Mass Spectrometric Studies of Molecular Ions in the Noble Gases

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Molecular ions of the rare gases (He₂⁺, Ne₂⁺, A₂⁺, Kr₂⁺, and Xe₂⁺) produced by electron impact at gas pressures from 10^{-4} to 10^{-2} mm Hg have been studied with a small mass spectrometer. The ion intensity increased linearly with electron current and with the square of the gas pressure. The form of the ionization versus electron energy curves resembles closely curves of excitation probability by electron collision. The

appearance potentials of the molecular ions were less than those of the atomic ions by 1.4 + 0.7 = 0.2 volts in He,

 $0.7^{+0.7}_{-0.3}$ volt in Ne, $0.7^{+0.7}_{-0.2}$ volt in A, $0.7^{+0.7}_{-0.3}$ volt in Kr. These results can be interpreted, we believe, only by assuming that the process of formation of the molecular ions observed in this experiment is, using helium as an example, an excitation by electron impact, $He+e+K.E. \rightarrow He^*+e$, followed by the collision process, $He^*+He \rightarrow He_2^++e$, where He^* stands for a helium atom raised to a high-lying excited state. Our results differ from those of Arnot and M'Ewen on helium particularly in that they reported the appearance potential low enough to permit metastable atoms to form molecular ions.

INTRODUCTION

OLECULAR ions of helium, neon, and argon were first identified by Tüxen¹ using a mass spectrometer. Later Arnot and M'Ewen² examined the appearance of He₂⁺ using an electron space charge detector, but they were unsuccessful in their attempts to find Ne_2^+ and A_2^+ in the same apparatus. Subsequently these authors³ reported mass spectrometric studies of He_2^+ . They concluded that the process of formation of He_2^+ involved two stages, (1) the excitation of a neutral helium atom by electron impact

 $He + e + KE \rightarrow He^* + e$,

and then, (2) collision between the excited atom, He*, and another neutral atom

$\text{He}^* + \text{He} \rightarrow \text{He}_2^+ + e.$

Arnot and M'Ewen interpreted their appearance potential measurements to mean that He* could be, among others, the metastable excited state at 19.8 electron volts. Because the lifetime of this state is, in general, many orders of magnitude longer than that of radiating states, they naturally supposed the important process of formation to be the one involving a metastable atom.

Independent evidence conflicts with this conclusion. Meyerott⁴ deduced from theory and from experiments on enhanced spectra in helium that 22.5 volts were required to form He₂⁺ in its ground state. In experiments⁵ at these Laboratories the molecular ions He_2^+ , Ne_2^+ , and A_2^+ which were observed were formed in less than 10^{-6} sec after excitation of the respective gases by a short (10^{-7} sec) pulse of electrons passing through them. Although these experiments would not detect molecular

ions formed from metastable atoms, by establishing that molecular ions could be formed in relatively large numbers from high-lying, short-lived excited states they indicated that formation from long-lived metastable states was guite unlikely. We, therefore, undertook to re-examine helium in a mass spectrometer and also to study the other rare gases in an attempt to establish more accurately the formation energies of the molecular ions and to clarify the understanding of at least one process⁶ by which they are formed.

We have found molecular ions in krypton and xenon as well as in helium, neon, and argon; radon was not examined. The pressure and electron energy data, which were obtained only in the three lightest gases, indicate that in each gas molecular ions are produced by the same two-stage mechanism described above. In all the noble gases except xenon, which was not studied in detail, the appearance potential of the molecular ions seems to be about one to two volts less than the ionization potential of the corresponding atomic ions. Thus we conclude that the excited state involved cannot be a metastable state, but rather is a high-lying radiating state, in agreement with the formation process which was deduced to account for the molecular ions observed in the Townsend discharge.⁵

EXPERIMENTAL METHOD

The apparatus used in this investigation was assembled by one of us for other purposes and was used here because it was available. It is shown schematically in Fig. 1. The mass spectrometer, known as the Diatron⁷ 20, is a small 180° spectrometer with an ion path of radius one centimeter. Electrons emitted by a tungsten filament are accelerated by an applied potential V_e before entering the ionization chamber where the

¹ O. Tüxen, Z. Physik 103, 463 (1936).

