiency.

As shown in Fig. 2 the photon intensity peaked at 550 Å and then decreased to only a few percent of the peak intensity by 350 Å. This was due to a near normal incidence reflection on one of the focusing mirrors in the 8° beam line. Because of it, second-order light interference was a serious problem only for wavelengths above 650 Å. The wavelength scales for these spectra were obtained by measuring the ionization thresholds for Ne and He. Due both to the beam-line optics and to variations in the electron beam position the accuracy of the wavelength scale could only be determined to within the half width at half maximum band pass of the monochrometer (0.4 Å). However, the relative wavelength scale was found to be reproducible to better than 0.1 Å.

III. RESULTS

The photoionization yield of Ne_2^+ recorded at a resolution of 2.5 Å (FWHM) is shown in Fig. 3. The threshold for production of Ne_2^+ was taken to be the point at which the signal rose above the background. The sensitivity of these signal measurements at threshold was 1 percent of the signal at 570 Å. Due to the cooling of internal modes in the supersonic expansion, no thermal corrections to the measured threshold were deemed necessary. The observed ionization potential of Ne_2 was found to be 20.33 ± 0.08 eV (610 ± 2.5 Å). This threshold energy is an upper bound to the adiabatic ionization potential of Ne_2 . Combining this number with the ionization potential of Ne (21.565 eV)²⁰ and the Ne_2 bond strength (0.004 eV)²¹ we obtain a lower bound to the dissociation energy of Ne_2^+ of 1.24 ± 0.08 eV. This value is slightly less than the 1.34 eV obtained by the dissociative recombination spectral line shape studies of Connor and Biondi.³ Taking into account the rather large errors in our measurements and remembering that our value is only a lower bound the difference is reasonable. The reported electron impact appearance potential measurement²² gives the dissociation energy of 0.69 ± 0.2 eV. This electron impact technique suffers from poor energy resolution and poor threshold sensitivity. The dissociation energy derived from interpretation of ion molecule scattering data ranges anywhere from 0.33 eV to 0.71 .²³ The ion beam method is limited by low energy ion source technology and difficulty in data interpretation due to possible interference of more than one potential energy surface.

The photoion yield signal rises slowly from threshold. Several broad, unresolved peaks are present in this spectrum, as was the case for the heavier rare-gas systems previously studied.^{4,5} A higher resolution scan (0.8 Å FWHM) over this same wavelength region is shown in Fig. 4, revealing many peaks with widths near instrumental resolution.

IV. DISCUSSION

A. Rare Gas Dimer Ionic States

The rare gas van der Waals molecules (Ne_2 and larger) can be described by a linear combination of atomic orbitals-molecular orbital (LCAO) single-determinant configuration of

$$\dots (\sigma_g ns)^2 (\sigma_u ns)^2 (\sigma_g np)^2 (\pi_u np)^4 (\pi_g np)^4 (\sigma_u np)^2$$

where $n = 2, 3, 4$ and 5 for Ne , Ar , Kr and Xe , respectively.

The ground states of the rare-gas dimers have $1\Sigma_g^+(0_g^+)$ symmetry and are overall repulsive with only long range van der Waals minima of 4 meV, 12 meV, 17 meV, and 24 meV at 3.1 Å, 3.76 Å, 4.00 Å, and 4.36 Å for Ne_2 , Ar_2 , Kr_2 and Xe_2 , respectively.^{21,24} The four lowest ionic states LCAO configurations, neglecting spin-orbit effects are:

$$\begin{aligned} &\dots (\sigma_g np)^2 (\pi_u np)^4 (\pi_g np)^4 (\sigma_u np)^1; \quad A^2\Sigma_u^+ \\ &\dots (\sigma_g np)^2 (\pi_u np)^4 (\pi_g np)^3 (\sigma_u np)^2; \quad B^2\Pi_g \\ &\dots (\sigma_g np)^2 (\pi_u np)^3 (\pi_g np)^4 (\sigma_u np)^2; \quad C^2\Pi_u \\ &\dots (\sigma_g np)^1 (\pi_u np)^4 (\pi_g np)^4 (\sigma_u np)^2; \quad D^2\Sigma_g^+ . \end{aligned}$$

The $A^2\Sigma_u^+$ and $B^2\Pi_g$ states result from removing an antibonding electron, producing attractive wells, while the $C^2\Pi_u$ and $D^2\Sigma_g^+$ repulsive. The $\sigma_u np$ is substantially more antibonding than the $\pi_g np$; thus, removing an electron from the former orbital makes the $A^2\Sigma_u^+$ considerably more attractive than the $B^2\Pi_g$ state.

