Letter

Measurement of the lifetime of a metastable excited state in Bi^-

M. K. Kristiansson,[1,*] J. Karls,[2] N. D. Gibson,[3] D. Hanstorp,[2] H. T. Schmidt,[1] and C. W. Walter[3]

[1]*Department of Physics, Stockholm University, Stockholm 10691, Sweden*

[2]*Department of Physics, University of Gothenburg, Gothenburg 41296, Sweden*

[3]*Department of Physics and Astronomy, Denison University, Granville, Ohio 43023, USA*

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The lifetime of the $^3P_0$ state of Bi^- has been measured by selective photodetachment in a cryogenic ion-beam storage ring. By measuring the lifetime as a function of applied laser powers and extrapolating to zero laser power, a lifetime of 16.0 ± 0.5 s is deduced for electric quadrupole decay of the excited state to the ground sate. The result provides a stringent test of recent state-of-the art theoretical calculations.

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Negative ions are important in a variety of physical situations, ranging from chemical reactions to planetary and stellar atmospheres to plasmas and discharges [1,2]. Since negative ions are not bound by a net Coulomb potential, correlation effects due to interactions of the electrons are relatively enhanced compared to neutral atoms and positive ions. Thus, negative ions present challenging but valuable opportunities to investigate electron correlation in atomic structure and dynamics, and they provide fertile testing grounds for state-of-the-art theoretical calculations [1,3–8].

The polarization potentials in negative ions are shallow and short ranged and can therefore only support one or at most a few bound states [1,5]. In most cases, any bound excited states are of the same parity as the ground state, so that electric dipole ($E1$) transitions are not allowed; indeed, $E1$ transitions have only been observed to date in the four atomic negative ions Os^- [9], Ce^- [10], La^- [11], and Th^- [12]. Transitions due to magnetic dipole ($M1$) and electric quadrupole ($E2$) interactions can occur between bound states of negative ions, but the transitions are weak and the lifetimes are consequently long (typically approximately seconds or greater) making experimental investigation very challenging. New capabilities to study such forbidden transitions have recently become available with the advent of new cryogenic storage ring facilities, such as the double electrostatic ion-ring experiment (DESIREE) [13–15] and the CSR [16,17] that can be used to measure decay rates of excited states of negative ions over unprecedentedly long time-scales of hours [18,19].

The ground state of the bismuth negative ion is the $6p^4\ ^3P_2$ level. The fine-structure levels are not ordered according to the J quantum number and the only excited bound state has $J = 0$ while the $J = 1$ level is unbound [8]. This change in the ordering is a result of the strong relativistic effects present in a heavy atomic system such as Bi^-. This leads to a breakdown of LS coupling and strongly complicates the theoretical description of such systems. We chose to keep the LS-coupling notation throughout this Letter for compatibility with the literature, even though the states are heavily mixed. With $|\Delta J| = 2$ and the same parity of both bound levels, the transition between them is an electric quadrupole ($E2$) transition. The observation of this transition by Walter *et al.* in 2021 was the first spectroscopic identification of an $E2$ transition in an atomic negative ion [20], while a lifetime measurement of an excited level in Pt^- decaying by an $E2$ transition was performed in DESIREE in 2017 [21]. $E2$ interactions in negative ions provide particularly useful opportunities to gain insight into detailed electron correlation effects, as the transition rates depend crucially on the wave functions.

Figure 1 shows the energy level diagram of the bismuth negative ion. The electron affinity of bismuth, corresponding to the binding energy of the Bi^- $(6p^4\ ^3P_2)$ ground state relative to the Bi $(6p^3\ ^4S_{3/2})$ ground state, is 942.369 ± 0.013 meV [22]. The binding energy of the $^3P_0$ excited state was measured by Walter *et al.* to be 373.09 ± 0.04 meV using threshold photodetachment [20]. In the same study, the Bi^- $^3P_2 \rightarrow {}^3P_0$ $E2$ transition energy was separately measured to be 569.27 ± 0.03 meV by a (1+1) resonant photodetachment method [20].

In 2019, Su *et al.* made the first theoretical calculations of the $E2$ radiative decay rate of the Bi^- $^3P_0$ excited state, obtaining a lifetime of 15.20 s (no uncertainty given) [8]. Recently as part of the 2021 study by Walter *et al.*, Safronova and Cheung calculated the same Bi^- $^3P_0$ lifetime to be 16.5 ± 0.7 s using the experimentally measured transition energy of 569.27 ± 0.03 meV [20]. While these two calculated lifetimes are fairly close, it is important to note that the quoted lifetime by Su *et al.* was obtained using their calculated transition energy for $^3P_2 \rightarrow {}^3P_0$ of 624.0 meV, which is larger than the subsequently measured energy by ~10% [20]. Since the $E2$ lifetime scales inversely with transition energy to the fifth power [8], revising the lifetime by Su *et al.* using the measured energy would yield an adjusted lifetime of 24.05 s, which is

