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PHOTOIONIZATION MASS SPECTROMETRY OF Ne_2 AND OF He CLUSTERS*

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We present the first measurements of the photoionization yield of Ne_2^+ and He_2^+ in the wavelength range of 650 Å to 520 Å and 750 Å to 480 Å, respectively. These experiments were performed at Stanford Synchrotron Radiation Laboratory on beam line I-2¹ (8° line) with our recently developed supersonic molecular beam photoionization mass spectrometer. The measurements were made by crossing the monochromatized photon beam with a differentially pumped supersonic molecular beam. The resulting ions were extracted, analyzed and detected by a quadrupole mass spectrometer.

The photoionization yield of Ne_2^+ recorded at a resolution of 0.8 Å is shown in Fig. 1. Ne_2 was prepared by expanding Ne gas at 77 K and 2000 torr through a 20 μm aperture. The threshold for production of Ne_2^+ was taken to be the point at which the signal rose above the background in a scan with 2.5 Å resolution shown in the insert on Fig. 1. The observed ionization potential of Ne_2 was found to be $20.21 \pm .05$ eV (613.6 ± 1.5 Å), which yields a lower limit to Ne_2^+ ground state binding energy of 1.36 ± 0.05 eV in agreement with the spectral line shape studies of Connor and Biondi.²

The photoion yield rises very slowly from threshold because of the unfavorable Franck-Condon factors for direct ionization. The neutral Ne_2 is bound by only 4 meV with an equilibrium distance of 3.03 Å^3 while the ion is strongly bound with an estimated equilibrium distance of 1.85 Å^4 . At 601 Å the first of a series of sharp peaks characteristic of autoionization are observed. Due to the large interatomic distance in the vertical transition region the molecular Rydberg states are expected to be almost atomic in nature. In Hund's case c with dipole selection rules the observable molecular states must be either 0_u^+ or 1_u , due to the ground molecular state being 0_g^+ . Although all excited atomic states with $J \neq 0$ can combine with a ground state atom to produce an 0_u^+ or 1_u molecular state, the observed spectrum can be accounted for by only the dipole allowed atomic states ($\Delta l = 0, \pm 1$). The

position of these atomic states are given in Fig. 1. The position of the peaks in the photoionization spectrum are seen to be slightly red shifted. These shifts are due to a combination of long range attractive forces and the variation in intensity of the unresolved vibrational bands.⁵

In Fig. 2 is shown the photoionization efficiency for He_2^+ from 545 Å to 490 Å at 0.8 Å resolution, which was obtained by expanding He gas at 4.2 °K and 700 torr through a 20 μm aperture. The spectrum is dominated by sharp autoionization structure corresponding to the Rydberg states $1s(2S_{1/2})np$ for $n > 3$. The signal arising from direct ionization was less than 1% of that observed at the autoionizing resonances. This very small direct ionization cross-section made it impossible to prove whether the He_2^+ originated from the supposed molecule He_2 or from dissociative ionization of larger clusters. No signal for He_3^+ could be detected above our background of about 0.1 count sec^{-1} . By comparison the He_2^+ signal was about 4 counts sec^{-1} at the autoionizing resonances, and the He^+ signal was typically 3000 counts sec^{-1} beyond threshold. The most plausible explanation for our data is that the He_2^+ signal arose from He_3 or higher clusters for which the parent ions were completely dissociated.

