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Isotopic effect of the mean lifetimes of the $NeAr^{2+}$ doubly charged rare-gas dimer

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It has been suggested recently by Chen *et al.* [Phys. Rev. A **49**, 3472 (1994)] that the measured long-lived $NeAr^{2+}$ formed in fast $NeAr^{+}$ + Ar charge-stripping collisions is mostly in its $v=12$ vibrational state bound to the electronic ground state, and that this molecular ion decays by tunneling through the potential barrier. Such a decay rate is expected to depend strongly on the reduced mass of the molecular ion leading to large isotopic effects. We have measured the mean lifetimes of the $^{20}Ne^{40}Ar^{2+}$ and $^{22}Ne^{40}Ar^{2+}$ isotopes in order to see this isotopic effect. Surprisingly, the mean lifetimes of both isotopes are similar to each other. Thus, it is suggested that the observed $NeAr^{2+}$ molecular ions do not decay via a tunneling mechanism, which would indicate that they reside in the metastable electronic ground state. Rather, electronic transitions from bound or metastable excited states into other repulsive states are the origin for the experimentally observed decay. Qualitative estimates for the shapes and ordering of these states in the electronic spectrum of $NeAr^{2+}$ are given.

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The first long-lived state of the $NeAr^{2+}$ molecular ion was recently discovered in charge-stripping collisions of 900-KeV $NeAr^{+}$ projectiles with Ar atoms, and its mean lifetime was determined to be 275 ± 25 ns by Ben-Itzhak, Gertner, and Rosner [1]. Following this measurement Koch, Frenking, and Gobbi [2] have performed *ab initio* calculations of the electronic ground state of $NeAr^{2+}$ and found a rather deep local minimum. They have suggested that this long-lived molecular ion is formed in this metastable ground state. In a very recent paper, Chen *et al.* [3] have reported phase-shift calculations of the energies and resonance widths of the vibrational states bound in this potential well. The calculated tunneling decay rates differ by more than three orders of magnitude from one vibrational state to the other. Only the $v=12$ vibrational state has a mean lifetime that is close enough to the experimental value, even though it is still underestimating the experimental value by about a factor of 3. This small discrepancy was attributed to an inaccuracy in the potential energy curve of the order of a few meV. It was concluded by Chen *et al.* that the long-lived $NeAr^{2+}$ molecular ion was formed in the $v=12$ vibrational state of the electronic ground state. Such highly excited vibrational states are expected to be populated by vertical transitions, because the two molecular ions involved have significantly different equilibrium internuclear distances.

One of the parameters to which the transition rates are most sensitive in a tunneling process is the reduced mass of the decaying system. Although the electronic potential energy curves do not depend on the masses of the atoms in the molecule, the energies of the vibrational states, which in turn determine the mean lifetime, do. This dependence of the transition rate on the reduced mass of the system can be experimentally studied for the $NeAr^{2+}$ system by measuring the mean lifetimes of the previously measured $^{20}NeAr^{2+}$ [1], as well as the $^{22}NeAr^{2+}$ isotopes (in both cases the ^{40}Ar isotope is used). The difference in the reduced mass μ of these two systems is only 6.5%; however, this small difference is sufficient to cause a factor of 20 difference between the mean lifetimes of the two isotopes. This large effect is due to the exponential dependence of the tunneling rate on $\sqrt{\mu}$, as can be seen from the known WKB decay rate formula

$$\tau^{-1}=\lambda=f_v e^{-2\sqrt{2\mu}\int_a^b dR\sqrt{V(R)-E_v}}. \quad (1)$$

The mean lifetimes of a few highly excited vibrational states that are calculated using the phase shift method, described in detail by Chen *et al.* [3], are presented in Table I for the $^{20}NeAr^{2+}$ and $^{22}NeAr^{2+}$ isotopes. The two vibrational states of the latter that are energetically close to the $v=12$ vibrational state of $^{20}NeAr^{2+}$ are the $v=12$ and 13. Thus, one expects a fast decaying component with $\tau\sim1$ ns and a long-lived component with $\tau\sim1500$ ns in decay rate measurements of the $^{22}NeAr^{2+}$. Molecular ions formed in the $v=12$ state will not dissociate within their flight time in our experiment.

