Radiative lifetimes of the $^1S_0$ metastable states of Kr^{2+} and Xe^{2+}

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(Received 5 February 1988)

The radiative lifetimes of the $^1S_0$ metastable states of Kr^{2+} and Xe^{2+} have been measured to be 13.1±0.6 and 4.5±0.3 msec, respectively. The ions were created by electron bombardment on the neutral parent gas and contained in a cylindrical radio-frequency ion trap. A single-photon-counting photomultiplier tube was used to observe directly the subsequent spontaneous emission. The transitions observed were, for Kr^{2+}, the $M1$ (magnetic dipole) transition at 350.5 nm from $^1S_0$ to $^3P_1$ in the $4p^4$ ground configuration, and, for Xe^{2+}, the $M1$ transition at 380.1 nm from $^1S_0$ to $^3P_1$ in the $5p^4$ ground configuration. The experimental results are in fair agreement with theoretical predictions.

I. INTRODUCTION

The high-vacuum, nearly perturbation-free environment characteristic of radio-frequency ion traps provides an almost ideal setting for experimental studies of long-lived states of atomic or molecular ions. The study of such states, known as metastable states, are of importance in the areas of astrophysics,[1,2] solar physics,[3–5] aeronomy,[6] plasma physics,[7] the development of laser systems,[8] and for the general testing and expansion of atomic and molecular structure theory. The method of using a radio-frequency quadrupole ion trap to study metastable states of atomic ions has become well established, as has the use of a cylindrical ion trap[9,10] which is simpler in design yet approximates well the ideal quadrupole potential well. The details of ion storage have been discussed in the review articles by Dehmelt[11,12] and by Wineland, Itano, and Van Dyck.[13]

In this paper we report on measurements of the radiative lifetimes of the metastable $^1S_0$ state in doubly-ionized krypton and xenon, both of which have an oxygenlike p^4 ground configuration. An energy-level diagram for Xe^{2+} is shown in Fig. 1; the corresponding diagram for Kr^{2+} is similar. The dominant decay channel from the $p^4\,^1S_0$ state is the magnetic dipole ($M1$) transition to the $p^4\,^3P_1$ state. This channel, with radiation at 350.5 nm in Kr^{2+} and 380.1 nm in Xe^{2+}, represents over 90% of the total transition probability for the decay and is the channel observed in these measurements. Weaker electric quadrupole ($E2$) transitions occur to $p^4\,^3P_2$ and $p^4\,^1D_2$.

Garstang[14] made a semiempirical calculation of the $M1$ and $E2$ transition rates from the $^1S_0$ state, from which lifetimes of 17.2 msec for Kr^{2+} and 4.4 msec for Xe^{2+} are obtained. These results are estimated by Garstang to be accurate to within 20% of the true values. Subsequently, Hansen and Persson[15] noted that the identification of the $^1S_0$ level in Xe^{2+} was in error by more than 1200 cm^{-1}. Their recalculation of the transition probabilities, using Garstang's method, yields a revised lifetime of 4.9 msec. Recent calculations by Biémont and Hansen[16] yield a lifetime of 17.3 msec for the $^1S_0$ state in Kr^{2+}.

A preliminary report by Johnson[17] presented experimental lifetime values of 16±2 msec for Kr^{2+} and 15±3 msec for Xe^{2+}. We note, however, that his measurements were conducted using the earlier value for the $^1S_0$ energy level in Xe^{2+} and that his observation window at 362 nm was considerably displaced from the reassigned wavelength of 380 nm. We have completed measurements on Kr^{2+} and Xe^{2+}, the latter using observations based on the revised $^1S_0$ energy level. Our results support the reassignment of $^1S_0$ in Xe^{2+}, but a similar reassignment of $^1S_0$ in Kr^{2+}, as suggested by Johnson and