Inclusion of spin-orbit effects will split the $B^2\Pi_g$ and $C^2\Pi_u$ states into their $\Omega = 1/2$ and $3/2$ components. At large internuclear distances, where spin-orbit interactions are comparable to chemical forces, these systems are best described in Hund's case (c) notation,²⁵ shown in Table 1. The $\Omega = 1/2$ component of the $C^2\Pi_u$ configuration is mixed with the $A^2\Sigma_u^+$ configuration by spin-orbit interactions, as is the $\Omega = 1/2$ component of the $B^2\Pi_g$ configuration mixed with the $D^2\Sigma_g^+$ configuration. The six case (c) states are designated $1/2u$ I, $1/2u$ II, $1/2g$ I, $1/2g$ II, $3/2u$ and $3/2g$, where I signifies the lowest lying state of $1/2u$ or $1/2g$ symmetry. The ground ionic state is the $1/2u$ I state. Recalling that the $A^2\Sigma_u^+$ configuration is attractive, and the $C^2\Pi_u$ repulsive, the resulting $1/2u$ I state will become less attractive (dissociation energy will decrease) and the $1/2u$ II state will become less repulsive (more like a bound state) as the mixing increases.

The experimental dissociation energies of Rg_2^+ decrease monotonically from Ar_2^+ to Xe_2^+ while the spin-orbit splitting of the atomic rare gas ionic states increases monotonically. Our measured lower bound of 1.24 ± 0.08 eV for Ne_2^+ dissociation energy is slightly less than the best value for Ar_2^+ of 1.33 ± 0.02 eV,²⁶ yet the value of Connor and Biondi³ of 1.34 eV for Ne_2^+ which is also only a lower bound is essentially equal to the value for Ar_2^+ . It is quite possible that the true Ne_2^+ dissociation energy is larger than the Ar_2^+ energy, following the same trend as the heavier rare gases. Recent theoretical calculations on the ionic states of the rare-gas systems indicate that spin-orbit interactions are primarily responsible for this trend.²⁷

At large R the $1/2u$ states are strong mixtures of the $\Lambda - \Sigma$ states, appropriate near the equilibrium internuclear distance, due to the strong spin-orbit interactions. At very large internuclear distances the potential is usually best described by dispersion forces. The dominant dispersing interaction is an ion-induced dipole,²⁸ for which the potential is $-\alpha/2R^4$, where α is the polarizability of the rare-gas atom. This potential is evaluated in Table 2 at the internuclear separation of the neutral rare-gas dimer. The vertical ionization potentials from the photoelectron spectroscopy studies of Dehmer and Dehmer²⁹ are also shown in Table 2 for comparison. In this region of R the ion-induced dipole interactions account for less than half of the total potential energy. Therefore, chemical forces are still very important even at these large internuclear distances.

The first excited ionic state, $B^2\Pi_{3/2g}(3/2g)$, is expected to be attractive but not nearly as much as the ground ionic state, because of the weaker π_g np antibonding. The minimum of the potential is also expected to lie at larger R than for the $1/2u$ I state, because as R decreases the $p\sigma_u - p\sigma_u$ antibonding dominates. The photoelectron spectra of Ar_2 , Kr_2 , and Xe_2 confirm these expectations.²⁹

The remaining ionic states $C^2\Pi_{3/2u}(3/2u)$, $C^2\Pi_{1/2u}(1/2uII)$, $B^2\Pi_{1/2g}(1/2gI)$, and $D^2\Sigma_g^+(1/2gII)$, are expected to be repulsive except for long range dispersion minima. A schematic representation of these potentials is shown for neon in Fig. 5. These ionic state curves are based on the potentials of Michels et al.²⁷

B. Excited States of Rare Gas Dimers

In order to assign the autoionization (AI) structure near threshold in the rare gas homonuclear diatomics detailed consideration must be given to the Rydberg states of these molecules. In the discussion that follows the symmetry and ionic core of the important excited states are derived. This information is used later to make rational assignments of the observed AI in neon dimer.