A general and detailed description of the experimental system for mean lifetime measurements of doubly charged molecular ions was reported by Gertner, Rosner, and Ben-Itzhak [4]. In the present experiment, both isotopes of the singly charged $NeAr^{+}$ molecular ion were formed in the rf ion source of the Technion Van de Graaff accelerator by using a ^{20}Ne, ^{22}Ne, and Ar gas mixture. The particular $^{22}NeAr^{+}$ or $^{20}NeAr^{+}$ molecular ion projectile was then

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TABLE I. Calculated mean lifetimes of some highly excited vibrational states of $^{20}NeAr^{2+}$ and $^{22}NeAr^{2+}$ in the electronic ground state.

	$^{20}NeAr^{2+}$		$^{22}NeAr^{2+}$	
v	E_v (a.u.)	τ	E_v (a.u.)	τ
10	0.023413	1.9 s	0.022887	65 s
11	0.025235	0.27 ms	0.024681	7.0 ms
12	0.026907	73 ns	0.026380	1.5 μs
13	0.028446	61 ps	0.027955	0.78 ns
14			0.029315	17.5 ps

selected simply by adjusting the magnetic field of the analyzing magnet, which is placed beyond the acceleration stage.

The mean lifetime of the $^{20}NeAr^{2+}$ molecular ion was determined previously from the measured number of counts under the full energy peak as a function of the distance between the target cell, where they were produced, and the electrostatic analyzer. The resulting exponential decay curve yielded $\tau=275\pm25$ ns [1]. However, the events where the full beam energy was deposited in the surface barrier detector consist of both nondissociated molecular ions as well as molecular ions, which dissociated after the analyzer and both fragments hit the detector simultaneously. The former might include molecular ions in very-long-lived states of $^{20}NeAr^{2+}$, thus reducing the accuracy of the measurement (as discussed below). With this effect included, a value of $\tau=275\pm^{25}_{100}$ ns was obtained [3].

The mean lifetime measurements were performed for both $^{20}NeAr^{2+}$ and $^{22}NeAr^{2+}$ using the method mentioned above in order to compare the mean lifetimes of these isotopes to each other. The number of doubly charged molecular ions reaching the detector as a function of their flight time to the exit of the electrostatic analyzer is shown in Fig. 1 for both isotopes. (These numbers were normalized to the number of neutral fragments detected by another detector covered with a low transmission mesh to reduce the rate on it.) It can be clearly seen that their mean lifetimes are similar, in contradiction with the large differences between the calculated values shown in Table I. The large uncertainty in the measured mean lifetime is due to the possible existence of $NeAr^{2+}$ in states that do not decay significantly during their flight time through the system, t. Thus, one has to fit

$$N(t)=N_{dis}\ \exp(-t/\tau)+N_{long} \tag{2}$$

to the data, where N_{dis} and N_{long} are the number of $NeAr^{2+}$ molecular ions formed in the target cell in dissociating and nondissociating states, respectively. The additional parameter, N_{long}, increases the range of τ to shorter values. Using this method the mean lifetimes were determined to be $\tau=275\pm^{25}_{100}$ ns for $^{20}NeAr^{2+}$ and $\tau=286\pm^{25}_{160}$ ns for $^{22}NeAr^{2+}$, which are surprisingly similar to each other.

In order to improve the accuracy of the mean lifetime measurements and verify that they are almost independent of the reduced mass, we have repeated the measurements using the "masked detector" method (described in detail in Sec. 3.4 of Ref. [4]). In this method only Ne and Ar fragments of the dissociated $NeAr^{2+}$ molecular ions are counted by the

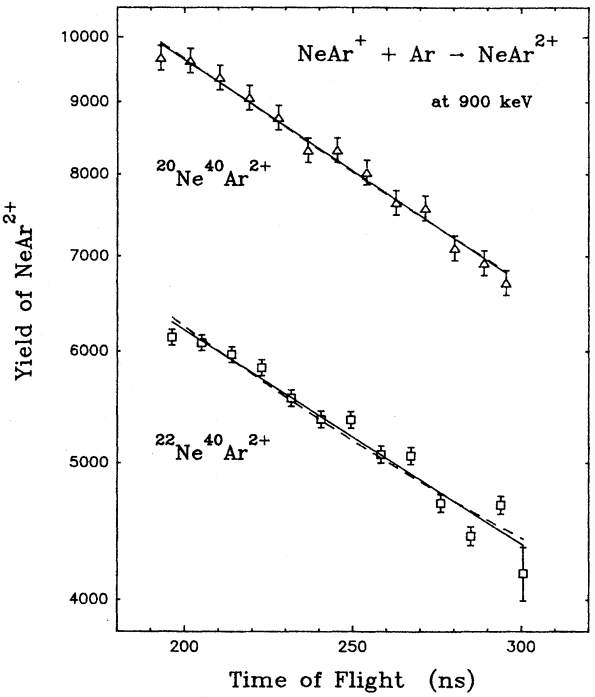

FIG. 1. The number of $^{20}NeAr^{2+}$ and $^{22}NeAr^{2+}$ molecular ions that passed the electrostatic analyzer as a function of their flight time from the target cell. The solid line is a single exponential fit to the data, while the dashed line includes an additional long-lived component, as given in Eq. (2).

