

## Mean-lifetime calculations of the metastable doubly charged $\text{NeAr}^{2+}$ rare-gas dimer

Z. Chen, I. Ben-Itzhak, and C. D. Lin

*James R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506*

W. Koch

*Institute für Organische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany*

G. Frenking

*Fachbereich Chemie, Universität Marburg, Hans-Meerweinstrasse, D-35032 Marburg, Germany*

I. Gertner and B. Rosner

*Department of Physics, Technion, Haifa 32000, Israel*

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The energies and mean lifetimes of the different vibrational states of the  $^1\Sigma^+$  electronic ground state of  $\text{NeAr}^{2+}$  have been calculated using the phase-shift technique. An efficient searching method for these narrow resonances was developed. The calculated lifetime of the  $v = 12$  vibrational state is in reasonable agreement with the experimental value of  $275 \pm 25$  nsec, reported recently by Ben-Itzhak, Gertner, and Rosner [Phys. Rev. A **47**, 289 (1993)], while the lifetimes of other states are more than three orders of magnitude off, thus determining the long-lived vibrational state detected unambiguously. From the difference between the calculated and measured mean lifetime, we have estimated that the potential curve of this 26-electron system is accurate to a few meV. We have also performed *ab initio* calculations of the  $^2\Sigma^+$  electronic ground state of  $\text{NeAr}^+$  and calculated the Franck-Condon factors for the final vibrational-state distribution of the  $\text{NeAr}^{2+}$  molecular ion produced in the  $\text{NeAr}^+$  charge-stripping collisions in order to estimate that high vibrational states are indeed produced in the experiment. We have also examined the validity of the WKB method for calculating the lifetimes of highly excited vibrational states.

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### I. INTRODUCTION

In recent years there has been an increasing interest in the theoretical and experimental studies of multiply charged rare-gas dimers. These molecular ions have bound states and metastable states despite the fact that the rare-gas atoms do not react chemically. The two-electron  $\text{He}_2^{2+}$  molecular ion has been discussed theoretically already in the 1930s by Pauling [1]. Since the first observation of the metastable electronic ground state of this molecular ion by Guilhaus [2], it has been followed by extensive experimental [3–5] and theoretical [6–10] works. The mean lifetimes of the different vibrational states of this metastable electronic state of  $\text{He}_2^{2+}$  have been calculated using the amplitude [8] and WKB [9–10] methods, but no measurements have been reported so far. A few long-lived many-electron doubly charged rare-gas dimers have been discovered experimentally [11–14] and their mean lifetimes were estimated from their flight time through the experimental setup. The experimental evidence is insufficient to identify specific states observed. Theoretical calculations of some of these molecular ions [15–17] provide some insight about the possible long-lived states, but given the scarce experimental data, these states cannot be determined conclusively. Some theoretical calculations predict the existence of other long-lived doubly charged rare-gas dimers which have not yet been detected. For example, Ackermann and Hogreve pre-

dicted that  $\text{Ar}_2^{2+}$  is metastable in its ground state [18].

Very recently, Ben-Itzhak, Gertner, and Rosner reported the production of  $\text{NeAr}^{2+}$  [19] in 0.9-MeV charge-stripping collisions in Ar gas. Furthermore, the mean lifetime of this molecular ion was measured directly. This measured mean lifetime can be calculated if the electronic potential curves of the molecular ion under consideration is known. Following the measurement, Koch, Frenking, and Gobbi [20] have performed elaborate *ab initio* calculations of the  $^1\Sigma^+$  electronic ground state of  $\text{NeAr}^{2+}$  and found a rather deep local minimum, shown in Fig. 1. These theoretical calculations indicate that the measured long-lived  $\text{NeAr}^{2+}$  was most likely produced in its metastable electronic ground state. Their mean-lifetime calculations for the different vibrational states using the WKB approximation are, however, orders of magnitudes off the experimental value. The discrepancy makes one doubt whether the long-lived state of  $\text{NeAr}^{2+}$  has been successfully determined.

