Formation and mean lifetime of the metastable doubly charged rare-gas dimer $NeAr^{2+}$

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The observation of a long-lived $NeAr^{2+}$ molecular ion is reported. This ion was obtained by charge stripping of a 900-keV $NeAr^{+}$ beam in an Ar gas target, and its mean lifetime was determined to be 275 ± 25 nsec. This is a direct measurement of the mean lifetime of a doubly charged rare-gas dimer. The ion decay is decribed well by a single exponential decay, suggesting that only one metastable state is populated in the collision. The cross section for the $NeAr^{2+}$ production was determined to be $(3\pm2)\times10^{-18}$ cm^2. The existence of this weakly bound molecular ion and the fact that its mean lifetime is known can serve to motivate better theoretical calculations of molecular structure and the dissociation process.

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I. INTRODUCTION

Multiply charged diatomic molecular ions containing a rare-gas atom are of increasing interest theoretically [1–4] as well as experimentally [5–8]. These molecular ions have bound states and metastable states even though the rare-gas atoms are not strongly active chemically. Furthermore, theoretical studies [1,2] have shown that the bond strength does not always decrease as electrons are removed from the molecule as one would expect intuitively. On the contrary, removing electrons sometimes may even strengthen the bond in spite of the increasing Coulombic repulsion. For example, theoretical calculations [1] predict that the ground state of CHe^{2+} is more stable than the ground state of CHe^{+} and CHe^{3+}.

Diatomic molecular ions containing two rare-gas atoms are expected to have even weaker bonds than those containing only one rare-gas atom. Stable or metastable states of these molecular ions can serve as a stringent test of molecular structure theory because of the small depth of the potential well which makes them very sensitive to small differences in the energy. It is therefore important to study the existence of such molecular ions and determine their mean lifetime and dissociation energy in order to improve our understanding of bonding and molecular dissociation.

In this paper we report the observation of a long-lived doubly charged rare-gas diatomic molecule, $NeAr^{2+}$. This long-lived molecular ion is formed in a metastable state which dissociates either by tunneling through the potential barrier or by an electronic transition to a repulsive state. Furthermore, for the first time the mean lifetime of such a metastable state has been determined directly. This information about the metastable state can serve as a test for mean lifetime calculations of molecular states which are more complicated than structure calculations.

II. EXPERIMENT

The $NeAr^{2+}$ molecular ion was produced by charge stripping of a 900-keV $NeAr^{+}$ beam in Ar gas target. The apparatus used in the present study has been described in detail previously by Heber *et al.* [9]. A schematic diagram of the experimental setup is shown in Fig. 1. A 900-keV $NeAr^{+}$ beam generated by the Technion 1-MV Van de Graaff accelerator was selected by a 15° analyzing magnet according to its momentum per unit charge. The beam was collimated to a parallel beam of about 0.4×0.4 mm^2 using two four jaw slits in front of the analyzing magnet in order to minimize contaminations, having a slightly different mv/q ratio, to the main beam. The beam was further collimated to less than 0.2×0.2 mm^2 by a four jaw slit before the entrance of the target cell. A subsequent velocity selector (Wien filter) was used before the target cell to clean the beam from any contamination having a different velocity than the $NeAr^{+}$ beam. The $NeAr^{+}$ molecular ions passed through a 50-mm-long differentially pumped gas cell containing argon with a 0.3-mm-diameter entrance and 1.0-mm-diameter exit collimators. The Ar gas pressure in the target cell was typically in the range of 0.1–3.5 mTorr while the pressure in the rest of the system was kept below 10^{-6} Torr.

