Double ionization of rare-gas dimers: $NeKr + e \rightarrow NeKr^{2+}$

K. Stephan, T. D. Märk, and H. Helm*

Abt. für Kernphysik und Gaselektronik, Institut für Experimentalphysik,
Leopold Franzens Universität, A 6020 Innsbruck, Austria

(Received 29 March 1982)

The existence of the doubly charged dimer ion $NeKr^{2+}$ is substantiated by electron-impact ionization of the mixed van der Waals dimer NeKr. The stability of this doubly charged molecule is discussed with the use of semiquantitative potential energy curves. The electron-impact-ionization appearance potential confirms the prediction from the potential-energy curves.

In this Brief Report we report the observation of long-lived species of the doubly charged molecular ion $NeKr^{2+}$. We produced this ion by electron-impact ionization of the mixed van der Waals dimer NeKr in the reaction

$$NeKr + e \rightarrow NeKr^{2+} + 3e \ . \tag{1}$$
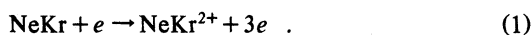
The neutral dimers were formed in a supersonic expansion of a mixture of 200-torr Ne, 50-torr Kr, seeded with 1750-torr He. The stagnation chamber and the nozzle (10-μm diam) were cooled to liquid-nitrogen temperature and the ions were analyzed in a conventional sector-type double-focusing mass spectrometer of reversed geometry. Details of the apparatus and the measuring technique are described in Ref. 1.

The doubly charged ions were uniquely identified through the observation of ions at $m/e = 51.5$ which arise from the isotopic combination $^{20}Ne\,^{83}Kr$. At electron energies around 100 eV the abundance of $NeKr^{2+}$ ions was found to be of the order of 1% of the singly charged ionization products $NeKr^{+}$.

Figure 1 shows the ionization efficiency curve for the formation of $NeKr^{2+}$ in reaction (1) close to threshold. For comparison the ionization efficiency curve for the formation of Kr^{2+} in the reaction

$$Kr + e \rightarrow Kr^{2+} + 3e \tag{2}$$

is also shown. It is apparent from Fig. 1 that the appearance potential for reaction (1) is close to that for reaction (2).

$NeKr^{2+}$ is the third doubly charged rare-gas molecule observed experimentally. Johnsen and Biondi[2] studied in a drift tube the formation of $NeXe^{2+}$ in a three-body reaction. We observed $NeXe^{2+}$ and $ArXe^{2+}$ by electron-impact ionization of
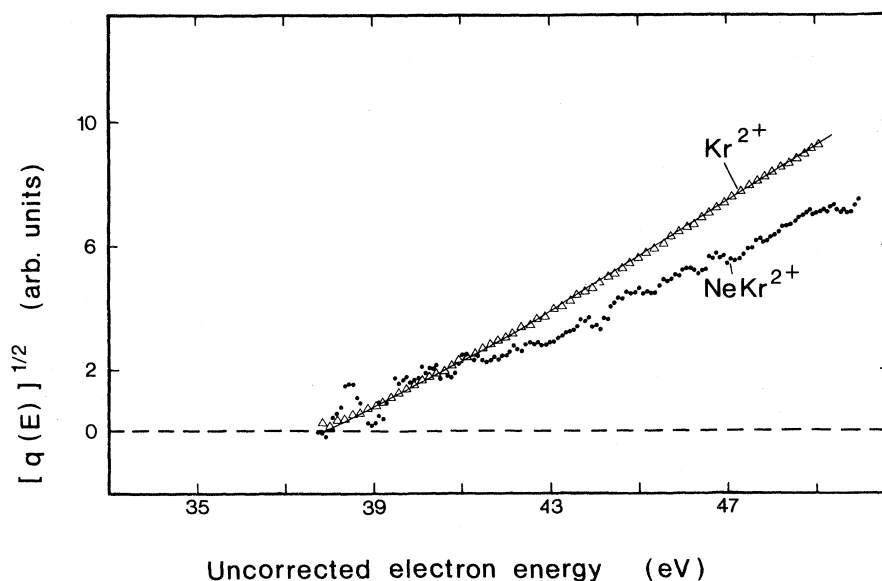

FIG. 1. Relative ionization-cross-section curves for the formation of $NeKr^{2+}$ in reaction (1) and for the formation of Kr^{2+} in reaction (2). To facilitate threshold extrapolation the square root of the relative cross section q is plotted along the ordinate.

the respective van der Waals dimers.[1]

The stability of $NeXe^{2+}$ is readily explained.[1] The lowest asymptotic limit in this doubly charged system is $Ne(^1S_0) + Xe^{2+} {}^3P_2$. This limit lies 355 meV below[3] the dissociation limit $Ne^+ {}^2P_{3/2} + Xe^+ {}^2P_{3/2}$. As a result of the weakly attractive interaction between $Ne + Xe^{2+}$ a truly stable molecular ion $NeXe^{2+}$ can be formed, lying ~33.3 eV above the neutral dimer NeXe.