All the excited states of the rare-gas molecules are expected to be of the Rydberg type. At small R , as the principal quantum number (n) increases, the potential energies of the molecular Rydberg states approach those of the ionic core states due to the high-lying Rydberg electron having less and less charge density in the region of the internuclear axis. This makes the low-lying ionic states very good approximations to the molecular Rydberg states. As an example, ab initio calculations by Cohen and Schneider³⁰ on one of the lowest Rydberg states for Ne_2 gave the sum of dissociation energy (D_e) and the height of its barrier to be 0.601 eV with $R_e = 1.79$ Å while their $\text{Ne}_2^+ 1/2u$ I values were $D_e = 1.20$ eV and $R_e = 1.75$ Å. Because of this similarity, molecular Rydberg states at small R are identified by the state of the ionic core and the n and l values of the Rydberg electron in the united atom (UA).

Mulliken³¹ has shown that for a molecular Rydberg state with an unpromoted³² Rydberg molecular orbital, its potential energy curve follows the ionic core at all R , while in the case of a promoted Rydberg molecular orbital the potential energy curve acquires an obligatory hump at intermediate R . In both the Ne_2 absorption spectra and theoretical calculations^{9,10} these humps have been found to be usually less than 600

cm^{-1} . This is in contrast to the He_2 Rydberg states with some humps larger than 4000 cm^{-1} .^{31,33} Therefore, within the relevant energy resolution of this treatment the Rydberg states approach their dissociation limits smoothly at large R .

At small R the possible states that arise from coupling the ionic cores with the different possible UA Rydberg electrons can be easily derived.³⁴

Considering only the lowest lying molecular ionic cores and the united Rydberg orbitals, $s\sigma_g$, $p\sigma_u$, $p\pi_u$, $d\sigma_g$, $d\pi_g$ and $d\delta_g$ 134 states are obtained. The higher lying ionic core states will be above the energy region of concern; i.e. below the $^2P_{3/2,1/2}$ atomic ionization potentials. Mulliken has shown that Rydberg states with $C^2\Pi_u$ and $D^2\Sigma_g^+$ core configurations dissociate to $\text{Rg}^+ + \text{Rg}^-$, or since Rg^- is unstable, to $\text{Rg}^+ + \text{Rg} + e^-$.⁸ Although some of these states are possibly attractive they lie much closer in energy to the atomic ionization potential than those of the $A^2\Sigma_u^+$ and $B^2\Pi_g$ cores. This eliminates half of the possible states. Of the remaining states only the following satisfy dipole selection rules for excitation from the Rg_2 ground state:

$A^2\Sigma_u^+ ns\sigma_g$	$0_u^+, 1_u$
$B^2\Pi_g np\sigma_u$	$0_u^+, (2)1_u$
$B^2\Pi_g np\pi_u$	$(2)0_u^+, (3)1_u$
$A^2\Sigma_u^+ nd\sigma_g$	$0_u^+, 1_u$
$A^2\Sigma_u^+ nd\pi_g$	$0_u^+, (2)1_u$
$A^2\Sigma_u^+ nd\delta_g$	1_u

Now that the possible molecular Rydberg states of interest have been identified their atomic dissociation limits need to be determined. These are obtained by constructing a correlation diagram in the usual fashion.

If the energy order of the UA Rydberg limits were known the exact state correlation diagram could be drawn. Mulliken has estimated these energies for Xe_2 6s and 5p Rydberg states creating approximate potential energy curves.⁸ Several reasonable assumptions were used concerning the UA limits. These assumptions are:

$$\begin{aligned} 2\text{Pns} + 1\text{S}_0 &\rightarrow \text{ns}\sigma_g \text{ or } (n+1)\text{p}\sigma_u \\ 2\text{Pnp} + 1\text{S}_0 &\rightarrow (n+1)\text{d}\sigma_g, \text{np}\pi_u, (n+1)\text{d}\pi_g, (n+2)\text{f}\sigma_u. \end{aligned}$$

The corresponding relationship for the d states is:

$$2\text{Pnd} + 1\text{S}_0 \rightarrow (n+3)\text{g}\sigma_g, (n+2)\text{f}\pi_u, \text{nd}\delta_g, (n+2)\text{f}\delta_u, (n+3)\text{g}\pi_g, (n+4)\text{h}\sigma_u.$$