One may address this discrepancy differently. Comparing the mean lifetimes, calculated for tunneling out of the  $^1\Sigma^+$  potential, to the experimental mean lifetime of  $\text{NeAr}^{2+}$ , one can determine the precision of the calculated potential curve and the vibrational levels bound in it. The vibrational states of the metastable  $^1\Sigma^+$  electronic ground state of this molecular ion dissociate by tunneling through the potential barrier. In the commonly used WKB approximation the tunneling rate is given by

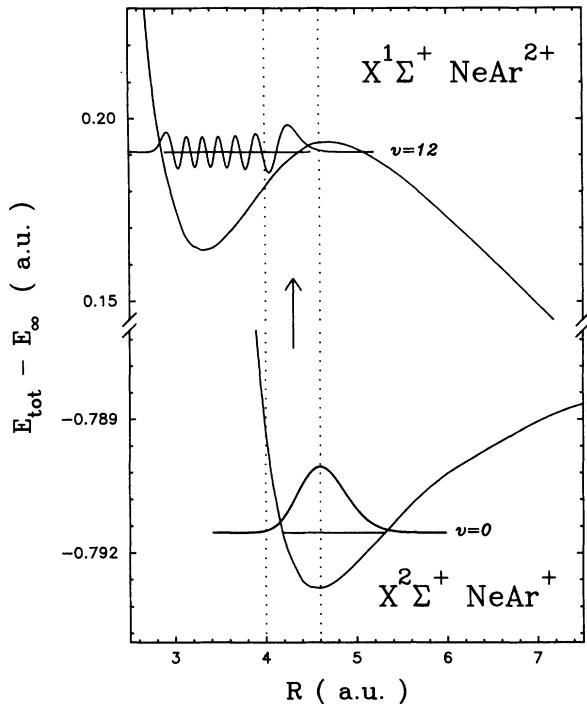


FIG. 1. Potential curves for the  $^2\Sigma^+$  and  $^1\Sigma^+$  electronic ground states of  $\text{NeAr}^+$  and  $\text{NeAr}^{2+}$ , respectively (notice the different energy scale used for each potential curve). Representative vibrational levels and wave functions are also shown.

$$\lambda = f_v \exp \left[ -2\sqrt{2\mu} \int_a^b dR \sqrt{V(R) - E_v} \right], \quad (1)$$

where  $f_v$  is the vibration frequency,  $\mu$  is the reduced mass of the molecule,  $V(R)$  is the potential energy,  $E_v$  is the vibration energy, and  $a$  and  $b$  are classical turning points. The tunneling rate is extremely sensitive to the exact value of  $V(R) - E_v$  because they appear in the exponent, especially for molecular ions with a large reduced mass. The fact that the mean lifetime was measured with an accuracy of about 10% ( $275 \pm 25$  nsec [19]) sets a stringent test on the precision of  $V(R) - E_v$ . We will show in this paper that mean-lifetime measurements and calculations of metastable molecular ions can be used to probe the precision of structure calculations of molecular potential curves.

In this paper we report our calculations of the energies and resonance widths of the vibrational states bound to the metastable  $^1\Sigma^+$  electronic ground state of  $\text{NeAr}^{2+}$ . The mean lifetime of the  $v=12$  vibrational state is in reasonable agreement with the measured value while the other states are more than three orders of magnitude off. The phase-shift method used for these calculations of extremely narrow resonances is described in Sec. II A. We have also performed *ab initio* calculations for the potential curve of the  $^2\Sigma^+$  electronic ground state of  $\text{NeAr}^+$  (Table I), which are described in Sec. II B. The vertical transition rates from the  $^2\Sigma^+$  state of  $\text{NeAr}^+$  to the  $^1\Sigma^+$  state of  $\text{NeAr}^{2+}$  caused by the collision were evaluated in Sec. II C in order to determine the final population of vibrational states of the  $\text{NeAr}^{2+}$ . In Sec. III we compare our mean-lifetime calculations to the measured value and

TABLE I. Total energies of the  $X^2\Sigma^+$  and  $X^1\Sigma^+$  electronic ground states of  $\text{NeAr}^+$  and  $\text{NeAr}^{2+}$ , respectively. D is the multireference analog of the Davidson correction to the MRCI total energies (see Ref. [20]).