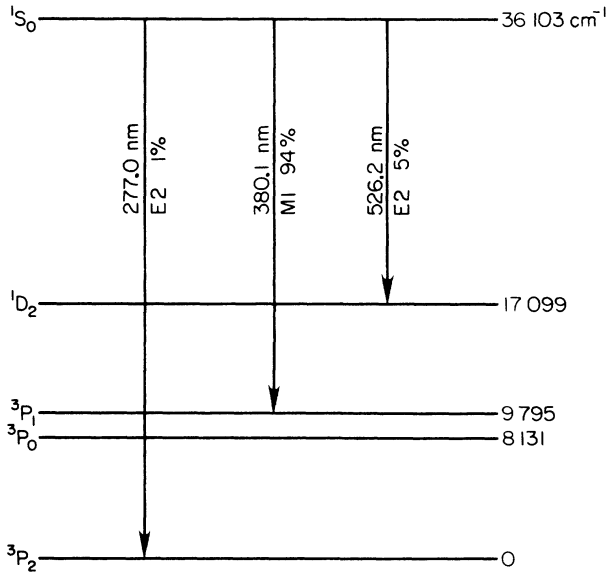

FIG. 1. Energy levels of the Xe^{2+} $5s^25p^4$ ground configuration. Transitions from the metastable $^1S_0$ level are shown.

Morrison,[18] seems unwarranted. Our results are in good agreement with the calculated lifetime for Xe^{2+} and in fair agreement for Kr^{2+}.

II. EXPERIMENTAL PROCEDURES

The measurements were performed in a cylindrical radio-frequency ion trap and were similar to previously reported measurements of metastable state lifetimes in N^+,[10] O^{2+},[19] and Si^{2+}.[20] The trap was 3.3 cm in diameter and 3.5 cm in height, and it was operated at a base pressure, determined with an uncalibrated, nude ion gauge, of 1×10^{-8} Torr. A simple, tungsten-filament electron gun, producing a 3-msec, 50-μA, 500-eV electron beam in the trap, was used to create the ions from neutral parent gas atoms introduced into the chamber at various pressures. Under the assumption that the cross section for collisional ionization to the $^1S_0$ state of Kr^{2+} or Xe^{2+} is approximately the same as that of Ar^{2+}, which has been measured to be 5.5×10^{-19} cm^2 at 500 eV,[21] it was estimated that roughly 15 000 $^1S_0$ ions were trapped.

The trap was operated at frequencies of 532 kHz for Kr^{2+} and 447 kHz for Xe^{2+}. Trapping voltages were applied which resulted in approximately spherical potential wells of depths 7 to 27 eV. Storage time was variable but was typically 60 msec for Kr^{2+} and 25 msec for Xe^{2+} during data collection. Ion numbers were monitored at the end of each cycle by pulsing the ions out through one endcap and detecting them with a magnetic electron multiplier (MEM). The various experimental parameters were optimized by maximizing the size of this signal.

The radiative lifetimes were determined by directly observing the time dependence of the spontaneous $M1$ emission that followed excitation. Observation was permitted by two 1.9-cm-diam holes in the ring electrode colinear with the optical collection axis. The holes were overlayed with a fine mesh that helped preserve the integrity of the trapping electric fields. A uv-reflective spherical concave mirror was situated behind one hole to enhance photon collection efficiency. The primary optics consisted of a three-lens system designed with the help of a computer program to maximize the amount of light collected from the central region of the trap while minimizing the throughput of stray light from the electron gun filament.

The optical system focused the decay photons through a narrow-band ($\Delta\lambda\sim10$ nm) interference filter onto a cooled, single-photon-counting photomultiplier tube (RCA 8850). The Kr^{2+} filter had a maximum 47% transmission at 348.6 nm and the Xe^{2+} filter had a maximum 43% transmission at 379.1 nm. Photon counts were collected in a multichannel scalar, and the information obtained was sent to a computer where data storage and analysis took place. Photons were collected in time bins of 1 and 0.5 msec for Kr^{2+} and Xe^{2+}, respectively, with the time base controlled by a crystal oscillator. Data collection followed excitation after a time delay of one time bin plus 0.6 msec and proceeded for several lifetimes of the gas being studied (25 msec for Xe^{2+} and 60 msec for Kr^{2+}). The time delay allowed cascading from higher levels and any rapid decay of excited background states to finish before data were collected. After data collection, the ions were electrically pulsed out of the trap onto the MEM and the cycle was repeated.