In the case of $ArXe^{2+}$ the dissociation limit $Ar\,{}^1S_0 + Xe^{2+} {}^3P_2$ lies energetically above the limits $Ar^+ {}^2P + Xe^+ {}^2P$. The weakly bound molecular state arising from $Ar\,{}^1S_0 + Xe^{2+} {}^3P_2$ are rapidly predissociated by the repulsive Coulomb interaction $Ar^+ + Xe^+$ (see Fig. 8 of Ref. 1). Long-lived species of $ArXe^{2+}$ can, however, be formed in states arising from the interaction of $Ar\,{}^1S_0 + Xe^{2+} {}^3P_{0,1}$ and higher states of Xe^{2+}. At distances ≥ 3 Å these states lie above the Coulomb potentials, hence decay only radiatively into the dissociative channels which give $Ar^+ + Xe^+$. The lowest long-lived state of $ArXe^{2+}$ lies approximatively 34.3 eV above the neutral ground-state dimer ArXe and was observed experimentally.[1]

In the case of $NeKr^{2+}$ the situation is yet different. Figure 2 shows schematic potential-energy curves for the lowest molecular states of $NeKr^{2+}$. The potential-energy curve arising from $Kr^{2+} {}^3P_2 + Ne\,{}^1S_0$ was approximated by the statistical average[1] $[\frac{2}{3}V_{3_{\Pi}}(R) + \frac{1}{3}V_{3_{\Sigma}}(R)]$ of the theoretical[4] curves for KrO to which a polarization term $-[2\alpha(Ne)]/2R^4$ was added. A better choice for an isoelectronic analog would be the molecule NeSe, for which, however, no potential-energy curves are known to date. At large molecular distances the interaction $Ne^+ {}^2P + Kr^+ {}^2P$ is purely repulsive and the curve shown for these asymptotes in Fig. 2 represents the pure Coulomb interaction e^2/R^2. These Coulomb potentials cross the weakly attractive potential-energy curves arising from $Ne\,{}^1S_0 + Kr^{2+} {}^3P_2$ at internuclear separation between ~4.8 and 5.5 Å. As a result the formation of quasibound molecular levels at energies below the lowest crossing point may be anticipated. The true $NeKr^{2+} {}^3P_2$ potential curve will be more bound than shown in Fig. 2 due to charge-exchange interaction with $Ne^+ {}^2P + Kr^+ {}^2P$. At internuclear separations near 3.5 Å, where the minimum in the lowest $NeKr^{2+}$ state is expected, the rate of predissociation by the Coulomb curves is sufficiently slow to permit the existence of long-lived ions $NeKr^{2+}$. Since the equilibrium separation[5] of the van der Waals dimer NeKr is 3.6 Å, favorable Franck-Condon factors
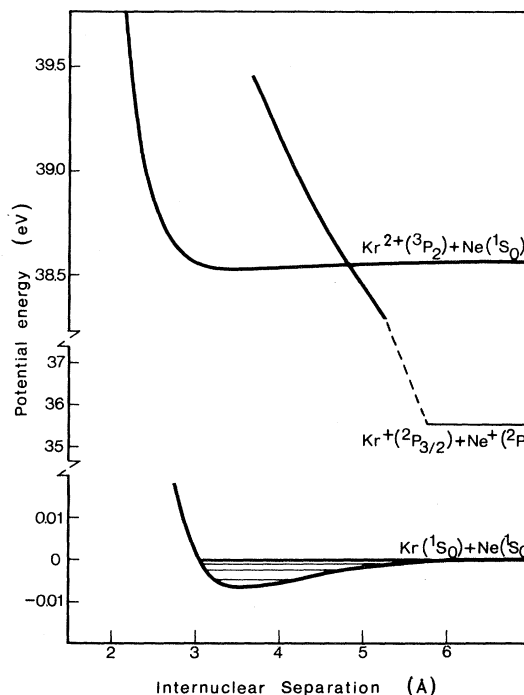

FIG. 2. Schematic potential-energy curves for the lowest states of $NeKr^{2+}$ and NeKr.

exist for the formation of $NeKr^{2+}$ in reaction (1). The observed appearance potential for reaction (1), 38.6 eV, is consistent with the interpretation that the dominant contribution to the observed $NeKr^{2+}$ signal arises from molecular states which diabatically relate to $Ne\,{}^1S_0 + Kr^{2+} {}^3P_2$. States arising from the higher fine-structure limits of $Kr^{2+} {}^3P$ cross the Coulomb potentials near their expected minimum position and should be predissociated more efficiently. A detailed discussion of the coupling phenomena at the intersections between the potential energy curves for $Ne\,{}^1S_0 + Kr^{2+} {}^3P$ and $Ne^+ {}^2P + Kr^+ {}^2P$ has been given by Maier.[6]

ACKNOWLEDGMENTS

*Permanent address: Molecular Physics Laboratory, SRI International, Menlo Park, Calif. 94025.

[1]H. Helm, K. Stephan, T. D. Märk, and D. L. Huestis, J. Chem. Phys. 74, 3844 (1981).

[2]R. Johnsen and M. A. Biondi, Phys. Rev. A 20, 87 (1979).

[3]C. E. Moore, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. 35 (1971).

[4]T. H. Dunning and P. J. Hay, J. Chem. Phys. 66, 3767 (1977).

[5]D. E. Freeman, K. Yoshino, and Y. Tanaka, J. Chem. Phys. 67, 3462 (1977).

[6]W. B. Maier, II, J. Chem. Phys. 60, 3588 (1974).