detector because of the mask covering half of its area. The $NeAr^{2+}$ molecular ions are directed to hit the mask near its straight edge, in such a way that no molecular ions are counted. Furthermore, only one of the fragments of each molecular ion can be detected, either Ne or Ar, because two-body breakup is collinear and the fragments, which move away from each other, hit on opposite sides of the beam spot (see Fig. 8 of Ref. [4]). As a result, only the dissociating channel is measured in this method, and the number of nondissociating molecular ions, N_{long} formed in the charge stripping collisions does not affect the measurement. The number of the Ne fragments (i.e., half of the number of the dissociated $NeAr^{2+}$) was measured as a function of their flight time from the target cell to the exit of the electrostatic analyzer, as shown in Fig. 2 for both isotopes. This number is the number of $NeAr^{2+}$ molecular ions that passed the analyzer and dissociated afterwards before reaching the detector. On the other hand, molecular ions that dissociate before or in the analyzer, whose number increases with increasing flight time, are deflected away from the $NeAr^{2+}$ trajectory.

The number of the Ne fragments detected with a half covered detector, assuming a single exponential decay, can be written as

$$N(Ne)=\tfrac{1}{2}[N(t)-N(t_d)]$$

$$=\tfrac{1}{2}N_0[\exp(-t/\tau)-\exp(-t_d/\tau)], \tag{3}$$

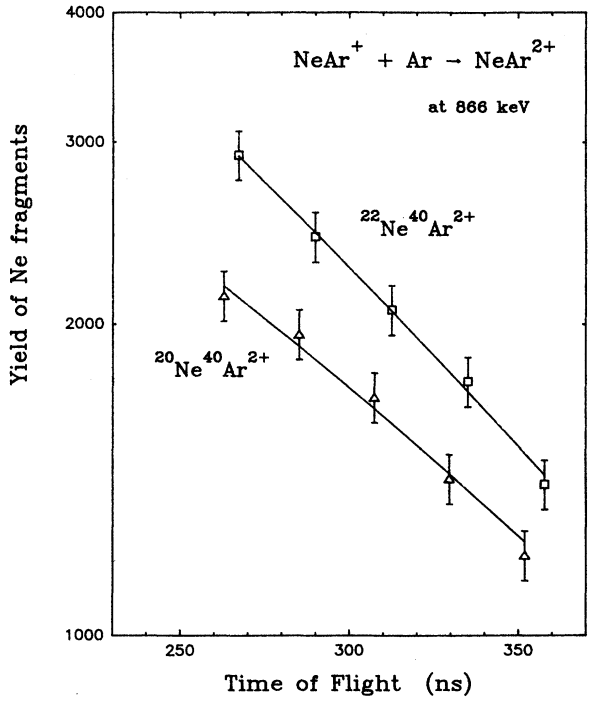

FIG. 2. The number of Ne fragments of $^{20}NeAr^{2+}$ and $^{22}NeAr^{2+}$ as a function of their flight time from the target cell to the exit of the electrostatic analyzer. The solid line is a fit of Eq. (3) to the data.

where t and t_d are the flight times from the target cell to the deflector exit and to the detector, respectively. The fraction of Ne fragments hitting the detector is slightly smaller than 50% because the midpoint of their spot is shifted from the mask edge by approximately the beam width (see discussion of this effect of the alignment on the error in [4]). This additional uncertainty was included in the error of each point on Fig. 2.