$R$ (a.u.)	$E(\text{MRCI}+\text{D})$ (a.u.)	
	$\text{NeAr}^+ \ ^2\Sigma^+$ (this work)	$\text{NeAr}^{2+} \ ^1\Sigma^+$ (Ref. [20])
2.4	-654.918 61	
2.5		-654.292 87
2.6	-655.088 94	
2.7		-654.370 35
2.8	-655.203 87	
2.9		-654.409 87
3.0	-655.278 74	
3.1		-654.427 26
3.2	-655.325 77	-654.430 78
3.3		-654.431 99
3.4	-655.354 28	-654.431 52
3.5		-654.429 86
3.6	-655.370 93	
3.7		-654.424 40
3.8	-655.380 25	
3.9		-654.417 82
4.0	-655.385 16	-654.414 54
4.2	-655.387 53	-654.408 68
4.4	-655.388 48	
4.5	-655.388 63	-654.403 03
4.6	-655.388 65	
4.7	-655.388 58	-654.402 18
4.8	-655.388 45	
4.9	-655.388 27	
5.0	-655.388 07	-654.404 08
5.2	-655.387 64	
5.5	-655.386 99	
6.0	-655.386 08	-654.422 89
7.0	-655.384 91	
8.0	-655.384 31	-654.471 08
10.0	-655.383 88	-654.496 66
20.0		-654.544 45
100.0		-654.585 86
$\infty$	-655.388 34	-654.595 86

to the commonly used WKB calculations. Atomic units are used throughout this paper (unless units are specified).

## II. THEORY

### A. Phase-shift method

For a single electronic state problem, given the Born-Oppenheimer potential, the resonance energy and width of the vibrational state can be obtained precisely by calculating the elastic scattering phase shift as a function of energy. Using this method, we first solve the Schrödinger equation

$$\left[ -\frac{1}{2\mu} \frac{d^2}{dR^2} + \frac{l(l+1)}{2\mu R^2} + V(R) - E \right] \psi_v(R) = 0 \quad (2)$$

numerically, where  $V(R)$  is the ground-state potential curve of the  $\text{NeAr}^{2+}$ . This potential has a deep well, but becomes repulsive at large  $R$  where it dissociates into  $\text{Ne}^+ + \text{Ar}^+$ . The solution of this radial equation has an

asymptotic form

$$\psi_v(R) \sim \sin \left[ kR - \frac{1}{k} \ln(2kR) - \frac{\pi l}{2} + \sigma_l + \eta(E) \right] \quad (3)$$

at large  $R$ , where  $\sigma_l$  is the Coulomb phase shift and  $\eta(E)$  is the phase shift due to the deviation from the Coulomb potential. The resonance energy and width can be obtained by fitting the phase shift in the following form:

$$\eta(E) = \eta_0 + \tan^{-1} \frac{\Gamma/2}{E - E_r}, \quad (4)$$

where  $\eta_0$  depends weakly on  $E$  near the resonance and can be taken as constant,  $E_r$  is the resonance energy, and  $\Gamma$  is the width.

The major difficulty in this procedure lies in locating the resonance. The typical energy widths are of the order of  $10^{-10}$  a.u. or less. For a given potential, a good estimate can give resonance energy as close as  $10^{-4}$  a.u. This means that millions of trials are needed just to locate the resonance unless a better procedure is found.

In Fig. 2 we plot the radial wave functions for several energies near the  $v=12$  vibrational resonance state, the energy of which is finally determined to be  $E_{v=12} = 0.1907534725$  a.u. The solid lines represent wave functions with energies below the resonance and the dashed lines represent wave functions with energies above

the resonance. The approximate positions of the resonances are first estimated by, say, the finite difference method, by assuming that the resonance is bound by the inner potential well only. This is done by setting the value of the potential to the top of the potential barrier for all the  $R$ 's beyond the top of the barrier. This procedure allows us to approach the resonance positions to within about four-digit accuracy for each given potential.

The next task is to locate the resonance to high accuracy. A "standard" approach would be simply to calculate the phase shifts at energies near the estimated position. This method is not practical since the width of the resonance for the present system is of the order of  $10^{-10}$  a.u. One thus needs to find an efficient method to narrow the intervals considerably. Furthermore, one would like to avoid calculating the phase shifts directly since this would require the integration of the differential equations to a much larger  $R$  value in the asymptotic region where the potential becomes Coulombic.