A correlation diagram, not drawn to scale, for an ns Rydberg state is shown in Fig. 6. Schematic potential energy curves for the 6s states of Ne_2^* are depicted in Fig. 5. Of the total 16 states only 5 are dipole allowed. Of these five, two are 0_u^+ and three are 1_u symmetry. The lowest lying 1_u state retains a significant $3\Sigma_u^+$ character at all internuclear distances, nearly coincident with the 0_u^- state. Therefore, transitions to this state are not expected to be intense. The next highest state, 0_u^+ , has the $A^2\Sigma_u^+$ core and closely resembles it. The next highest 1_u state has a $B^2\Pi_{3/2g}$ core. This core state is overall repulsive but with a long-range minimum as previously described. The Rydberg state should resemble the core state at small R but dissociate

over a maximum, characteristic of a promoted MO. Thus, this state is most likely repulsive in the vertical transition region of the van der Waals molecule.

The remaining two dipole allowed states, 0_u^+ , 1_u , which correlate to $2p_{1/2}ns + 1s_0$ atoms, have $B^2\Pi_{1/2g}$ cores. The $B^2\Pi_{1/2g}$ ionic state is believed to be repulsive, aside from a possible attractive dispersion minimum. However, the Rydberg states of 0_u^+ symmetry are a mixture of several LCAO configurations at large R , due to spin-orbit interactions. One of these configurations is primarily responsible for the attractiveness of the lowest 0_u^+ ($A^2\Sigma_{1/2u}^+$ core) state. The other configurations are more repulsive. The spin-orbit interaction mixes these configurations. Therefore, the higher lying 0_u^+ state is less repulsive than its predominant ionic core configuration, $B^2\Pi_{1/2g}$. This effect, as well as the attractive dispersion force, suggests that this state will have a long range minimum.

The energy order of the UA molecular np Rydberg states is not known, making a definitive correlation diagram impossible to construct. Mulliken estimated both the energy order for the lowest UA states and Rydberg potential energy curves for Xe_2 .⁸ Using an ordering similar to Mulliken for the UA states a correlation diagram can be constructed.³⁴ Guided by this simple approach there should exist two 0_u^+ and two 1_u states with $A^2\Sigma_{1/2u}^+$ cores that dissociate to $2p_{3/2}np + 1s_0$ and also a 0_u^+ state with $B^2\Pi_g$ core dissociating to $2p_{1/2}np + 1s_0$.

The nd Rydberg states are even more numerous than the np Rydberg states making predictions even more tenuous. The $2p_{3/2}nd + 1s_0$ limits should have molecular states of 0_u^+ symmetry with both $A^2\Sigma_{1/2u}^+$ and $B^2\Pi_g$ type cores, while the $2p_{1/2}nd + 1s_0$ limits are predicted to have at least one 0_u^+ state with a $B^2\Pi_g$ core. This is very similar to the $2p_{3/2}ns$ and $2p_{1/2}ns$ manifolds.

C) High Resolution VUV Absorption

High resolution VUV absorption spectra of the rare gas dimers have been reported.¹⁰⁻¹⁶ All of the states observed were molecular Rydberg states in character, formed from Rydberg atomic states and ground state atoms. These studies were limited to relatively-low lying Rydberg states because extensive broadening of the numerous atomic lines makes it extremely difficult to study higher Rydberg states. This is in contrast to the photoionization studies reported here which (although of much lower resolution) are not sensitive to the atomic transitions or to strongly dissociative molecular states. For both Ne_2 and Ar_2 , except for the lowest lying states, few states above the adiabatic IP have been assigned from the absorption spectra. Nevertheless, several generalizations are made from the reported absorption data.

Two Rydberg molecular states are observed which arise from the $2p_{3/2}ns + 1s_0$ atomic limits. The lower of these is assigned to the 1_u state which consists of an extensive v' progression up to the dissociation limit (10 bands) and is about a factor of 10 less intense than the higher energy state. The higher states are most likely 0_u^+ and

display a somewhat shorter v' progression to the dissociation limit. As suggested by the correlation diagram, these states have a $A^2\Sigma^+_{1/2u}$ core.