An electrostatic analyzer was used to identify all the charged products produced in the collision of $NeAr^{+}$ with Ar. This analyzer consisted of a horizontal electrostatic parallel plate deflector D2, which directed the ions through an exit slit, S5, 0.45 mm wide and 3 mm high, located at a distance of 18.5 mm off the beam axis giving a resolution in the deflection voltage $\delta V/V$ of about 2.5% for each ion. This deflector is mounted on a movable stage such that the distance between it and the target cell can be varied to allow measurements of mean lifetimes [11]. The height and orientation of the target cell were

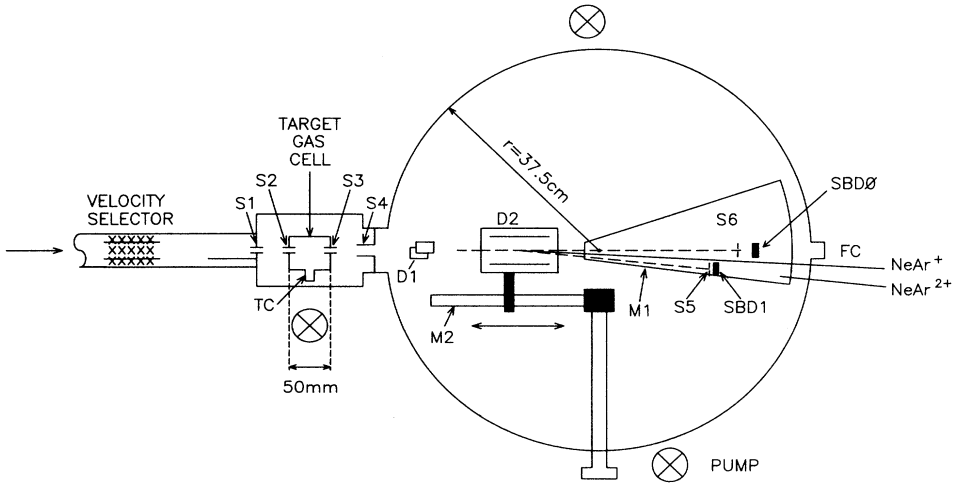

FIG. 1. The experimental set-up. The ion trajectories through the analyzer are drawn for a deflection voltage at which the $NeAr^{2+}$ goes through the exit slit S5. (Note that the deflector D2 and the arm M2 can be moved externally.)

adjusted so that it would be aligned with the beam axis. This alignment was verified by ensuring that the beam current has a maximum for zero deflection voltage on an additional vertical electrostatic parallel plate deflector D1, located beyond the target cell. The ions passing through the analyzer exit slit S5 were detected by a surface-barrier detector (SBD1). These detectors produce a signal which is proportional to the total energy of the particles detected. The detector was positioned directly on the beam axis, by rotating the arm M2 on which the detectors are attached, so that it detected the $NeAr^{+}$ beam passing through the target cell with zero deflection voltage on D2. A typical energy spectrum obtained by the surface-barrier detector SBD1 is shown in Fig. 2. In the energy spectrum shown on the top for background pressure, i.e., no Ar in the target cell, only the wide $NeAr^{+}$ peak can be seen. On the other hand, in the energy spectrum shown in the bottom, for a target pressure of 3.5 mTorr, three wide peaks can be seen. At this pressure a significant fraction of the $NeAr^{+}$ molecular ions break into Ne and Ar fragments whose charge states are not identified because there is no deflection voltage. These fragments have approximately the beam velocity, because the breakup energy which is typically a few eV is much smaller than the beam energy of 900 keV. Thus the Ne and Ar fragments have approximately 300 and 600 keV, respectively, according to their mass ratio, while the molecular $NeAr^{+}$ ion has the full 900-keV beam energy. These three ions produce the well-distinguished peaks seen in the energy spectrum shown in Fig. 2(b). The small deviations of the peaks' positions from the energy ratios expected are due to known nonlinear pulse height defect effects in surface-barrier detectors due mainly to saturation effects [10]. To summarize, in the analyzer used the ions can be identified by their energy recorded in the energy spectrum obtained by the surface-barrier detector, as well as by the voltage needed to direct them through the exit slit.