² F. L. Arnot and M. B. M'Ewen, Proc. Roy. Soc. (London) A166, 543 (1938).

F. L. Arnot and M. B. M'Ewen, Proc. Roy. Soc. (London) A171, 106 (1939).

⁴ R. Meyerott, Phys. Rev. 70, 671 (1946). ⁵ J. A. Hornbeck, Phys. Rev. 84, 615 (1951).

⁶ It is likely that there exists more than one process of formation of the molecular ions, e.g., a three-body collision among two neutral atoms and an atomic ion.

⁷ Manufactured by the Consolidated Engineering Corporation, Pasadena, California.



FIG. 1. Schematic diagram of mass spectrometer and associated electrical circuits. The resolving power of the apparatus was sufficient to separate the neon isotopes of masses 20, 21, and 22. Since the spectrometer was operated with a single vacuum pump, i.e., the pressure in the analyzer was the same as in the ionization chamber, the resolution was degraded somewhat at the higher gas pressures necessary to observe molecular ions. Noise in the dc amplifier restricted the detection of ion currents to values greater than 10^{-14} amp.

ions are formed. Collimation of the electron beam is achieved by the same magnetic field that bends the ions around the semicircular path of the analyzer, which is "unfolded" in Fig. 1. The electron beam on leaving the chamber is accelerated by the voltage V_c and collected. The ions formed by electron impact are repelled from the chamber by a small potential into a region where the ion accelerating voltage, V_I , draws them into the analyzer chamber. The values of V_I and the externally applied magnetic field determine the mass to charge ratio of the ions that go through the small exit slit of the analyzer and strike the ion collector. This ion current is amplified by a direct coupled amplifier, developing a voltage that is fed to the vertical plates of a No. 304-H Dumont dc oscilloscope. The voltage V_I is varied as a function of time at a pre-set repetition rate, usually about one cycle every two seconds, and connected to the horizontal plates of the cathode-ray tube. This gives a horizontal scale that depends (nonlinearly) on the mass/charge ratio. The oscilloscope trace, therefore, plots ion intensity versus the mass-to-charge ratio of the ions formed by the electron beam.

When measuring the intensities of two ion peaks, such as He⁺ and He₂⁺, as a function of the energy of the ionizing electrons, the magnetic field of several thousand gauss was adjusted so that the same value of V_I applied in each case. This assured the maintenance of the same electric fields within the spectrometer, an important feature when one is concerned about tenths of an electron volt in appearance potential measurements.

All the metal parts of the Diatron 20 except the collector are mounted on one press and fit into a small

glass envelope, which was baked out at a temperature of 400°C before the gas was introduced. The gas pressure was measured by an ionization gauge.

Normally we admitted a single rare gas into the spectrometer and established the horizontal mass scale by marking the positions of the prevalent atomic ions, once, twice, or three times ionized. We also admitted on one occasion a small admixture of neon in helium



FIG. 2. Composite photograph of oscilloscope traces showing A_2^+ peaks for various electron accelerating voltages. The voltage corresponding to each trace is given.

permitting observation of He⁺, Ne⁺, and He₂⁺ simultaneously. This mixture was useful in providing a cross check of the (relative) energy scale of the electrons; for with it we measured the difference in the appearance potentials of He⁺ and Ne⁺ to be 3.2 volts, whereas the more precise spectroscopic difference is 3.021 volts. With this internal consistency the accuracy in determining the appearance potentials of the molecular ions was limited mainly by the small number which were formed.

In the pressure and filament emission measurements the height of the ion peaks was read directly from the cathode-ray tube screen. The remainder of the data were obtained by photographing the *CRT* traces and subsequently measuring the peak heights on the photographic negatives.



FIG. 3. Composite photograph showing atomic and molecular ion peaks. The mass value is given below each peak. The increased amplification of the molecular ion peak relative to the adjacent atomic ion peak is indicated.

