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Very-long-lived metastable vibrational states of Ba_2^{++}

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Potential-energy curves for the $^1\Sigma_g^+$ states of Ba_2^{++} are exhibited. The ground-state curve shows a local minimum lying 0.0562 a.u. above the energy at infinite separation, and a local maximum lying at 0.0618. These features form a potential well in which metastable vibrational states can exist. The lifetimes are estimated as high as 10^{197} sec, using the WKB method. Considerations regarding experimental formation and detection of bound Ba_2^{++} are discussed.

INTRODUCTION

True bound states of doubly ionized diatomic molecules almost certainly do not exist. The Coulomb repulsion of two positive ions is energetically stronger than any chemical binding effects, so that the electronic energy of the molecule's ground state is lower at infinite internuclear separation than at any smaller separation. However, over short intervals at intermediate internuclear separations, the forces associated with binding effects can be somewhat stronger than the repulsive Coulomb force. In such cases, the ground-state-energy curve shows a local minimum at some intermediate separation, as reported in several published calculations.¹⁻⁴ These minima always lie energetically above the infinite-separation ground-state energies, so that the potential wells associated with such minima cannot support true bound states. These wells can support scattering resonances, however. In this paper we show that, in some cases, such metastable states are so long lived that the doubly ionized diatomic systems can be regarded as stable molecules. The Ba_2^{++} molecule treated here is far more stable than any of the systems treated by previous authors.¹⁻⁴ This greater stability is due to the greater mass of the Ba_2^{++} system. Atomic units are used throughout this work, except where otherwise specified.

THEORY

We have computed the potential-energy curves for the $^1\Sigma_g^+$ molecular eigenstates of the Ba_2^{++} system, for use in reaction rate studies. The curves were obtained by the multiconfiguration-valence-bond (MCVB) method.^{5,6} We used a $(7s, 6p, 2d)$ set of basis orbitals on each Ba nucleus, for a total of 70 basis orbitals. The details of this calculation have been reported elsewhere, and need not be

repeated here.⁷

Figure 1 shows our three lowest potential-energy curves. Curve 1, the ground-state curve, represents a state which, at infinite internuclear separation, dissociates into two Ba^+ ions in their ground states. Curve 2 represents a state which dissociates into two Ba^+ ions, one in its ground state and one in its lowest 2P state. Curve 3 represents a state which dissociates into a Ba atom and a Ba^{++} ion, each in its ground state. The ground-state curve $E_1(R)$ shows a local minimum of the sort described in the Introduction. This minimum, at internuclear separation $R = 10.22$, lies at an energy of 0.0562 above the $R = \infty$ energy. The local maximum at $R = 13.34$ lies at an energy of 0.0618. The potential-well depth with respect to the top of the potential barrier is thus 0.0056. The harmonic-oscillator frequency associated with the local minimum is 0.00021.

For sufficiently low energies, the relative nuclear motion can be treated by modeling the Ba_2^{++} system as two massive elementary particles inter-

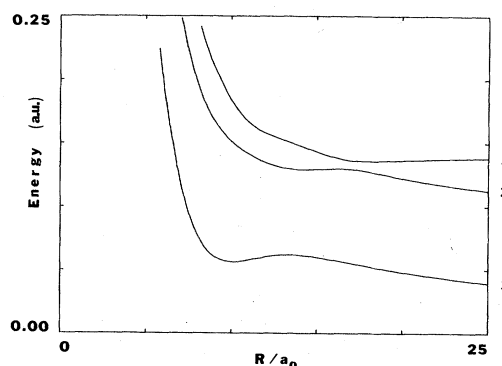


FIG. 1. The three lowest $^1\Sigma_g^+$ potential-energy curves of Ba_2^{++} . The ground-state curve $E_1(R)$ shows a local maximum and a minimum which lead to the formation of metastable vibrational states.

acting via a central potential $E_1(R)$. This potential's attractive well should produce metastable states resembling harmonic-oscillator eigenfunctions. The number of such scattering resonances is roughly given by the ratio between the well depth and the oscillator frequency: $0.0056/0.00021 \approx 27$. The lowest collision energy T for which resonance formation occurs is near $T=0.0562$, the energy at the local minimum in $E_1(R)$. For this energy, the exponential decay length associated with the wave function's behavior in the classically forbidden region, near the local maximum in $E_1(R)$, is 0.027. Because this length is so small compared with the width of the classically forbidden region (see Fig. 1), the metastable states can decay by tunneling through this region only very slowly, and should be very long lived.