While scanning the voltage of the analyzer the yield of ions detected was normalized to the number of neutral fragments and molecules detected by a second surface-barrier detector located directly on the beam axis as shown in Fig. 1. A small 0.5-mm-diameter collimator was placed on the normalization detector in order to reduce the high rate of neutrals to a reasonable value. The yield of Ne^{q+}, Ar^{p+}, and $NeAr^{2+}$ ions, defined as the number of counts under their respective peaks in the energy spectrum, similar to the one presented in Fig. 2(b), is shown in Fig. 3 as a function of the deflector voltage for a target pressure of 2.5 mTorr. The ions are directed onto the exit slit S5 according to their energy per charge unit. Thus the $NeAr^{2+}$ molecular ion is expected to peak

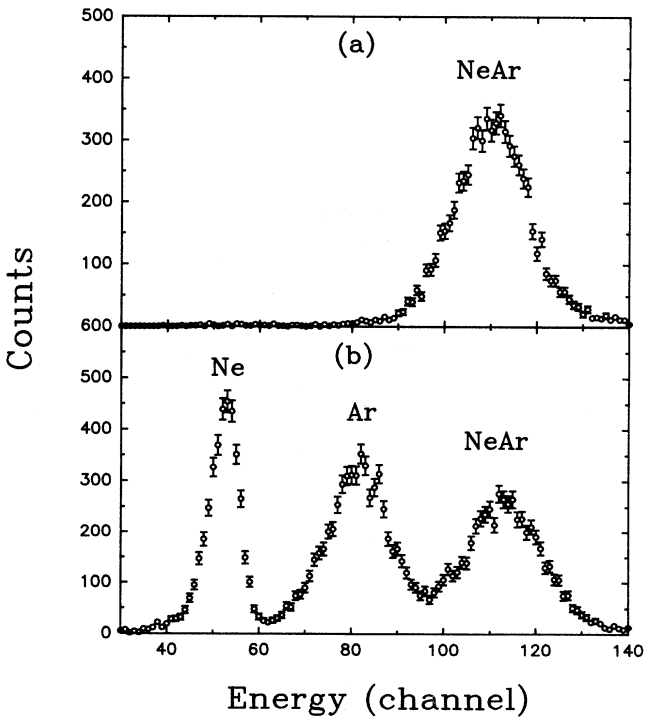

FIG. 2. Energy spectra of (a) $NeAr^{+}$ main beam, (b) $NeAr^{+}$ after passing through the target cell with no deflection voltage. The $NeAr^{n+}$, Ar^{n+}, and Ne^{n+} ions have 900, 600, and 300 keV, respectively.

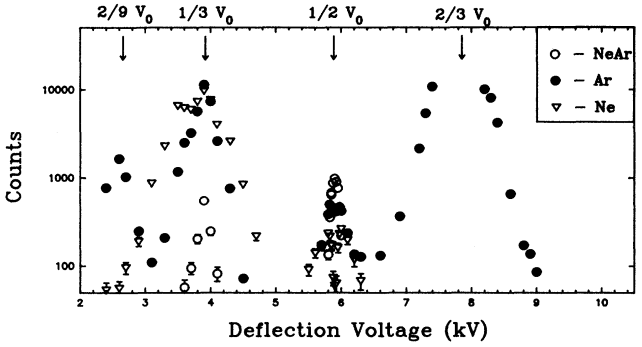

FIG. 3. The number of $NeAr^{n+}$, Ar^{n+}, and Ne^{n+} ions as a function of the deflection voltage.

at $\frac{1}{2}V_0$, where V_0 is the voltage needed to direct the main $NeAr^+$ beam through the exit slit. In addition to the molecular ion peaks at V_0 and $\frac{1}{2}V_0$ a few more peaks are expected. The Ar^+, Ar^{2+}, and Ar^{3+} fragments produced in the target cell, which have $\frac{2}{3}$ of the beam energy, are expected to peak at $\frac{2}{3}V_0$, $\frac{1}{3}V_0$, and $\frac{2}{9}V_0$, respectively, while the Ne^+, Ne^{2+}, and Ne^{3+} fragments, which have only $\frac{1}{3}$ of the beam energy, are expected to peak at $\frac{1}{3}V_0$, $\frac{1}{6}V_0$, and $\frac{1}{9}V_0$, respectively. These expected voltages are marked on a horizontal axis of Fig. 3. The peaks associated with the molecular ions $NeAr^+$ and $NeAr^{2+}$ as well as the Ar^{p+} ($p=1-3$) and the Ne^+ are clearly seen. The additional peaks of Ne and Ar at $V_0/2$ will be discussed later. The "NeAr" peak at $V_0/3$ is a real peak, but is not due to $NeAr^{3+}$: It is due to true coincidences between Ne^+ and Ar^{2+} from the $Ne^+ + Ar^{2+}$ breakup channel which have the same energy per charge as the $NeAr^{3+}$. This peak is as narrow as a molecular ion peak because the narrow slit S5 selects only a small fraction of coincidences between fragments originating from molecules which dissociated approximately parallel to the beam axis.