*moa.kristiansson@fysik.su.se

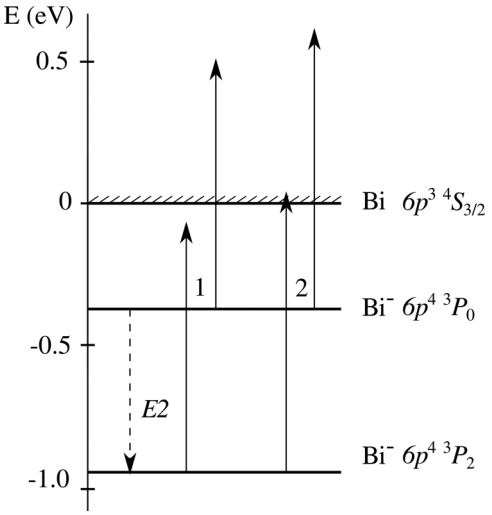

FIG. 1. Energy level diagram for Bi^- showing $E2$ radiative decay from the Bi^- $^3P_0$ excited state to the $^3P_2$ ground state. The two photon energies that are used to photodetach the two bound states are indicated by the two sets of upward arrows. Arrow set 1 corresponds to 0.886 eV (1400 nm) and photodetaches only from the excited state. Arrow set 2 corresponds to 0.954 eV (1300 nm) and photodetaches from both the ground state and the excited state of Bi^-. In the experiment, the time evolution of the Bi^- $^3P_0$ population in the storage ring is monitored to measure its lifetime by photodetaching either just the excited state or both states.

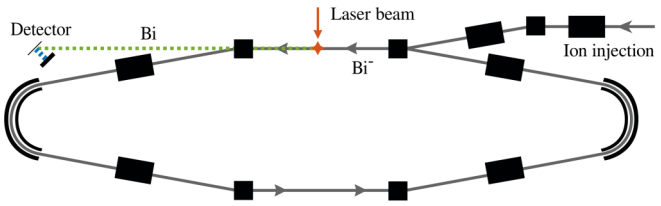

FIG. 2. Schematic of the ion storage ring used in the experiment. Bi^- ions of 10 keV energy are injected and stored in the ring. A transverse pulsed laser beam interacts with the ion beam. The neutral Bi atoms created in photodetachment travel straight forward and hit the micro-channel-plate detector.

significantly longer than that predicted by the calculations of Walter *et al.* [20].

In the present study, we used state-selective photodetachment of Bi^- ions in a storage ring to monitor the time evolution of both the ground and excited state populations. The extremely low pressure in the storage ring, coupled with the high sensitivity of the detection system, enables measurements of the ion populations over hundreds of seconds [18,21,23] allowing precise observation of the weak $E2$ radiative decay of the excited state. The results yield the first measured lifetime of the $^3P_0$ state, providing a stringent test of the two different theoretically calculated lifetimes [8,20] and giving new insights into the dynamics of this complex system.

The DESIREE at Stockholm University [13,14] was used to store Bi^- ions and through photodetachment, measure the lifetime of the excited state. DESIREE consists of two storage rings with a common straight section for studies of ion-ion collisions with sub-eV center-of-mass energies. The storage rings are contained in a vacuum chamber and kept at a temperature of 13.5 ± 0.5 K. The cryogenic temperature reduces the particle density of the rest gas in the vacuum chamber to a particle density of less than 10^4 cm^{-3}. Bi^- ions are produced in a cesium sputter source where the high sputtering energy of several keV produces a relative population in the excited state that is many orders of magnitude larger than the Boltzmann factor at room temperature. The ions are injected into one of the storage rings and the excited state is allowed to equilibrate with the blackbody radiation of the chamber. This decay of the excited state is probed with photodetachment using light from a pulsed optical parametric oscillator laser system. The laser system has a repetition rate of 1 kHz and a pulse duration of 5 ns. The two photon energies used are 0.886 and 0.954 eV with varying average power from 0.2 to 11.5 mW. The laser power is measured before the entrance window to the vacuum chamber. Due to divergence of the laser beam (the estimated diameter of the laser beam is about 1 cm) and losses when passing through the vacuum chamber windows, the effective laser power interacting with the ions is at least a factor of 2 smaller than this. The laser light interacts with the ions in a transverse configuration in the straight section along the injection line on the storage ring according to Fig. 2. Neutral atoms resulting from photodetachment are detected using a detector placed after the straight section. The detector consists of a glass plate covered by a single graphene layer for optimum surface conduction and secondary electron emission [24] followed by a microchannel plate triple-stack assembly. The signal resulting from photodetachment is collected during a time window of 10 μs, starting 16.7 μs after the laser firing time, corresponding to the time of flight from the laser interaction region to the detector. This scheme results in a drastically reduced background from the detector (typically $\sim$3–5 s^{-1}) and the ion-residual gas collisions. A second time window of 500 μs placed 130 μs after the signal gate is used to monitor and correct for the background signal.