Signal collection rates of approximately 40 counts per cycle were typical. With an estimated optical collection efficiency of 0.03 and a photomultiplier (PMT) quantum efficiency of about 0.3, it is inferred that approximately 6000 metastables were trapped. This is roughly one third the number estimated from cross section and electron current considerations but, considering the uncertainties in these estimates, is not seriously in disagreement. A weak background was detected, primarily from the dark rate of the PMT and secondarily from the electron gun filament. Total collection times were about 1 h per decay curve, with typically 1×10^6 or more signal counts being accumulated. No signal was observed from the background gas alone, from other gases, or if other interference filters were used.

Although their numbers were minimized by careful choice of the trap operating parameters, some other ions, mostly singly- and triply-ionized parent gas atoms, were trapped along with the species of interest. However, it was determined[22,23] that no long-lived states in these ions radiate at wavelengths that would have been transmitted by the filters. Also ruled out were transitions from the neutral parent atoms or from any background species. As a further precaution against collecting photons from unwanted decays and also against long-term drifts in the characteristics of the system, the trap was "detuned" every alternate cycle by switching the dc voltage on the ring electrode to +100 V, a value that would not permit the ions of interest to be stored. The background data collected in this fashion were then subtracted on a channel-by-channel basis from the background-plus-signal data collected during the previous cycle.

III. RESULTS AND DISCUSSION

The decay curves thus obtained represent the total rate of change with time of the number of trapped metastables. Figure 2 for Xe^{2+} shows a typical example. A total

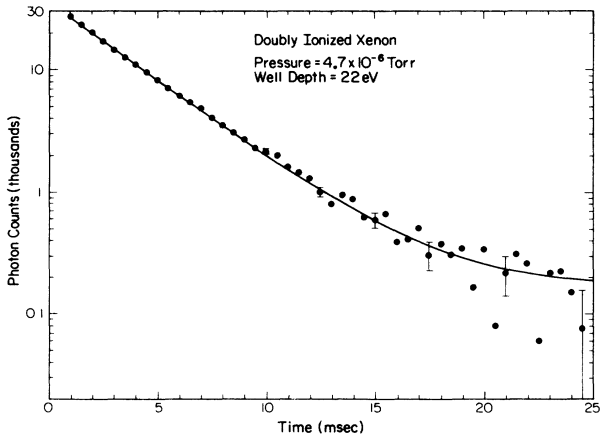

FIG. 2. Typical photon decay curve for Xe^{2+}, showing the number of counts collected per channel. The solid line is the result of a nonlinear least-squares fit to the data.

of 33 such decay curves, covering a wide range of pressures, were used in the final analysis for Kr^{2+} and 57 were used for Xe^{2+}. Data were taken at potential well depths of 7 (Xe^{2+} only), 9, 12, 17, 22, and 27 eV, although the data for 27 eV were not used because of very poor statistics and inconsistencies with other data. The reasons for these are unclear, though one possible explanation is that the increased rf heating of the ions at this largest well depth altered the ion distribution in, or loss from, the trap. Other than this anomaly at 27 eV, the measured lifetimes were found to be independent of well depth.

Measurements were made for sample gas pressures ranging between 2.0×10^{-7} Torr and 1.0×10^{-5} Torr. At gas pressures below this range, the signal-to-noise ratio was too low to be usable without excessively long collection times. For pressures above this range, the decay rate versus pressures curves showed a slight leveling off, as was also seen by Knight.[10] Over the pressure range used, covering a factor of 50, the decay rate was linear with pressure, as expected.