III. RESULTS AND DISCUSSION

The molecular ion of interest in this study, $NeAr^{2+}$, is expected to hit the detector at half the voltage of the main beam, namely, $V_0/2$. At this voltage no other fragment of the $NeAr^+$ projectile, produced in the target cell, is expected to go through the exit slit. For this deflection voltage the $NeAr^{2+}$ ion goes through the exit slit located at a distance of 18.5 mm from the beam axis, whereas the Ar^+ ion hits 4.5 mm toward the beam axis, and the Ne^+ and Ar^{2+} both hit 9 mm further away than the $NeAr^{2+}$, as shown in Fig. 4. This was the reason for choosing a heteronuclear molecule over a homonuclear molecule, for which the singly charged fragments and the doubly charged molecular ion hit the deflector at the same deflection voltage [7,8]. The trajectories followed by the neighboring ions on both sides are the Ne and Ar fragments which make spots on the plane of the exit slit that are much broader than the 0.2×0.2 mm^2 beam spot because of the additional energy obtained by the fragments in the dissociation process. This energy is sufficient to increase the size of the spots produced by the fragments on the exit slit plane to a couple of millimeters without changing the ions' energy significantly. The spot of the lighter Ne fragment is expected to be larger due to linear momentum conservation in the two-body breakup. For this reason the exit slit was chosen to be only 0.45 mm wide in order to reduce the chances that a Ne or Ar fragment exits through the slit when the voltage is set for the $NeAr^{2+}$ molecular ion detection. As seen in Fig. 3 the Ar^+ on one side and the Ne^+ and Ar^{2+} on the other side fall off to a low yield for the range of voltages of interest. At the center of this voltage range (i.e., $V=V_0/2$), which is expanded in Fig. 5, a narrow peak at the full energy can be clearly seen. This peak has to be a doubly charged molecule or atom at full beam energy, most likely the

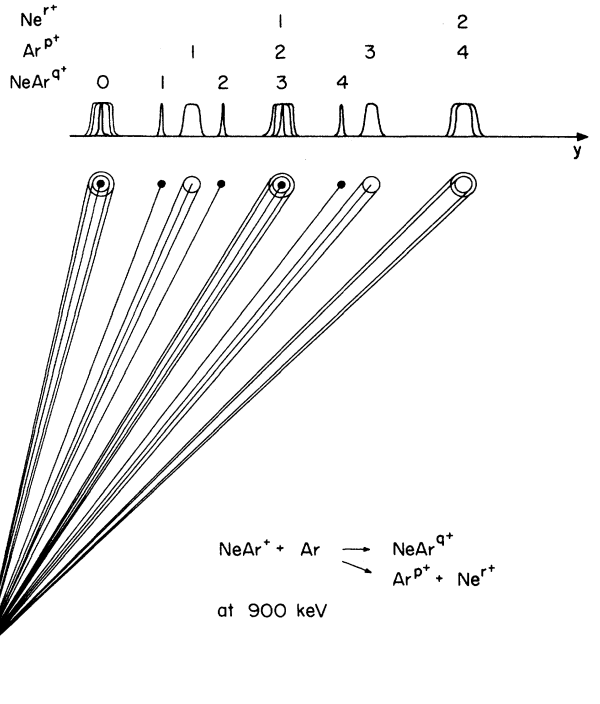

FIG. 4. Ion trajectories for a deflection voltage of $V_0/2$.