We estimate the metastable state lifetimes by assuming that the harmonically oscillating system makes $\omega/2$ attempts per unit time to tunnel through the forbidden region, where ω is the oscillator frequency.⁸ The probability of success on each attempt is determined by a barrier penetration factor computed by the WKB method⁹:

$$B(T) = \exp\left(- (8M)^{1/2} \int_{R_1}^{R_2} [E_1(R) - T]^{1/2} dR\right),$$

where M is the Ba_2^{++} reduced mass, T is the collision energy, and R_1 and R_2 are the classical turning points at the inside and outside of the barrier. The estimated lifetime is then given by

$$t = 2\pi/\omega B(T).$$

Figure 2 shows the potential $E_1(R)$ with an expanded vertical scale. The horizontal solid line inside the well represents the resonance state of vibrational quantum number $v=10$. On this same scale, a line representing the $v=0$ vibrational state would be indistinguishably close to the well bottom. The horizontal dashed line through the barrier represents the classically forbidden region through which the system must tunnel. Its end-points are the limits R_1 and R_2 of the WKB integration.

RESULTS

Figure 3 shows the computed Ba_2^{++} lifetime plotted as a function of the collision energy. The vertical dashed lines indicate energies corresponding to the top and bottom of the potential well. The lifetimes are extremely long. The lowest metastable state, of energy $T \approx 0.0563$, has a lifetime $\log_{10} t \approx 213.8$; the $v=10$ metastable state, of energy $T \approx 0.0584$ and indicated in Fig. 2, has a lifetime $\log_{10} t \approx 135.5$. For t expressed in seconds, these two logarithms are 197.2 and 118.9, respectively. We conclude that the life-

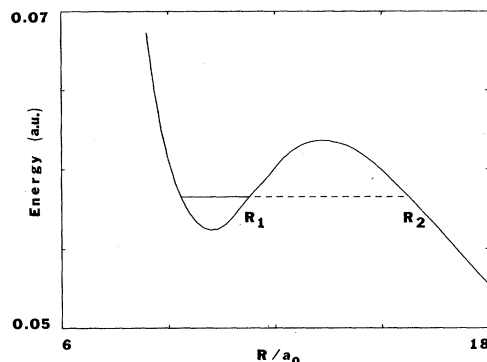


FIG. 2. $E_1(R)$ with energy scale expanded. The solid horizontal bar indicates the $v=10$ metastable vibrational state. The dashed line indicates the range of the WKB integration used to compute this state's lifetime.

times of these metastable states against tunneling decay are so long that Ba_2^{++} can be regarded as a stable molecule.

Potential-energy curves computed for He_2^{++} by McLean, Weiss, and Yoshimine,¹ and for N_2^{++} , O_2^{++} , and NO^{++} by Thulstrup, Andersen, and co-workers,²⁻⁴ show local minima in the ground-state curves similar to the minimum shown in our Ba_2^{++} curve. We have estimated lifetimes for the lowest metastable vibrational states of these systems, for comparison with our Ba_2^{++} results. These lifetimes were again estimated by the WKB method, using the potential energies obtained by the previous workers.¹⁻⁴ These lifetimes are listed in Table I, along with the lifetime of the lowest Ba_2^{++} resonance.