In the region of the $^2P_{1/2}ns$ atomic limit, an O_u^+ state which has a much smaller vibrational spacing, but an intensity comparable to that of the lower O_u^+ state is observed. This lower vibrational frequency is anticipated for a Rydberg state with a $B^2\Pi_{3/2g}$ core.

At least three systems are observed near the np atomic states. The highest energy state has the longest v' progression and the most intensity. It is assigned to a O_u^+ state, dissociating to $^2P_{1/2}np$ ($J = 0$) and 1S_0 atoms. The lower systems of bands are approximately one fourth as intense, with only a few v' states observed. These systems have not been conclusively assigned. As a whole the np systems in Ne_2 are a factor of 200 less intense than the O_u^+ states observed in the ns series, but they increase in intensity for the heavier rare gases.

Several of the band systems for Ne_2 and Xe_2 in the region of the $^2P_{3/2}nd$ states appear to be similar in structure and only slightly less intense than the O_u^+ states derived from $^2P_{3/2}ns$ atoms. Only two systems in the region of the $^2P_{3/2}$ states are observed in Ne_2 , being assigned to O_u^+ molecular states dissociating to $^2P_{3/2}3d[1/2]_1$ plus 1S_0 and $^2P_{3/2}3d[3/2]_1$ plus 1S_0 atoms. Many additional systems are observed in Xe_2 ; however, state symmetries are not assignable, due to irregular vibrational spacing, which might be evidence of a curve crossing.

A $2p_{1/2}$ nd and a $1s_0$ atom can couple to form two 0_u^+ and four 1_u molecular states. Only in Ne_2 , have systems in this energy range been reported, but atomic limits were still not assigned. The vibrational spacings are irregular, suggesting the possibility of two states or a curve crossing. It is reasonable to assume that at least the highest of these systems would have $B^2\Pi_g$ core.

D. Ionization of Rare Gas Dimers

The rare gas van der Waals minimum lies at a much larger internuclear distance than the ionic state minimum. Therefore, direct ionization populates only the very high vibrational levels of the ground state of the ion. This results in much higher vertical ionization potential for the $A^2\Sigma_u^+$ state than the adiabatic IP. For example, the Ar_2^+ , $2\Sigma_{1/2u}^+$, vertical ionization potential is 15.55 eV while the adiabatic ionization potential is around 14.44 eV, a difference of 1.11 eV.²⁹ The vertical transition will populate approximately $v' = 34$ to $v' = 49$ of the ground ionic state.³⁵ Schneider and Cohen³⁶ calculated Franck-Condon factors for the theoretical potential for a similar state in Ne_2 and found them to be exceedingly small, less than 10^{-10} for the lowest v' levels. This evidence as well as the measured intensity in the photoionization efficiency curves rule out direct ionization as an important mechanism for production of the dimer ions near threshold. The sharp structures in the yield curves are most certainly due to AI of the molecular Rydberg states of the rare gas dimers. In fact, these states must have significant cross-sections very close to the adiabatic ionization potential to account

for the observed signal. There are two possible AI processes that need to be considered, vibrational autoionization and electronic autoionization.

The type of state necessary for vibrational AI is one that is very similar in shape to the ionic state. Since the ground ionic state is $A^2\Sigma_{1/2u}^+$ (indeed, quite different from the other ionic states) the Rydberg states involved must have this core. There are several states of this type with the proper symmetry that can be reached by dipole selection rules. However, like the A state, in the vertical transition region (at large R) they can only be populated in high v states. Due to the propensity for small changes in the vibrational quantum number, for this type of autoionization only high v states of the ion can be produced. Consequently, vibrational AI will not produce ions near the adiabatic threshold.

On the other hand, electronic AI is not restricted by this propensity. The vibrational states populated are governed by Franck-Condon type factors and electronic matrix elements. The Rydberg states with $B^2\Pi_g$ core at large R will have some A core character due to spin-orbit interactions. This A character should enhance the electronic matrix elements between the Rydberg states with $B^2\Pi_g$ cores and the A ionic state. In addition, the Rydberg states with predominantly $B^2\Pi_g$ cores have significant Franck-Condon overlap with the ground state, due both to their large R_e and widths. They will also have significant Franck-Condon factors with the ground ionic state. This makes them very good candidates for electronic AI.