The method we developed for searching for the narrow resonances is as follows. First, we use two energy points near the estimated resonance position and integrate the differential equation to some points beyond the outer classical turning point. We focus on the wave function in the classical forbidden region. As an example, we show in Fig. 2(a) the two wave functions, one below and one above the resonance. If the energy is below the reso-

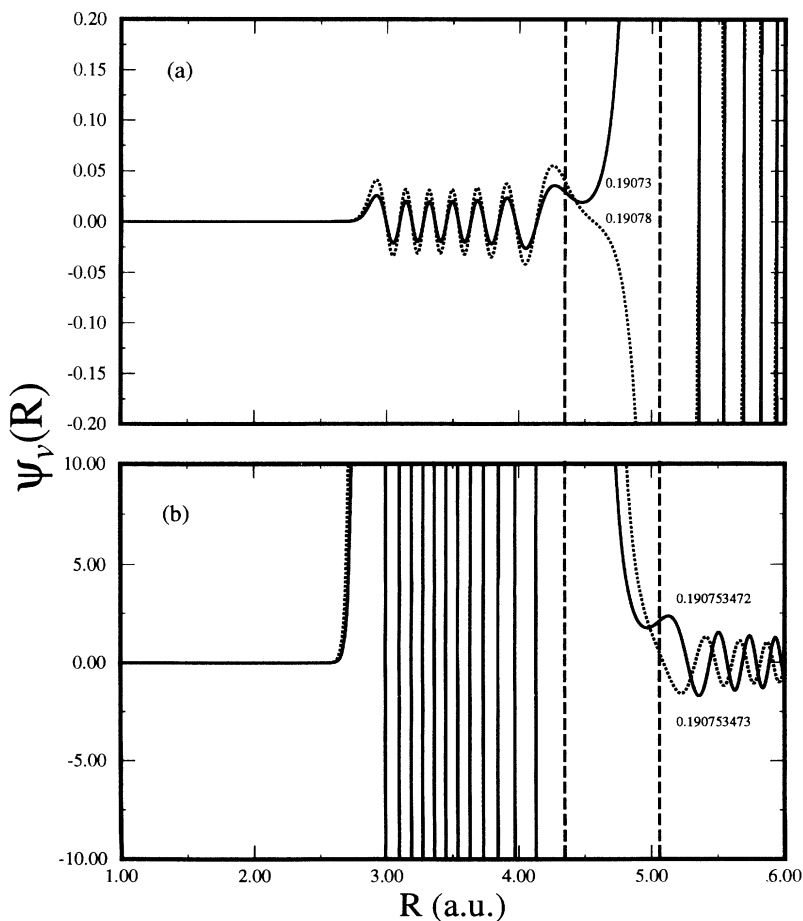


FIG. 2. The vibration wave function  $\psi_v(R)$  calculated by the phase-shift method (solid lines represent energies above the resonance and dashed lines represent energies below). The vertical dashed line marks the position of the classical turning points. The numbers next to each line indicate its energy.

nance, its wave function in the classical forbidden region (the two classical turning points are marked by short thick vertical dashed lines) should exhibit no node. Actually the derivative of the wave function should vanish at some point within this interval. If the energy is above the resonance, its wave function should have a node within the classical forbidden region. This feature of the wave functions in the classical forbidden region is expected since the phase shift has to undergo an increase of  $\pi$  across the resonance. This procedure allows one to narrow the interval where the resonance is located rapidly by using the information provided by the relative amplitudes. It has the advantage that one does not need to integrate the differential equation to the large  $R$  region where the wave function oscillates rapidly. A standard binary search method can also be used.

When the energy is still far from the resonance (measured in terms of the width of the resonance), the wave functions are mostly concentrated in the region outside the potential barrier, as seen in Fig. 2(a) where the amplitude in the outer region is normalized to one and the oscillation inside the potential barrier is of the order of 0.05. As the energies become close to the resonance, the wave functions in the region inside the potential barrier become very large, as seen in Fig. 2(b) where we have normalized the amplitude of the oscillatory wave function to unity and the wave functions in the inner region has oscillations with amplitudes of the order of  $10^4$ . Once the resonance region has been narrowed to the order of its width, the phase shifts can be calculated and the actual position and width are then obtained by fitting to Eq. (4). One can tell if the two energy points are very close to the resonance when the approximate phase shifts are less than  $\pi$ .