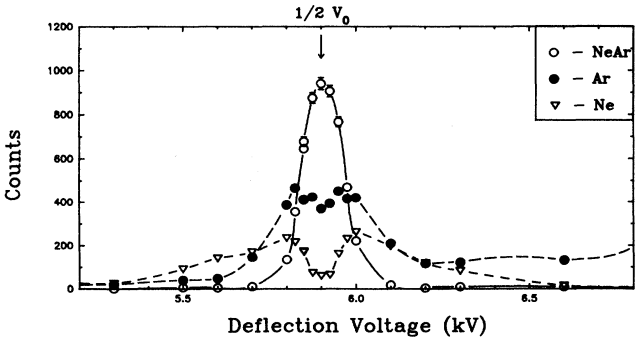

FIG. 5. The number of $NeAr^2$, Ar^{n+}, and Ne^{n+} ions as a function of the deflection voltage around the voltage $V_0/2$ where the doubly charged molecular ion is expected.

$NeAr^{2+}$ molecular ion. At the same deflection voltage, $V_0/2$, there are unexpected peaks of Ne and Ar fragments, which have to be produced by dissociation after the deflector D2. These peaks are wider due to the kinetic energy release in the dissociation as explained before. A careful study of the fragment's peaks shows a small dip at the place where a peak is expected. These dips are caused by events where both fragments of a broken molecule hit the detector simultaneously, thus depositing the full energy in the detector and contributing to counts under the full energy $NeAr^{2+}$ peak. These Ne and Ar fragment peaks, at exactly the voltage associated with the doubly charged molecule, can be caused by metastable $NeAr^{2+}$ molecular ions dissociating in flight after they have been analyzed by the electric field. These fragments are an indication that the $NeAr^{2+}$ molecular ion is metastable. In order to ensure that the full energy peak is really a molecule and not an ion of $^{60}Ni^{2+}$, for example, the yield under the full energy peak was measured as a function of the pressure in the target cell. The yield under the full energy peak increases with the pressure and then drops as expected because of the competition between electron stripping and collision induced dissociation. A careful search for C, N, O, and Si ions coming from molecules with mass 60, both in the energy spectrum taken at $V_0/2$ and the voltage scan shown in Fig. 3, show no indication of these ions, thus contaminations caused by molecules of these light atoms, like CO_3^+ or $^{30}Si_2^+$, which have the same mv/q and velocity, were ruled out. The existence of a metastable doubly charged $NeAr^{2+}$ molecular ion was established at this point.

The measurement of the $NeAr^{2+}$ mean lifetime was performed using a technique similar to one we have used previously to determine the mean lifetime of the metastable Ar^- ion [11]. For this measurement the distance between the target cell and the horizontal deflector D2 was varied by a known amount and the number of counts under the full energy peak at each distance was measured. The number of $NeAr^{2+}$ ions measured when the distance between the deflector D2 and the target cell was l_1 is given by

$$N_1 = N_0 e^{-t_1/\tau} , \tag{1}$$

where N_0 is the number of $NeAr^{2+}$ ions produced in the target cell and t_1 is their flight time to the deflector which is given by

$$t_1 = l_1/v , \tag{2}$$

where v is the beam velocity. Now, the number of metastable $NeAr^{2+}$ ions which passed the deflector can be measured as a function of the deflector distance from the target cell. If the molecular ion is formed in one metastable state we expect an exponential decay curve with a slope of $1/v\tau$ from which the mean lifetime can be evaluated as the beam velocity is known.

For the evaluation of the mean lifetime described above it is important that all $NeAr^{2+}$ metastable ions which passed the deflector are accounted for as molecular ions (i.e., counts under the full energy peak) even if they decayed in flight on the way to the detector after being analyzed by the electric field. As we have seen before for a 0.45×3.0 mm^2 exit slit this assumption is not valid. Using an iris aperture instead of the narrow exit slit, the number of $NeAr^{2+}$ ions as a function of the aperture's radius was measured and is shown in Fig. 6. From this figure it can be seen that all the $NeAr^{2+}$ fragments which had dissociated in flight after the electrostatic deflector are collected when the radius is larger than 2.5 mm. A 4-mm-aperture radius was used to collect the data used for the mean lifetime measurement. For such a large exit slit both the Ne and Ar fragments of a $NeAr^{2+}$ molecular ion which passed the deflector hit the detector simultaneously thus being counted as a full energy event. The increase of the slit also increases the amount of Ne^+ and Ar^+ fragments which can hit the detector, but the slit size was still small enough so random coincidences of Ne^+ with Ar^+ were negligible.