These results indicate that all of these ion pairs except He_2^{++} can be considered stable molecules. Our estimated lifetime for He_2^{++} is approximately an hour, but lifetimes estimated by such a crude method could be in error by a few orders of mag-

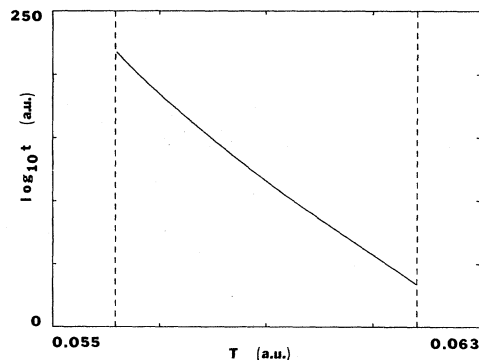


FIG. 3. Ba_2^{++} resonance lifetime as a function of collision energy. The dashed lines represent the energies corresponding to the local minimum and maximum in the ground-state-energy curve.

TABLE I. Computed lifetimes for the ground ($v=0$) metastable vibrational states of five doubly ionized diatomic molecules. To convert the lifetimes to seconds, subtract 15.6.

Species	$\log_{10} [t \text{ (a.u.)}]$
He ₂ ⁺⁺	19.9
N ₂ ⁺⁺	98.3
O ₂ ⁺⁺	27.6
NO ⁺⁺	45.8
Ba ₂ ⁺⁺	213.8

nitide. The other lifetimes are all extremely long. The lifetimes are strongly affected by the ion pair's reduced mass; it is well known that barrier penetration effects proceed much more slowly for heavy systems than for light systems. We conclude that there exists a fairly large class of effectively stable doubly ionized diatomic molecules, and that heavy ions are much more likely to form such molecules than light ions.

FURTHER DISCUSSION

In order to understand the physical mechanism underlying the Ba₂⁺⁺ binding effect, we must examine the molecule's electronic wave function in detail. Such an examination reveals that covalent bonding and ion-induced dipole interaction are roughly equally important in producing the attractive interatomic force. The latter form of binding occurs when an electron migrates from one ion to the other; the resulting neutral Ba atom is then polarized by the Ba⁺⁺ ion. Terms in the wave function representing both forms become prominent when R decreases below the position of the local maximum in $E_1(R)$.

We expect that the experimental formation and detection of bound Ba₂⁺⁺ are very difficult. The extremely long lifetimes imply that the scattering resonances are far too narrow to allow formation

by direct two-body collision. Formation by three-body collisions in hot dense gases is probably feasible. But the depth of the potential well (0.0056) is considerably smaller than that well's height above the $R=\infty$ energy (0.0562). Therefore, a temperature high enough to generate bound Ba₂⁺⁺ will also cause rapid thermal dissociation of any molecules produced. This difficulty could perhaps be overcome by use of a laser-blowout technique.

Detection of bound Ba₂⁺⁺ by mass spectroscopy may be possible. Molecules formed from two nuclei of the same isotope are indistinguishable from single Ba⁺ ions because such homonuclear Ba₂⁺⁺ molecules have the same charge-to-mass ratio as a Ba⁺. But heteronuclear Ba₂⁺⁺ might be detectable because in some cases its charge-to-mass ratio is not equal to any single Ba⁺ ratio. In particular, pairs formed from ¹³⁸Ba (71.7% abundance) and ¹³⁷Ba (11.3%) have a ratio that can be interpreted as a single Ba⁺ ratio only by postulating the existence of a Ba isotope of half-integral nucleon number. Observation of such a charge-to-mass ratio in a Ba⁺ experiment would demonstrate the existence of bound Ba₂⁺⁺.

To summarize, our calculations indicate that metastable bound states of Ba₂⁺⁺ exist, with lifetimes so long that this species can be regarded as a stable molecule. Other calculations¹⁻⁴ indicate that other metastable doubly ionized diatomic species also exist, but with lifetimes shorter than Ba₂⁺⁺. Experimental formation of these species is difficult because of rapid thermal dissociation occurring in the source. Detection of these species by mass spectroscopy is possible because of isotope mixing.

ACKNOWLEDGMENTS

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