Because of the large reduced mass of  $\text{NeAr}^{2+}$ , the wave functions oscillate very rapidly. To make sure of numerical accuracy, we have used quadruple precision in integrating the Schrödinger equation. As a test case for our method we have calculated the mean lifetimes of  $\text{He}_2^{2+}$  vibrational states with  $l=0$  and compared them to previous calculations by Babb and Du [8], who have used the amplitude method. The results from both methods are in good agreement, as shown in Table II, for example, for the  $v=2$  vibrational state of  ${}^3\text{He}{}^4\text{He}^{2+}$ . The difference between the resonance energies is about 3 meV ( $\delta E/E \sim 0.03\%$ ), while the relative difference in the resonance width and mean lifetime are about 15%. The present phase-shift method is considered to be the more accurate since the other method uses additional approximations.

### B. *Ab initio* calculations of potential curves

The calculation of the potential curve for the  ${}^2\Sigma^+$  electronic ground state of  $\text{NeAr}^+$  involved two steps. Opposite to our previous investigation of the  ${}^1\Sigma^+$  electronic ground state of the  $\text{NeAr}^{2+}$  dication [20], the molecular orbitals were generated by simple restricted open-shell Hartree-Fock (ROHF) calculations and not through multiconfiguration self-consistent field (SCF) calculations. The latter were not necessary since nondynamical electron correlation is not an issue for the  $\text{NeAr}^+$  ground state. Exploratory calculations revealed that the Hartree-Fock determinant is by far dominating and that the occupation numbers of the formally doubly occupied orbitals is virtually identical to two for all geometries. Actually, full valence complete active space SCF [21] calculations lead to erratic results, since due to the strongly occupied orbitals, orbital flipping between the inactive and the active orbital spaces occur. The one-particle basis set was a generally contracted Gaussian basis of the atomic natural orbital type as introduced by Almlöf and Taylor [22]. The exponents and coefficients have been taken from Widmark *et al.* [23] and the final basis set included  $5s, 4p, 3d, 2f$  and  $6s, 5p, 4d, 3f$  contracted functions for Ne and Ar, respectively. Since for the construction of these basis sets the positive atomic ions were also included, we expect a balanced description for the  $\text{NeAr}^+$  cation. In the second step the ROHF molecular orbitals were subjected to multireference configuration-interaction (MRCI) [24] calculations. The reference space consisted of all electron configurations of the correct spatial and spin symmetry generated by distributing 23 electrons (i.e., all but the Ne and Ar  $1s$  electrons) in the  $3-8\sigma$  and  $1-3\pi$  orbitals. All single and double replacements from the six reference configurations were included in the CI, leading to a CI expansion of 1 351 536 configuration-state functions. The multireference analog of the Davidson correction [25] was applied to the MRCI total energies to account for higher than double excitations. All calculations have been performed employing the MOLCAS-2 program installed on an IBM RS/6000-computer workstation [26]. The computed  $D_e$  of 0.13 eV is slightly larger than our previous result of 0.08 eV obtained using a smaller one-particle basis set and many-body perturbation theory to fourth order to account for the dynamical electron correlation [27].

### C. Transition rate calculations

The  $\text{NeAr}^+ + \text{Ar}$  charge-stripping collisions at 0.9 MeV are very fast relative to the nuclear motion. Under

TABLE II. Energy and width of the  $v, l=2, 0$  state of  ${}^3\text{He}{}^4\text{He}^{2+}$  calculated by the amplitude method (Ref. [8]) and the phase-shift method (this work).

State	Amplitude method Ref. [8]			Phase-shift method		
	$E$ (a.u.)	$\Gamma$ (a.u.)	$\tau$ (sec)	$E$ (a.u.)	$\Gamma$ (a.u.)	$\tau$ (sec)
$v, l=2, 0$	0.354 86	$1.49 \times 10^{-9}$	$1.62 \times 10^{-8}$	0.354 74	$1.75 \times 10^{-9}$	$1.39 \times 10^{-8}$

TABLE III. Transition rates from  $\text{NeAr}^+(v_i)$  to  $\text{NeAr}^{2+}(v_f)$  for  $v_i=0$  and 1.