E. Autoionization Structure Assignments

Because the states involved in the AI of the rare gas dimers are the same as those observed in absorption but modified in intensity by their efficiency to autoionize, the following predictions are made:

- I) Of the molecular Rydberg states derived from $^2P_{3/2}ns$ or nd atoms and a ground state atom, the ones with an $A^2\Sigma^+_{1/2u}$ core will be more intense in absorption than in photoionization near threshold, because of the ineffectiveness of vibrational AI.
- II) Considering the states with atomic limits of $^2P_{1/2}ns$ or nd plus 1S_0 , the most intense will have 0^+_u symmetry with a $B^2\Pi_g$ core and appear with comparable intensity in both absorption and in photoionization, due to the effectiveness of electronic AI.
- III) The states with $^2P_{1/2,3/2}np$ atomic limits will be weak for Ne_2 and increase in intensity for the heavier systems. We expect the $B^2\Pi_g$ core Rydberg states to be as pronounced in photoionization spectra as in absorption.

Figure 7 shows the photoionization efficiency of Ne_2 in the region of the sharp AI structure near threshold. In the top part of this figure, the absorption data of Tanaka and Yoshino¹⁰ are plotted. The first peak in the photoionization efficiency at 600.7 Å, which is red-shifted from the atomic $^2P_{1/2}5s$ state, agrees with system XII in absorption. This is an 0^+_u state with a $B^2\Pi_{1/2g}$ core. The absence of an intense peak corresponding to system XI (0^+_u from $^2P_{3/2}5s$) is consistent with prediction I, namely, that a $A^2\Sigma^+_{1/2u}$ core Rydberg state will not be

efficient in autoionization near threshold. The second peak in the efficiency curve at 599.0 Å lies coincident in energy with the $2p_{3/2}4d$ atomic states. Based on a correlation diagram of the UA states³⁴ there will be two 0_u^+ states and three 1_u states with $B^2\Pi_g$ cores and two 0_u^+ states and four 1_u states with $A^2\Sigma_{1/2}^+$ cores. It is possible that, again, the B core states yield significant intensity; however, the A core states can not be ruled out. If the A core states makes a significant contribution to this peak, prediction I would be contradicted. Unfortunately, only diffuse absorption bands have been reported in this energy region, leaving these assignments questionable.

The peak at 596.6 Å is red-shifted from $2p_{1/2}4d$ atomic state which produces two 0_u^+ states and three 1_u states, all certainly with B core. The observed red-shift of this state is in excellent agreement with the $2p_{1/2}3d$ state reported from absorption measurements. The intensity of this peak is as expected from prediction II. There are several $2p_{3/2}5p$ atomic states in this energy region whose molecular states might also contribute intensity.

There is a weak feature at 594.2 Å well removed from Ne s and d atomic states and red-shifted from the $2p_{1/2}5p$ states. The molecular state expected in this region will have $B^2\Pi_g$ cores.³⁴ Although this peak is weak and of the same magnitude as the scatter in the data, it is twenty times as intense as $2p_{1/2}3p$ and $4p$ analogues seen in absorption studies. This behavior is as expected from prediction III.

The $2p_{3/2}6s$ state of neon lies slightly to the red of the maximum of the peak at 591.7 Å. There are no other known atomic states between the

$2p_{3/2}6s$ and $2p_{3/2}5d$ states of Ne. Therefore this peak's blue shift is assigned as AI through the repulsive 1_u state derived from $2p_{3/2}6s$, $J = 1$ and $1s_0$ combination. This type of state is believed to be responsible for the broadening, toward the blue, of the atomic line in absorption at high pressures. It has a $B^2\Pi_{1/2g}$ core, a positive dispersion force, and a promoted Rydberg MO. All of these effects make this state repulsive; however, an avoided crossing at large R can yield a local minimum. The red-shifted portion of this peak in the photoionization efficiency could be due to the 0_u^+ state with an $A^2\Sigma_{1/2u}^+$ core. It would then be the higher energy analog of the state responsible for system XI in the absorption spectra of Tanaka and Yoshino.¹⁰

The feature at 590 Å is coincident with $2p_{3/2}5d$ states, red-shifted from the $2p_{1/2}6s$ state and broader than the other intense peaks. This peak is assigned to molecular states arising from both of the atomic states. This assignment is consistent with the first and second peaks both in red-shift and intensity.