The best fit to the data of the equation above, using N_0 and τ as free parameters, yields $\tau=220\pm^{30}_{55}$ ns for the $^{20}NeAr^{2+}$ isotope, and $\tau=152\pm^{25}_{30}$ ns for the $^{22}NeAr^{2+}$ isotope. These results are consistent with the measurements presented above, and they also indicate an isotopic effect that is much smaller than expected if the $NeAr^{2+}$ decays by tunneling. The calculated mean lifetimes (presented in Table I) of the $v=12$ vibrational states of the two isotopes are 73 and 1500 ns, i.e., a factor of 2 smaller and a factor of 8 larger than the measured values, respectively. The agreement between the calculated and measured mean lifetimes of the $^{20}NeAr^{2+}$ isotope can be improved if a small change of the ground state potential energy curve will shift down its $v=12$ vibrational state by a few meV [3]. However, such a change in the potential energy curve will shift the mean lifetime of the $v=12$ vibrational state of the $^{22}NeAr^{2+}$ isotope further away. Such a correction might bring the $v=13$ vibrational state of the latter closer to the measured value, but given that it is a factor of 170 off the measured value it is not very likely that the $v=12$ vibrational state of $^{20}NeAr^{2+}$ accidentally has a mean lifetime similar to the $v=13$ state of $^{22}NeAr^{2+}$. Thus, one is faced with two problems: (i) The isotopic difference is much smaller than expected for a tunneling decay, and (ii) the measured mean lifetimes are not even close to the theoretical values, especially for the heavier isotope.

On the basis of the proximity of these two values of the mean lifetimes to each other we can only deduce that if an isotopic effect exists it is very small. Such a conclusion is in accord with decay by dipole transitions from a bound or metastable excited state to a rapidly dissociating state. In such cases small changes in the energy of the vibrational states lead to much smaller changes in the transition rates (see, for example, calculations for the HeH^{2+} system [5]). On the other hand, for a decay by tunneling through a potential energy barrier, which is the decay mode of the electronic ground state of $NeAr^{2+}$, the expected difference due to the isotopic effect should be much larger. We can therefore conclude that the $NeAr^{2+}$ molecular ions for which we have measured the mean lifetimes are not in their electronic ground state but rather in an excited state. Additional bound or metastable electronic states must therefore exist for this molecular ion, for which calculations are needed.

To guide the way for such calculations, qualitative estimates for some low-lying excited states of $NeAr^{2+}$ are discussed below. The lowest dissociation channel in this system corresponds to $Ne^+(^2P)+Ar^+(^2P)$, giving rise to the states $^1\Sigma^+(I)$, $^1\Pi(I)$, $^3\Sigma^+(I)$, and $^3\Pi(I)$ [6]. The low-lying excited dissociation channels [7] are $Ne(^1S)+Ar^{2+}(^3P)$ (+6.06 eV above the lowest channel), $Ne(^1S)+Ar^{2+}(^1D)$ (+7.80 eV), and $Ne(^1S)+Ar^{2+}(^1S)$ (+10.18 eV). These give rise to the states $^3\Sigma^-(I)$ and $^3\Pi(II)$, $^1\Delta(I)$ and $^1\Pi(II)$, and $^1\Sigma^+(II)$ and $^1\Sigma^+(III)$, respectively. At large internuclear separations the four states correlating with the lowest atomic limit are purely Coulomb-repulsive, while those connected with the excited dissociation channels are attractive due to charge induced dipole interaction. So far, it is known that the $^1\Sigma^+(I)$ ground state arising from the lowest dissociation channel is metastable with a minimum at 3.3 a.u. and the barrier at 4.7 a.u. [2]. Qualitatively, the $^3\Sigma^-(I)$ and $^1\Delta(I)$ states should be bound by charge-induced dipole forces, and their minima are expected at larger internuclear distances than the minimum of the ground state, based on earlier calculations on the $HeAr^{2+}$ system [8] and our experience with $HeNe^{2+}$ [9]. The $^1\Pi(I)$ and $^3\Pi(I)$ states corresponding with the lowest dissociation channel are expected to be metastable due to avoided crossings with the $^1\Pi(II)$ and $^3\Pi(II)$ states from higher dissociation channels. Thus, their potential energy curves should be qualitatively equivalent to the metastable ground state with local minima and barriers to Coulomb-explosion. Because of the lack of avoided crossings, the $^3\Sigma^+(I)$ state will probably be purely Coulomb-repulsive. Whether minima actually occur for the excited $^1\Pi(II)$ and $^3\Pi(II)$ states depends on the locations of the crossing points and cannot be stated without computation, and the same applies to the excited $^1\Sigma^+(II)$ and $^1\Sigma^+(III)$ states. In particular, the bound $^3\Sigma^-(I)$ and $^1\Delta(I)$ states are likely candidates for the detected long-lived $NeAr^{2+}$. They are expected to have low spontaneous emission rates to the repulsive asymptotes of the states deriving from the lowest atomic channel because they have no sym-

metry equivalents among the latter. Furthermore, their minima are better aligned with the minimum of the $NeAr^+$ parent molecular ion, and thus they are more likely to be populated in the charge-stripping collision than the electronic ground state $^1\Sigma^+(I)$.

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