Final state $v_f$	Transition probability $T(v_i \rightarrow v_f)$	
	$v_i=0$	$v_i=1$
10	0.009 256	0.025 514
11	0.026 265	0.054 744
12	0.068 239	0.092 753
13	0.184 366	0.088 576

these conditions the transition rates from the  $^2\Sigma^+$  state of  $\text{NeAr}^+$  to the  $^1\Sigma^+$  state of  $\text{NeAr}^{2+}$  (shown in Fig. 1) are approximately proportional to the Franck-Condon factors, i.e., the square of the overlap integral between the initial and final vibrational wave functions,

$$P(v_i \rightarrow v_f) \propto \left| \int dR \psi_{v_i}^*(R) \psi_{v_f}(R) \right|^2. \quad (5)$$

The vibrational wave functions for the electronic ground state of  $\text{NeAr}^+$  were calculated using the finite-difference method while the ones for the metastable electronic ground state of  $\text{NeAr}^{2+}$  were calculated by the phase-shift method as described in Sec. II A. The overlap integrals were then evaluated by numerical integration and the transition rate matrix is shown in Table III for  $v_i=0$  and 1. The  $\text{NeAr}^+$  molecular ions that are produced in the rf source of the Technion Van de Graaff accelerator are mostly in the vibrational ground state with a small fraction in the first vibrational excited state. Taking into account only the  $\text{NeAr}^+(v_i=0)$  initial state, the dominant final vibrational states populated are the  $v=12$  and 13 states and the distribution is shown in Fig. 3. The

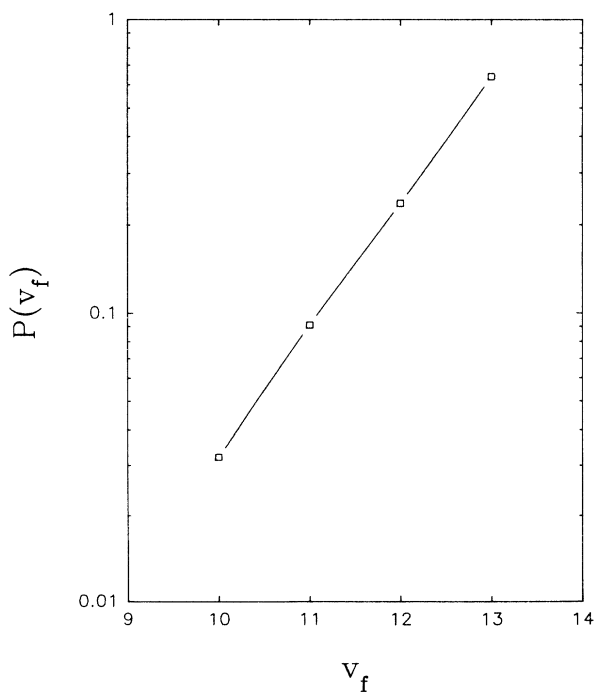


FIG. 3. Final vibration state population of  $\text{NeAr}^{2+}$  assuming vertical transition only from  $\text{NeAr}^+(v_i=0)$  and using the Franck-Condon principle.

lower vibrational states are practically not populated since the equilibrium internuclear distance of  $\text{NeAr}^+$  aligns with the barrier peak position of the  $\text{NeAr}^{2+}$ , thus the overlap of the wave functions with low-energy vibrational states is very small.

### III. RESULTS AND DISCUSSION

#### A. Comparison with the measured mean lifetime

The mean lifetimes of the highly excited vibrational states ( $v \geq 10$ ) of the  $^1\Sigma^+$  electronic ground state of  $\text{NeAr}^{2+}$ , shown in Table IV, were calculated using the phase-shift method. These mean lifetimes decrease rapidly with increasing vibrational quantum numbers. In fact, the mean lifetime changes by about three orders of magnitude for each increase in  $v$ . Since the measured mean lifetime is of the order of hundreds of nanoseconds, only the mean lifetime of the  $v=12$  state is determined. For  $v < 12$ , the  $l=0$  states are essentially stable and for  $v=13$  the state decays immediately.