The highest energy peak to be assigned in this wavelength region is red-shifted from the $2p_{1/2}5d$ just as the peak at 596.6 Å is from the 4d state. Its intensity is consistent with prediction II.

At higher photon energy the density of states increases, thereby blending the peaks together and preventing further assignments with the available resolution. Below the onset of the sharp structure, the photoionization efficiency decays very slowly to threshold. Several processes contribute to the intensity in this region. The largest of these must still be autoionization. The atomic states in this energy region are

$2p_{3/2}5s$, $2p_{1/2}4p$ and $2p_{3/2}4p$. The observed ionization potential is in the region where AI states from $2p_{1/2}4p + 1s_0$ are predicted to have intensity in analogy with the peak at 594.2 Å.

The photoionization efficiencies of Xe_2 , Kr_2 and Ar_2 studied in this laboratory were comprised of many rather broad features.⁵ The smaller dissociation energy of these ions, the stronger spin-orbit interactions, and the poorer resolution made assignments similar to those for Ne_2 impossible. However, an obvious trend is observed in going from Ar_2 to Xe_2 . The major intensity in Ar_2 is in the region of the ns and nd states, while for Kr_2 considerable intensity is observed between these states. For Xe_2 this tendency is lost. In the absorption studies for these systems, the np type states increase in intensity in going from Ne to Xe. In addition any propensity towards $\Omega = 0$ instead of $\Omega = 1$ is expected to decrease with increasing spin-orbit interaction. Therefore, the number of accessible states will increase in going from Ne_2 to Xe_2 , resulting in the observed trend in the photoionization efficiencies of the rare gas systems.

High resolution photoionization mass spectrometric results on Ar_2 reported by Dehmer and Poliakoff⁶ show that indeed the broad structure observed in the earlier work⁵ is comprised of several electronic states. They assigned the first band system above threshold, which is also observed in absorption spectra by Tanaka et al.,¹¹ to a state derived from $2p_{1/2}5p + 1s_0$ atoms. Similarly, an analogous state in Ne, $2p_{1/2}4p + 1s_0$, is predicted to be responsible for the observed threshold signal in this work. This high resolution study of Ar_2 also

found that a significant fraction of the states observed in absorption does not produce Ar_2^+ and therefore must predissociate or dissociatively ionize.⁷ This is also found to be the case for Ne_2 .

IV. CONCLUSIONS AND SUMMARY

The dissociation energy of Ne_2^+ is determined to be greater than 1.24 ± 0.08 eV by photoionization mass spectroscopy. The supersonic molecular beam technique and intense continuum synchrotron radiation source employed in this work yielded sufficient signal to resolve a few of the lowest autoionizing molecular Rydberg states. Careful consideration of the autoionization mechanisms, absorption spectra, and electronic configurations of the molecular Rydberg states led to several assignments in the photoionization efficiency. The molecular Rydberg states with $B^2\Pi_g$ core configurations are found to make the most important contribution to the photoionization cross-section near threshold, due to their ability to bridge the excitation between the large initial R of the van der Waals dimer and the small R of the ionic molecular state. Vibrational autoionization is shown not to be a plausible mechanism near threshold, due to the vertical transition region being at the large internuclear distance of the van der Waals molecule. Electronic autoionization is not restricted as such and is expected to be further assisted by the ability of spin-orbit interaction to mix A core character into a B core molecular Rydberg state.

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Table 1. Correlations between Λ - Σ states and ω - ω (case (c)) states from $2P_{3/2}$, $2P_{1/2}$ states coupled to a $1S_0$ state.

Λ - Σ coupling	Case (c)	Atomic limits
$A^2\Sigma_u^+$	$A^2\Sigma_{1/2u}^+$	$np^5 2P_{3/2} + 1S_0$
$B^2\Pi_g$	$B^2\Pi_{3/2g}$	
	$B^2\Pi_{1/2g}$	
$C^2\Pi_u$	$C^2\Pi_{3/2u}$	
	$C^2\Pi_{1/2u}$	$np^5 2P_{1/2} + 1S_0$
$D^2\Sigma_g^+$	$D^2\Sigma_{1/2g}^+$	

Table 2. The ion induced dipole potential evaluated at R_e of the van der Waals dimer.