The number of metastable $NeAr^{2+}$ ions which passed the deflector as a function of the deflector distance from the target cell are shown in Fig. 7. From this figure it can be clearly seen that a single exponential decay curve is in good agreement with the data suggesting the existence of a single metastable state. We have tried to add a constant number of counts to the exponential decay function in order to check the possibility of ions which are long lived relative to the flight time through the detection system. The best fit gives no such contribution. The mean lifetime of the $NeAr^{2+}$ metastable state evaluated from the slope is

$$\tau = \frac{1}{vS} = 275\pm25 \text{ nsec} , \tag{3}$$

where $v = 1.70\pm0.01$ mm/nsec is the beam velocity and S is the slope. The main contribution to the error in the mean lifetime evaluation is an instability of the target pressure.

The dissociation of the weakly bound $NeAr^{2+}$ molecular ion can be collisionally induced by the residual gas atoms in the target chamber if the cross section for such a process is large enough. This will also cause a reduction in the number of $NeAr^{2+}$ ions as a function of the distance from the target cell where they were created. The number of $NeAr^{2+}$ counts decreased only when the

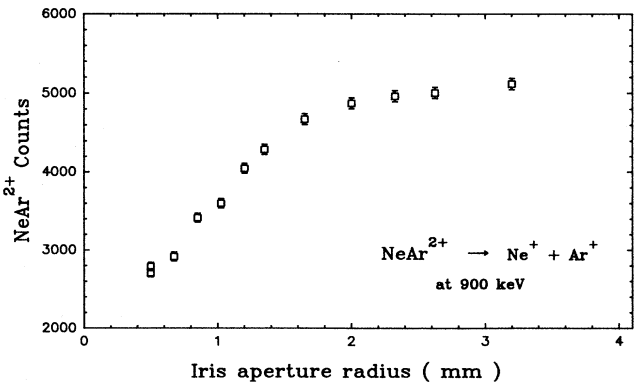

FIG. 6. The number of $NeAr^{2+}$ ions as a function of the radius of the iris aperture S5 in front of the detector.

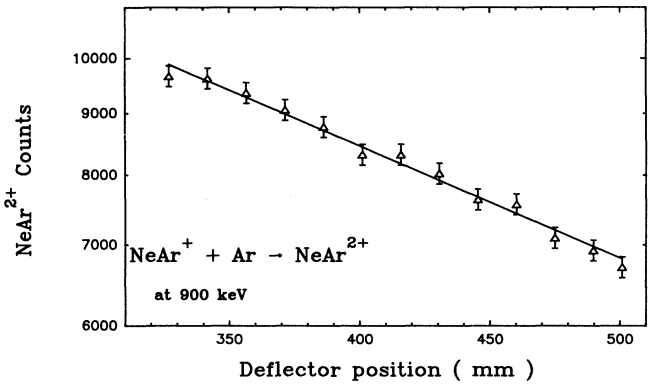

FIG. 7. The number of $NeAr^{2+}$ ions as a function of the distance between the exits of the target cell and the electrostatic deflector.

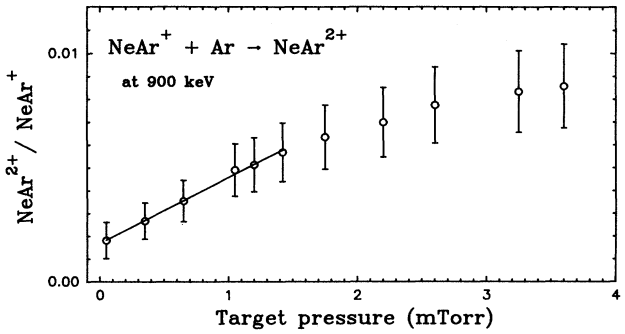

FIG. 9. The number of $NeAr^{2+}$ ions as a function of the pressure in the target cell.

pressure in the scattering chamber was increased dramatically as can be seen from Fig. 8. The cross section for dissociation caused by a collision with a residual gas atom was estimated to be about 3×10^{-16} cm^2. Thus, for the typical working pressure in the scattering chamber, which was less than 10^{-6} Torr, the fraction of $NeAr^{2+}$ dissociating because of collisions is negligible (i.e., less than 0.06%).