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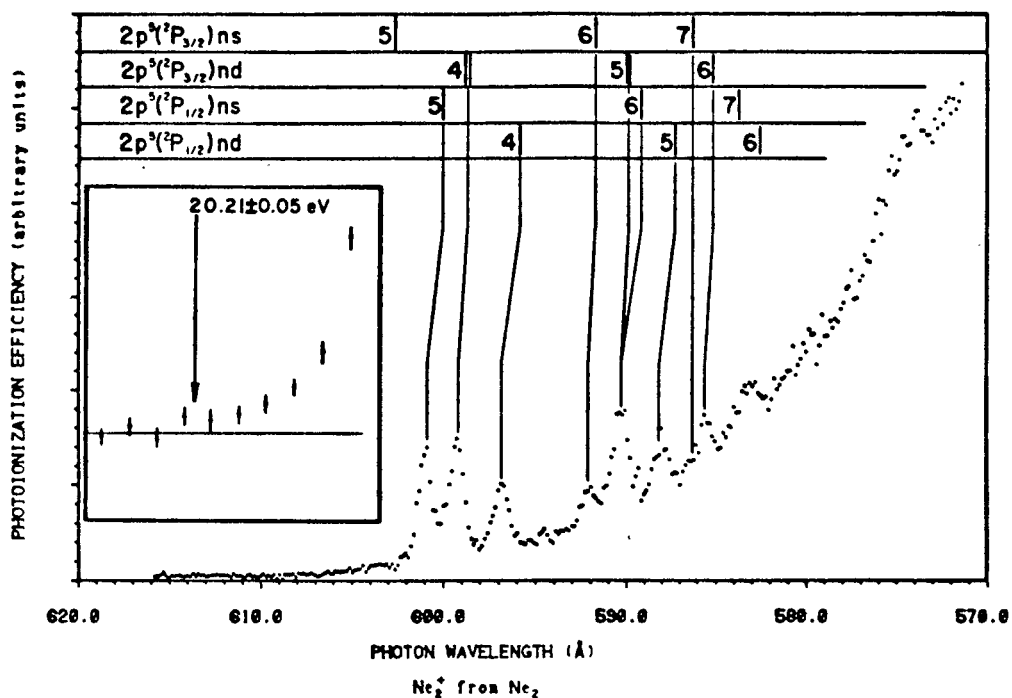


Figure 1. Photoionization efficiency curve for Ne_2^+ from Ne_2 taken at a wavelength resolution (FWHM) of 0.8 \AA with Ne gas expanded from 2000 torr at $77 \text{ }^\circ K$.

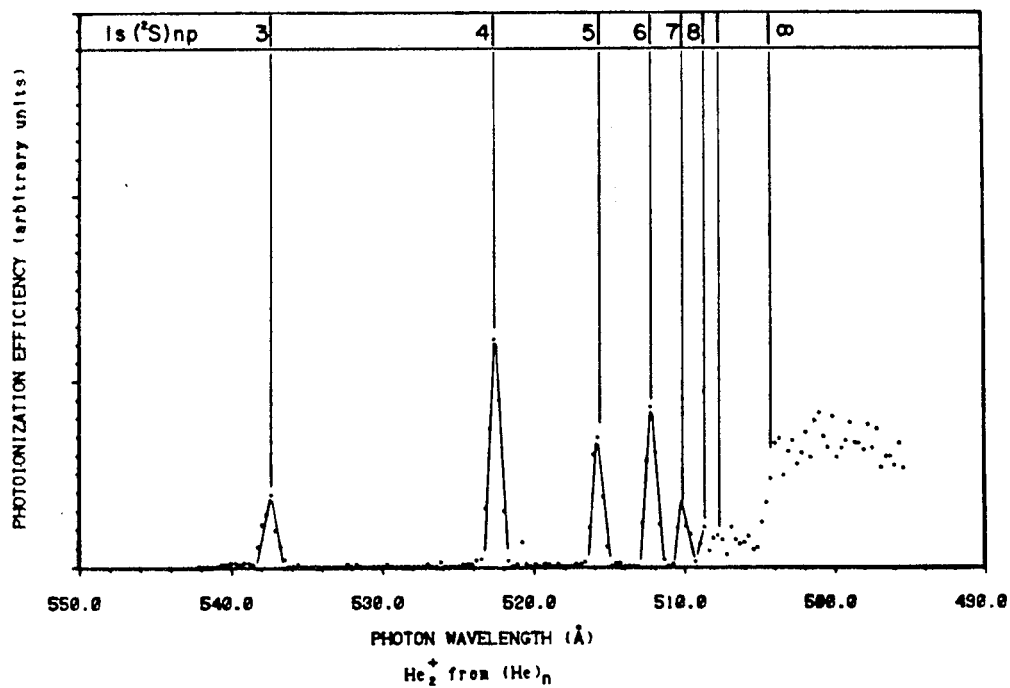


Figure 2. Photoionization efficiency curve for He_2^+ from $(He)_n$ taken at a wavelength resolution (FWHM) of 0.8 \AA with He gas expanded from 700 torr at $4.2 \text{ }^\circ K$.