Molecular Ion	Polarizability ^a $\alpha(\text{\AA}^3)$	$R_e(\text{\AA})^b$	$-\alpha/2R^4$ (eV)	Vertical ^c IP of 1/2u I (eV)	$E(R_e)^d$ of 1/2u I (eV)	Adiabatic ^e IP of (eV)	D_0^f 1/2u II (eV)
He_2^+	0.2051	2.96	-0.019	--	--	--	--
Ne_2^+	0.395	3.03	-0.034	--	--	--	--
Ar_2^+	1.64	3.761	-0.059	15.55 ± 0.025	-0.227 ± 0.025	15.85 ± 0.015	0.10 ± 0.015
Kr_2^+	2.48	4.007	-0.069	13.76 ± 0.03	-0.257 ± 0.02	14.54 ± 0.015	0.14 ± 0.015
Xe_2^+	4.04	4.361	-0.080	11.85 ± 0.015	-0.304 ± 0.015	13.27 ± 0.015	0.19 ± 0.015

^aAtomic polarizabilities from index of refraction measurements, A. Dalgarno and A. E. Kingston, Proc. Roy. Soc. (London) A259, 424 (1961).

^bEquilibrium internuclear distance of van der Waals dimers Ref. 21 and 24.

^cVertical ionization potentials from Ref. 29.

^dPotential energy of the 1/2u I state at R_e , with respect to the $2P_{3/2}$ ionic state by $E(R_e) = \text{IP}(2P_{3/2}) + D_0(R_g)_2 - \text{VIP}(1/2u \text{ I})$ where $\text{IP}(2P_{3/2})$ is the atomic ionization potential, $D_0(R_g)_2$ is the rare gas van der Waals binding energy (Ref. 21 and 24) and $\text{VIP}(1/2u \text{ I})$ is the vertical ionization potential of Ref. 29.

^eAdiabatic ionization potentials of Ref. 29.

^fThe dissociation energy of the 1/2u II state (Ref. 29).

FIGURE CAPTIONS

- Fig. 1. Cross-sectional view of supersonic molecular beam photoionization mass spectrometer used at SSRL. The photon beam is coming out of the plane of the paper. 1. Beam source differential pumping wall; 2. Outer dewar and heat shield; 3. Inner dewar; 4. Nozzle; 5. Skimmer; 6. Ion extraction field lens; 7. Focussing lenses; 8. Quadrupole mass filter; 9. Spiraltron ion detector; and 10. Gas catch.
- Fig. 2. The photon flux as a function of wavelength on the 8° (I-2) line at SSRL after passing through a 1500 Å thick Al/Si window and a 1200 lines/mm osmium coated grating blazed at 540 Å, measured, using a sodium salicylate VUV to visible converter and a RCA 8850 photomultiplier tube calibrated with a NBS photodiode at 584 Å, on May 8, 1980 during dedicated operation of SPEAR with a stored electron beam current of 42 mA.
- Fig. 3. Photoionization efficiency of Ne_2 measured with a photon resolution of 2.5 Å FWHM.
- Fig. 4. Photoionization efficiency of Ne_2 measured with a photon resolution of 0.8 Å FWHM. Plotted, in the upper portion, are the energies of the dipole allowed atomic transitions for Ne.
- Fig. 5. Schematic molecular potential energy curves of Ne_2 , Ne_2^* (in the region of the 6s Rydberg states) and Ne_2^+ .
- Fig. 6. Correlation diagram for the p^5ns Rydberg states. The atomic limits are on the left-hand side while the UA states are on the right.

Fig. 7. The photoionization efficiency of Ne_2 at 0.8 Å FWHM in the region, near threshold, of the sharp autoionization structure. The insert near the top shows the absorption spectra of Ref. 8 on the same wavelength scale. The atomic transitions are indicated by lines drawn beneath the data at the appropriate wavelengths.

Fig. 1

XBL 828-11043

Fig. 2

Fig. 3

XBL 828-11039

XBL 828-11045

Fig. 4

XBL 834-9012

Fig. 5

Fig. 6

XBL 809-11859

XBL 828-11044

Fig. 7

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