Since the background has been subtracted away, one might expect the decay curves to be described by functions of the form $C\exp(-At)$, where A is a metastable ion-loss rate due to a combination of radiative loss plus other loss mechanisms linearly proportional to the pressure. The latter would include metastable loss due to collisions resulting in deexcitation (quenching) and also general ion loss due to charge exchange, scattering out of the trap, etc. A simple linear fit of the logarithms of the data could then be performed to find the two unknowns, C and A. Because of the statistical nature of the signal and background, however, some data in the "tail" of the decay curves have negative values after the background subtraction, thus precluding this simple analysis. Instead, we performed a nonlinear fit to functions of the form $C\exp(-At)+B$, where B is expected to be consistent with zero. This nonlinear fit was accomplished using a least-squares approach modeled after Bevington.[24]

The data for Xe^{2+} were well fit using this method, but the data for Kr^{2+} were not. Ion-loss studies, made by monitoring ion number as a function of storage time, revealed a two-component ion-loss profile for Kr^{2+}. The first component consisted of a faster exponential decay, having a time constant of approximately 3 msec, and the second consisted of a slower exponential decay with a time constant inversely proportional to the pressure. A five-parameter, nonlinear, least-squares fit of the Kr^{2+} photon data to functions of the form

$$C_1\exp(-A_1t)+C_2\exp(-A_2t)+B$$

yielded good χ^2 statistics and a value for B that was consistent with zero. The shorter time constant obtained with these fits agreed well with the smaller time constant obtained in the ion-loss measurements. The larger time constant was then interpreted as due to radiative loss plus other losses directly proportional to the pressure, and it was subsequently used for the determination of the radiative lifetime.

There was no evidence of nonexponential ion loss for Xe^{2+}. However, even though good statistics resulted from three-parameter fits to the photon data, it was found that small but significant nonzero values for B ensued. This anomaly was ascribed to the occurrence of a weak discharge, discovered after the Xe^{2+} data were collected, taking place between the ring electrode and a lens holder. This discharge may have resulted in broadband uv radiation which was then scattered into the collection optics. It is likely that the discharge intensity was dependent on the ring electrode dc voltage, which changed in value as the trap was alternatively tuned and detuned, and that this asymmetry led to the nonzero value for the subtracted background. There was, however, no time dependence to this extra light and there is no evidence that it affected the final results for Xe^{2+}. This problem was corrected before data were collected for Kr^{2+}.

Although all statistics were generally good, the three-parameter fits for Xe^{2+} were found to have slightly better values for χ^2 and slightly decreased values of the decay rates if the first few data channels were deleted from the fit. The shifts in the time constants were only a few percent but were statistically significant. Values for χ^2 and the decay rate asymptotically approached constants as more channels were deleted, and essentially no further change was observed for fits starting after channel five. This implies that the decay curves were not exactly single exponential but, instead, also included a weak, rapid decay. Two-exponential, five-parameter fits, as applied to the Kr^{2+} data, did not improve the statistics in this case. The small shifts in the decay rates returned by the three-parameter fits were found to vary roughly linearly with the inverse of the time delay to the channel used to start the fit. Extrapolation to infinite time delay produced the decay rates used in subsequent analysis.

The purely radiative decay rate for each ion was determined by plotting the total decay rates obtained from the photon data fits against the pressure. These plots, known as Stern-Volmer plots, were made for each well depth studied and showed good linearity, with correlation coefficients typically around 0.97. Extrapolation to zero

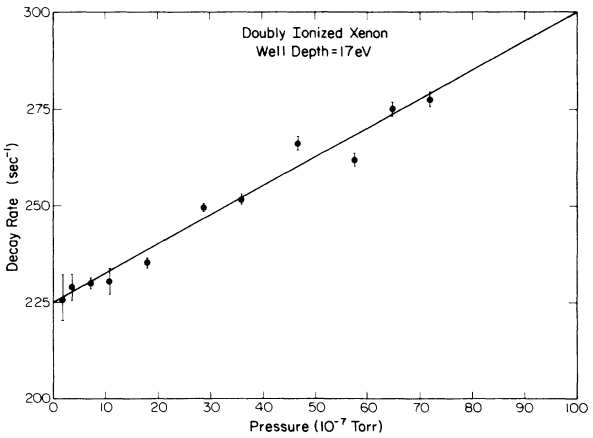

FIG. 3. Typical Stern-Volmer plot of decay rate vs pressure for Xe^{2+}. The straight line is a linear least-squares fit to the data. Extrapolation to zero pressure gives the purely radiative decay rate.