Photographs of CRT traces showing the variation in A_2^+ peak height with the electron accelerating voltage are shown in composite form in Fig. 2. The peak is seen to fall on top of a background ion current that is decreasing in the direction of larger mass. The background effect is typical of all the molecular ions we observed and can be explained in the following way. At pressures low enough to avoid excessive scattering, the number of molecular ions formed is quite small compared with the number of atomic ions. As shown in Fig. 3, for example, the ratio of peak heights of atomic to molecular ions was about 500 to 1 in neon, 1200 to 1 in argon, 20,000 to 1 in krypton, and 40,000 to 1 in xenon. The same ratio in helium is 85 to 1. Hence the gain of the amplifier must be increased in order to observe the molecular ions at all. The increased amplification "blows up" the wings of the atomic ion peaks, which are broadened by scattering, so as to overlap the adjacent molecular ion



FIG. 4. Variation of ion peak height in helium with pressure. The electron current was constant at 150 μ amp; the electron accelerating voltage was 25 volts for He₂⁺ and 30 volts for He⁺. The broken lines have slopes of one and two.

peaks. This increases the difficulty of making reliable peak height measurements on the molecular ions; in fact, krypton, and xenon were extremely troublesome.

VARIATION WITH FILAMENT EMISSION AND PRESSURE

Both the molecular and atomic ion peaks were found to vary linearly with the electron beam current, in agreement with Arnot and M'Ewen. This indicates that only one excited atom (or ion) is involved in the formation mechanism.

With a fixed electron energy somewhat above the ionization potential of the atomic ion, the peak heights of the atomic and molecular ions were measured as a function of gas pressure, p. The results for helium and argon are shown in Fig. 4 and Fig. 5 on a log-log plot.



FIG. 5. Variation of ion peak height in argon with pressure. The electron current was constant at 200 μ amp; the electron accelerating voltage was 19 volts for both ions. The broken lines have slopes of one and two.



FIG. 6. The ratio of peak heights of molecular to atomic ions versus pressure. Conditions are as given in Figs. 4 and 5.

Within the experimental error these data indicate that the production of the molecular ions varies with p^2 whereas the atomic ion production is a linear function of p, as expected. The divergence of the experimental points at the highest pressures from the straight lines of slopes one and two in the figures is undoubtedly of instrumental origin. Above 10^{-3} mm Hg, measurement of the pressure with an ion gauge is obviously unsatisfactory, and also scattering in the analyzer of the spectrometer is a limitation. However, the ratios of the molecular to atomic ion peak heights versus p, plotted in Fig. 6, show a linear variation with pressure over a pressure range of a factor of ten.

We consider the above data sufficient evidence to conclude that the molecular ions are formed in a twostage process involving first excitation (or ionization) and then collision of the excited atom (or ion) with a neutral one.

VARIATION WITH ELECTRON ENERGY

Measurements on traces similar to those in Fig. 2 give the ion peak heights as a function of the electron



FIG. 7. Ionization in helium versus the electron accelerating voltage (uncorrected for contact potential difference). The broken line indicates a "ghost," as explained in reference 8.

accelerating voltage, as plotted in Figs. 7, 8, and 9 for helium, neon, and argon. In each case we find, within experimental error, a typical ionization probability curve for the atomic ion production. For the molecular ions we find in each case a curve very similar to published curves of atomic excitation efficiency as a function of electron energy. In helium the results⁸ are not dissimilar to calculations of excitation cross-sections by Massey and Mohr⁹ for the optically allowed transitions $1s^2 {}^1S$ - $1s3p {}^1P^o$ and $1s^2 {}^1S$ - $1s3d {}^1D$. The curve is not so similar to the calculations for transitions to the 1s3p ³ P^{o} and 1s3d ³D states, which cannot decay directly to the ground state, and to states of the configuration 1s2p. The inference is strong that the formation mechanism involves the excitation rather than the direct ionization of a neutral helium atom by electron impact. Since a mixture of several atomic states is probably involved, and also because of uncertainties in the experimental data, it does not seem profitable to speculate



FIG. 8. Ionization in neon versus the electron accelerating voltage (uncorrected for contact potential difference).

from these data as to the particular states involved other than to notice the similarities pointed out above.