The very long-lived  $\text{NeAr}^{2+}$  molecular ions (i.e.,  $\tau \gg 1$   $\mu\text{sec}$ ) have not been seen experimentally [19]. A careful analysis of the number of  $\text{NeAr}^{2+}$  counts as a function of the distance (Fig. 7 of Ref. [19]) enabled us to set an upper limit of 10–15% on the fraction of  $\text{NeAr}^{2+}$ , which has mean lifetimes much longer than the typical flight time through the apparatus. This fraction is smaller than the one estimated by the Franck-Condon principle and the discrepancy may be attributable to the failure of the latter. Given the relatively wide range of internuclear distances which contribute to the stripping and that stripping is expected to be more effective with increasing internuclear distances since the valence electrons become more delocalized, it is plausible that the failure of the Franck-Condon principle will result in more favorable population of higher vibrational states. Any quantitative discussion can be carried out only if the electronic transition amplitude  $D_{\text{elec}}(R)$  is calculated. If we assume that the fraction of very long-lived states relative to the total  $\text{NeAr}^{2+}$  is the maximum permitted by the experimental value, then the measured mean lifetime is

$$\tau = 275_{-100}^{+25} \text{ nsec}, \quad (6)$$

which is to be compared to the calculated lifetime of 72.5 nsec for  $v=12$  and  $l=0$ .

The mean lifetimes discussed above were calculated assuming that the rotational quantum number is  $l=0$ . For the heavy  $\text{NeAr}^{2+}$  molecular ions the dependence of the mean lifetime on the rotational quantum number is rather weak. In Table IV, the mean lifetimes calculated for a few  $v=11, 12$  and  $l>0$  are shown. For  $v=12$  and  $l=15$  the mean lifetime decreases by about a factor of 2 as compared to the mean lifetime for  $l=0$  for the same  $v$ . The mean lifetimes decrease with increasing  $l$ , thus highly excited  $l$  states of the lower  $v$  states might have mean lifetimes comparable with the experimental value. For example for  $v=11$ ,  $l$  has to be about 50, but it is difficult to believe that such highly excited  $l$  states are populated, especially in a narrow distribution. We mention that the dependence of the mean lifetime on the rotational quan-

TABLE IV. Energy and width of the vibration energy levels of  $\text{NeAr}^{2+}$  calculated by the phase-shift method, the WKB method, and the WKB' method. The numbers in brackets denote multiplicative powers of ten.

State $v, l$	WKB method		Phase-shift method			WKB' method
	Energy (a.u.)	$\tau$ (sec)	Energy (a.u.)	$\Gamma$ (a.u.)	$\tau$ (sec)	$\tau$ (sec)
10,0	0.023 475 4	1.33	0.023 413	1.30[17]	1.87	1.80
11,0	0.025 317 8	1.55[-4]	0.025 235	8.90[-14]	2.72[-4]	2.30[-4]
11,10					1.75[-4]	
11,20					6.78[-5]	
11,30					2.00[-5]	
11,40					1.85[-6]	
11,50					1.44[-7]	
11,60					7.63[-9]	
12,0	0.027 104 0	3.08[-8]	0.026 907	3.34[-10]	7.25[-8]	7.74[-8]
12,10					5.30[-8]	
12,15					3.72[-8]	
13,0	0.028 839 4	1.08[-11]	0.028 446	3.98[-7]	6.09[-11]	6.33[-11]

tum number is expected to be much stronger for the lighter molecular ions such as  $\text{He}_2^{2+}$ . However, no mean-lifetime measurement has been reported so far for the  $\text{He}_2^{2+}$  molecular ion.

By comparing the calculated mean lifetimes with the experimentally determined mean lifetime, we are able to identify the vibrational state of the doubly charged molecular ions that are produced in the stripping reaction. Although the calculated lifetime is about a factor of 3 shorter than the measured one, this discrepancy is most likely due to the accuracy of the calculated potential curve. We will come to this aspect later again.