TABLE I. Metastable $^1S_0$ lifetimes for Kr^{2+} and Xe^{2+}. Units are msec.

Authors	Kr^{2+}	Xe^{2+}	
Garstang[a]	17.2	4.4[e]	theoretical
Biémont and Persson[b]	17.3		theoretical
Hansen and Persson[c]		4.9	theoretical
Johnson[d]	16±2	15±3	experimental
This work	13.1±0.6	4.5±0.3	experimental

[a]Reference 14.
[b]Reference 16.
[c]Reference 15.
[d]Reference 17. Xe^{2+} measurement based on unrevised energy level.
[e]Based on unrevised energy level.

pressure gives the purely radiative decay rate or, its inverse, the radiative lifetime. Figure 3, for Xe^{2+}, is a typical example. With 27 eV excluded, no dependence on well depth was found. The radiative decay rates obtained for each of the remaining well depths were averaged together to give final lifetime values of 13.1±0.4 msec for Kr^{2+} and 4.5±0.3 msec for Xe^{2+}, where the uncertainties are statistical only.

Reaction rates for metastable ion loss, thought to result primarily from charge exchange with the parent gas, were deduced from the slopes of the Stern-Volmer plots. The average rates were 4.6×10^{-10} cm^3/sec for Kr^{2+} and 3.0×10^{-10} cm^3/sec for Xe^{2+}, although it should be noted these values could be in error by a factor of 2 or more since the pressure readings were made with an uncalibrated ion gauge. These values are very similar to that of $(5.5\pm0.8)\times10^{-10}$ cm^3/sec obtained by Prior[25] for the same $^1S_0$ state in Ar^{2+}. However, these rates are three to four orders of magnitude larger than room-temperature charge-exchange rates measured by Johnsen and Biondi[26] for the $^1S_0$ state of doubly-ionized rare gases. As suggested by Prior, this discrepancy may be due to the fact that the average kinetic energy of the trapped ions is roughly two orders of magnitude larger than the ion energies in the measurements of Johnsen and Biondi.

In addition to the lack of any well-depth dependence (within the limits previously described), the results obtained were found not to depend on the electron beam energy or any other trapping parameter. The only other known systematic factor is possible reactions with the residual gas in the vacuum chamber at a pressure of 1×10^{-8} Torr. This would require a small correction to the rates obtained from the Stern-Volmer plots. The composition of the residual gas was unknown, but it was likely a combination of H_2, H_2O, and CO. A rough measurement of the reaction rates of the $^1S_0$ state of Xe^{2+} in H_2 and CO produced rates not significantly different than those measured in the parent gas, thus implying a correction of around 0.1 sec^{-1}. This effect makes a negligible change in the reported lifetimes. Our final value for the radiative lifetime of the $^1S_0$ state of Xe^{2+} is therefore 4.5±0.3 msec. In the case of Kr^{2+}, again, no correction was made to the reported lifetime. Since, however, Kr^{2+} is expected to be more sensitive to reactions due to the longer lifetime, and since no H_2 or CO reaction rate measurements were made with Kr^{2+}, we have slightly increased our quoted uncertainty. This results in a final value for the radiative lifetime of the $^1S_0$ state of Kr^{2+} of 13.1±0.6 msec. We compare our results to previous theoretical and experimental work in Table I.