The yield of $NeAr^{2+}$ was measured as a function of the target pressure as shown in Fig. 9. Its linear dependence at low pressure indicates that single collision conditions are fulfilled. From the slope shown in the figure the cross section for $NeAr^{2+}$ production was evaluated. When evaluating the production cross section the decay of the metastable $NeAr^{2+}$ ions in flight has to be considered. Using the mean lifetime of 275±25 nsec evaluated before and the data in Fig. 9 the $NeAr^{2+}$ production cross section in $NeAr^{+}$ + Ar collisions at 900 keV is

$$\sigma=(3\pm2)\times10^{-18}\ \text{cm}^2\ . \tag{4}$$

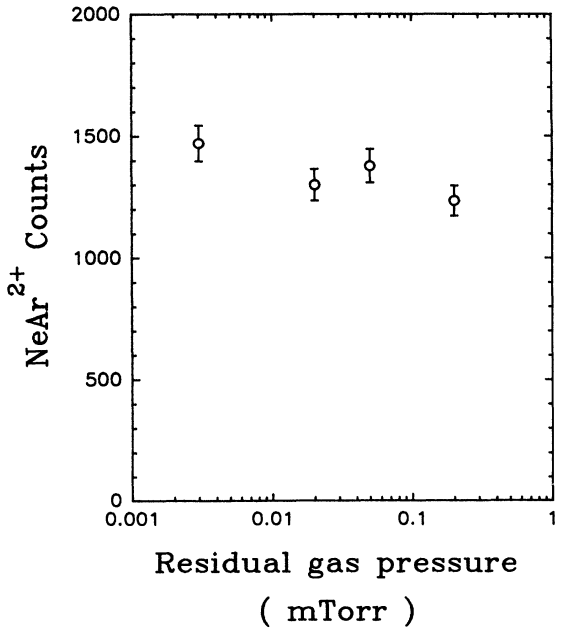

FIG. 8. The number of $NeAr^{2+}$ ions as a function of the pressure of the residual gas in the scattering chamber.

Only a few doubly charged rare-gas dimers have been detected so far [6–8,13–15]. Two-electron systems are easier to handle theoretically. Metastable He_2^{2+} was predicted theoretically by Yagisawa, Sato, and Watanabe [12] and its existence has been reported by Guilhaus *et al.* [6] and by Heber *et al.* [7]. The existence of a few many-electron metastable doubly charged rare-gas dimers have been reported: $NeXe^{2+}$ by Johnsen and Biondi [13], $ArXe^{2+}$ by Helm *et al.* [14], $NeKr^{2+}$ by Stephan, Mark, and Helm [15], and Ne_2^{2+} by Ben-Itzhak *et al.* [8]. Mean lifetimes of these molecular ions have not been measured but are known to be long from estimates based on their typical flight time. Furthermore, no theoretical calculations of the mean lifetimes have been done to the best of our knowledge. Calculations for the many-electron systems are much more demanding than those for a two-electron system and only a few potential curves have been computed. For example, Penkina and Rebane [16] predicted that Ne_2^{2+} has no minimum in the ground-state potential curve, while a metastable state of this ion has been detected [8]. The state of the metastable Ne_2^{2+} was not determined in the measurement, thus no conclusions can be reached about the validity of the theoretical prediction above. Another example is the theoretical prediction [3,4] that the $^1\Sigma_g^+$ ground state of $HeNe^{2+}$ is very unlikely to be detected because of the flatness of the potential energy curve. No experimental work has been done to find this ion to the best of our knowledge.

IV. SUMMARY

A long-lived doubly charged rare-gas dimer, $NeAr^{2+}$, was detected. Its mean lifetime was determined directly to be 275±25 nsec. This metastable molecular ion was formed by electron stripping collisions of 900-keV $NeAr^{+}$ in Ar target. The production cross section is

$(3\pm2)\times10^{-18}$ cm^2. The fact that a single exponential decay curve fits the data suggests that only one metastable state is populated in the collision. We hope that this direct measurement of the mean lifetime of a doubly charged rare-gas dimer will motivate detailed theoretical calculations of the potential curves as well as calculations of the mean lifetime and the kinetic energy released in the dissociation.

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