#### B. The WKB method

One commonly used method for the evaluation of tunneling rates is the WKB method; see Eq. (1). The same method can be used to evaluate the vibrational energy levels bound within the potential curve (Table V). The energy levels are given by

$$\int_a^b dR \sqrt{2\mu[E_v - V(R)]} = (v + \frac{1}{2})\pi, \quad (7)$$

where  $a$  and  $b$  are the inner and outer classical turning

TABLE V. Energy and mean lifetime of all vibrational states (with  $l=0$ ) of  $\text{NeAr}^{2+}$  calculated by the WKB method. The numbers in brackets denote multiplicative powers of ten.

State	Energy (a.u.)	$\tau$ (sec)
0	0.001 267 30	1.27[55]
1	0.003 761 34	1.02[44]
2	0.006 203 26	2.59[41]
3	0.008 591 83	1.57[35]
4	0.010 921 4	2.06[29]
5	0.013 188 5	5.52[23]
6	0.015 391 8	2.88[18]
7	0.017 527 7	2.85[13]
8	0.019 588 8	5.40[8]
9	0.021 569 6	1.97[4]
10	0.023 475 4	1.33
11	0.025 317 8	1.55[-4]
12	0.027 104 0	3.08[-8]
13	0.028 839 4	1.08[-11]

points, respectively. The energy levels calculated by the WKB method deviate slightly from the ones calculated by the phase-shift method for states far from the barrier maximum, as expected. In contrast, significant deviations occur for the highly excited states; see Table IV. The deviations of the mean lifetimes calculated by the WKB method are even more significant. For example, the energy of the  $v=12$  vibrational state, which is our main interest, is over estimated only by 5.4 meV by the WKB method relative to the more accurate phase-shift method. On the other hand, the mean lifetime is off by more than a factor of 2. In order to check if this large deviation in the WKB calculation of the mean lifetime is caused by the decay rate calculation [Eq. (1)] or the relatively small inaccuracy in the energy level, we have carried out WKB' calculations of the mean lifetimes using the energy levels calculated by the phase-shift method. These values are in excellent agreement with the ones calculated by the phase-shift method, as seen from Table IV, indicating that the WKB method fails mainly because of insufficient precision of the energy levels. In cases where the energy levels are known with enough precision an accuracy of about 10% is reasonable for this method. On the other hand, for highly excited states the small error in the energy is sufficient to make WKB calculations of mean lifetimes accurate only within an order of magnitude.

As stated earlier, the extreme sensitivity of the dependence of the mean lifetime on the exact values of the potential curve can be used as a powerful tool for probing the precision of existing molecular structure calculations. Using the WKB' method, we estimated that if the resonance energy is lower by about 7 meV, then the calculated mean lifetime will be in good agreement with the measurement. To reach such an accuracy in potential curve calculation for a 26-electron diatomic molecule is not trivial, particularly at large internuclear separations.

#### IV. SUMMARY

The energies and mean lifetimes of the highly excited vibrational states of the metastable  $^1\Sigma^+$  electronic

ground state of  $\text{NeAr}^{2+}$  have been calculated using the phase-shift method. An efficient searching method for these narrow resonances was presented. The mean lifetimes of the different vibrational states decrease rapidly with increasing vibrational quantum number and for each increase of  $v$ , the mean lifetime decreases by about three orders of magnitude. The mean lifetime of the  $v=12$  vibrational state (with  $l=0$ ) is in reasonable agreement with the experimental value of  $275_{-100}^{+25}$  nsec [19]. The difference between the calculated and measured mean lifetime indicates that the potential curve of this 26-electron system is probably accurate to a few meV. We have also performed *ab initio* calculations of the  $^2\Sigma^+$  electronic ground state of  $\text{NeAr}^+$ . Franck-Condon factors have been calculated for the  $\text{NeAr}^+ + \text{Ar} \rightarrow \text{NeAr}^{2+}$  vertical transitions in order to determine the population of final vibrational states of  $\text{NeAr}^{2+}$ . This population peaks at the highest vibrational level and decreases rapidly

ly with decreasing energy. Thus only the first vibrational state whose mean lifetime is within the measurement range is expected to be detected, as have been observed experimentally [19]. We have also compared our phase-shift calculations to the commonly used WKB method which gives reasonable mean lifetimes, even near the potential barrier, if the "correct" energy of the level is used.

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