In summary, we have measured the radiative lifetimes of the $^1S_0$ states of Kr^{2+} and Xe^{2+}. The result for Kr^{2+} is in fairly good agreement with the less accurate preliminary result of Johnson and is just outside the estimated 20% uncertainty of Garstang's theoretical value. The result for Xe^{2+} is in good agreement with the theoretical value but disagrees with Johnson's work. As noted earlier, his measurement apparently was made using the unrevised value for the wavelength. One possible explanation for the larger discrepancy between theory and experiment in the case of Kr^{2+} is that the branching ratio for $E2$ decay is higher in Kr^{2+} than in Xe^{2+} (9% versus 6%), and $E2$ rates are generally much more difficult to calculate than $M1$ rates. We note that we could, in principle, measure the $E2/M1$ branching ratio by also observing the $E2$ emission line with a wavelength-calibrated PMT. In practice, however, the greatly increased background light seen at the longer wavelengths from the electron gun filament, combined with the more than 90% signal reduction on the $E2$ line, makes this measurement not feasible in our present apparatus.

ACKNOWLEDGMENTS

This research has been supported, in part, by National Science Foundation Grant No. PHY-8503424 and by The Ohio State University.

[1]A. H. Gabriel and C. Jordan, in *Case Studies in Atomic Collision Physics 2,* edited by E. W. McDaniel and M. R. C. McDowell (North-Holland, Amsterdam, 1971), pp. 211–291.
[2]A. K. Dupree, Adv. Atom. Mol. Phys. **14**, 393 (1978).
[3]R. Smitt, Sol. Phys. **51**, 113 (1977).
[4]T. Garz, M. Kock, J. Richter, B. Baschek, H. Holweger, and A. Unsöld, Nature **223**, 1254 (1969).
[5]J. E. Ross and L. H. Aller, Science **191**, 1223 (1976).

[6]R. W. Nicholls, Ann. Geophys. **20**, 144 (1964).
[7]M. Klapisch *et al.*, Phys. Rev. Lett. **41**, 403 (1978).
[8]W. R. Bennett, Jr., Appl. Opt. Suppl. **2**, 3 (1965).
[9]F. Plumelle, M. Desaintfuscien, J. L. Duchene, and C. Audoin, Opt. Commun. **34**, 71 (1980).
[10]R. D. Knight, Phys. Rev. Lett. **48**, 792 (1982).
[11]H. G. Dehmelt, Adv. Atom. Mol. Phys. **3**, 53 (1967).
[12]H. G. Dehmelt, Adv. Atom. Mol. Phys. **5**, 109 (1969).
[13]D. J. Wineland, W. N. Itano, and R. S. Van Dyck, Jr., Adv. Atom. Mol. Phys. **19**, 135 (1983).
[14]R. H. Garstang, J. Res. Nat. Bur. Stand. **68A**, 61 (1964).
[15]J. E. Hansen and W. Persson, Phys. Scr. **25**, 487 (1982).
[16]E. Biémont and J. E. Hansen, Phys. Scr. **34**, 116 (1986).
[17]C. E. Johnson, Bull. Am. Phys. Soc. **32**, 1274 (1987).
[18]L. P. Johnson and J. D. Morrison, Int. J. Mass Spectrom. Ion Phys. **18**, 355 (1975).
[19]P. L. Smith, B. C. Johnson, H. S. Kwong, W. H. Parkinson, and R. D. Knight, Phys. Scr. T **8**, 88 (1984).
[20]H. S. Kwong, B. C. Johnson, P. L. Smith, and W. H. Parkinson, Phys. Rev. A **27**, 3040 (1983).
[21]K. Wiesemann, J. Puerta, and B. A. Huber, J. Phys. B **20**, 587 (1987).
[22]C. E. Moore, *Atomic Energy Levels,* Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1958), Vols. II and III.
[23]H. O. DiRocco, J. G. R. Almandos, M. Gallardo, and W. Persson, Phys. Rev. A **33**, 2114 (1986).
[24]P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969), Chap. 11.
[25]M. H. Prior, Phys. Rev. A **30**, 3051 (1984).
[26]R. Johnsen and M. A. Biondi, Phys. Rev. A **20**, 87 (1979).