APPEARANCE POTENTIAL MEASUREMENTS

Careful studies of the toes of the atomic ion curves, Figs. 7–9, and of the appearance of molecular ion peaks above the noise level of the apparatus yield information on the minimum energy of formation of the molecular ions. Characteristic data in this region are plotted in Fig. 10 for helium, neon, and argon. In these illustrations the zero of ordinates of the atomic ion curves has been adjusted so that the significant regions of the data can be shown in the same plot. The horizontal scale is electron accelerating voltage as indicated by a volt-

⁸ The dip shown in Fig. 7 is a "ghost" which we do not explain. It was found only in helium, and its position on the voltage scale varied with gas pressure, repeller voltage, and other instrument settings. By making several "runs" under different conditions the entire excitation curve (solid line, Fig. 7) could be plotted. ⁹ H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London)

⁹ H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) A132, 605 (1931).



FIG. 9. Ionization in argon versus the electron accelerating voltage (uncorrected for contact potential difference).

meter, i.e., uncorrected for contact potential difference, for we are concerned only with the voltage difference between the appearance potentials of the molecular and atomic ions.

In the conventional way we interpret the onset of atomic ionization as the voltage at which the atomic peak increases abruptly with increased electron accelerating voltage. The ionization observed below this break in the curves is accounted for by recognizing that a small amount of ionization can occur whenever there is a voltage in the apparatus greater than the ionization potential. The electron collecting voltage, for example, meets this requirement.

The simplest interpretation of the data in Fig. 10 would be that the appearance potential of He_{2}^{+} is 1.5 volts less than that of He⁺, and that of A_2^+ is 0.7 volt less than A⁺; and we would conclude that Ne⁺ appears at 3.2 volts less than He⁺. Because the number of molecular ions produced is so small, however, there is considerable difficulty in picking the voltage where the molecular ions are first detectable. Increasing the detection sensitivity of the instrument would probably increase the difference between the appearance potentials of the atomic and molecular ions. This problem is illustrated in Fig. 10 in which the Ne⁺ curve is plotted on a scale reduced ten times. It is clear that if the uncertainty in the peak height measurement were to be increased also by a factor of ten, the observed appearance potential of Ne⁺ would be about 0.5 volt higher.

In order to estimate the error in the above determinations, relative appearance potentials of the two ions were also measured when the amplifier gain was readjusted so that the maximum signal voltage (i.e., maximum peak height) of the two peaks was about the same at the optimum accelerating voltage in each case. This test indicated a probable error of slightly less than an electron volt in determining the appearance potentials from the data of Fig. 10. Since atomic excitation efficiency curves rise more sharply as a function of



FIG. 10. Ionization versus the electron accelerating voltage (uncorrected) in argon and also in helium with a small admixture of neon. The zero of ordinates of the atomic ion data has been adjusted so that these curves can be plotted conveniently in the same figure. The arrows at the top give the relative appearance potentials of the ions.

electron energy than the corresponding ionization efficiency curves, this estimate of the probable error seems reasonable. Our data, which include at least two "runs" in each gas, indicate that by taking the atomic ionization potentials of He⁺, Ne⁺, A⁺, and Kr⁺ to be 24.58, 21.56, 15.76, and 13.93 volts,¹⁰ respectively, the appearance potentials of He₂⁺, Ne₂⁺, A₂⁺, and Kr₂⁺, respectively, are 23.18+0.2, 20.86+0.3, 15.06+0.2, and -0.7 -0.7 -0.7

13.23 \pm 0.3 volts. These values are higher than the -0.7

energies of the metastable atoms by amounts believed to be outside the limit of experimental error. The metastable levels are listed¹⁰ here for comparison: 19.81 and 20.61 in helium, 16.61 and 16.71 in neon, 11.55 and 11.72 in argon, and 9.77 and 10.52 in krypton. The data on helium are entirely consistent with the deduction of Meyerott⁴ that the ground state of He₂⁺ is very close to 22.5 volts. It may be noted that the lower value reported by Arnot and M'Ewen³ does not seem to be well established even by their own data.

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¹⁰ The values quoted here for helium, neon, and argon are taken from *Atomic Energy Levels*, by Charlotte E. Moore, National Bureau of Standards circular No. 467 (1949). Krypton is not included in this reference so the "old value" is given here. Likewise the energies of the metastable states are "new values" except for krypton.



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