In order to accurately measure the storage lifetime of an excited state, it is advantageous if the storage lifetime of the total ion beam is several times longer than the excited state lifetime. This is beneficial, since the decay of the excited state then can be distinguished from the decay of the ion beam. The lifetime of the ion beam was monitored by using a photon energy of 0.954 eV. This energy detaches both the ground state and the excited state corresponding to the arrows labeled 2 in Fig. 1. The storage lifetime was measured to be 1190 ± 350 s, which is much longer than the expected lifetime of the excited state. Another important factor is the ion-beam current; if a too high current is used the beam current has been found to decay faster than the characteristic exponential decay [14]. Using experience from dealing with ions of similar mass-to-charge ratio and energy, an ion-beam current of about 0.5 nA (in the beginning of the measurement cycle) was used in order to avoid ion-ion interactions affecting the beam lifetime.

A photon energy of 0.886 eV (arrow set 1 in Fig. 1) was used to probe the excited state as a function of storage time. This is shown in Fig. 3, where an average laser power of 8.2 mW is used. An exponential fit is made to extract the decay rate Γ_{tot} which is a sum of several different effects according

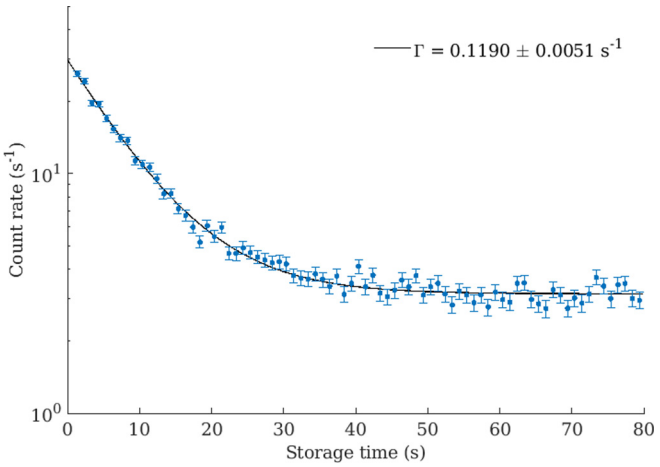

FIG. 3. Photodetachment signal as a function of storage time using a photon energy of 0.886 eV and a laser power of 8.2 mW. An exponential fit to the decay yields a decay rate of $0.1190 \pm 0.0051\ \mathrm{s}^{-1}$.

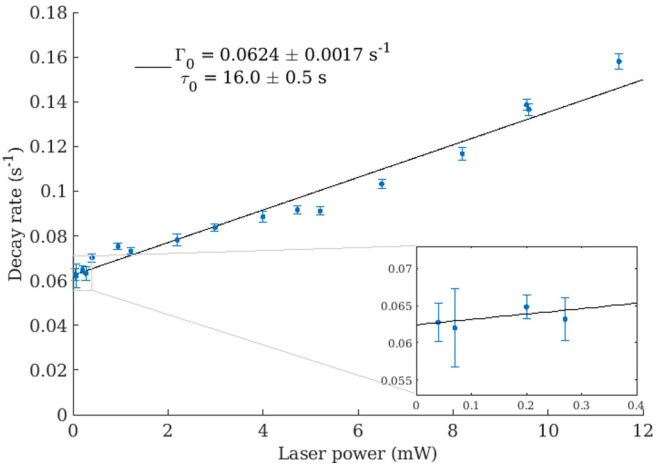

FIG. 4. The measured decay rate as a function of average laser power going from 0.02 to 11.5 mW. A first-order polynomial is fitted to the data in order to extract the radiative decay rate Γ_0 which yields $\Gamma_0 = 0.0624 \pm 0.0017\ \mathrm{s}^{-1}$. This gives a lifetime of $\tau_0 = \frac{1}{\Gamma_0} = 16.0 \pm 0.5$ s. The inset in the bottom right shows a zoomed-in view in the low power region, close to the intersection with the decay-rate axis.

to

$$\Gamma_{\mathrm{tot}} = \Gamma_0 + \Gamma_{\mathrm{laser}} + \Gamma_{\mathrm{other}}, \tag{1}$$

where Γ_0 is the radiative decay rate of the excited state, Γ_{laser} is the decay rate due to the photodetachment process itself, and Γ_{other} represents all other effects determining the undisturbed storage lifetime of the ion beam. Γ_{other} can be taken into account by dividing the photodetachment signal by a fitted linear function to the background measured in between the laser pulses. Since the background mainly depends on the storage lifetime of the ion beam which is about 20 min, a linear dependence is a good approximation of the exponential decay of the beam over the timescale of 80 s which is the time of a measurement cycle. In order to investigate the contribution of Γ_{laser} to Γ_{tot}, a series of measurements were made where the laser power was varied. In Fig. 4 the decay rate is shown as a function of laser power. A linear decrease of the decay rate is expected with increasing laser power if only one-photon detachment is the process involved. A fit to a polynomial of first order $y = ax + b$ gives the unaffected radiative decay rate $b = \Gamma_0$ by extrapolation to zero laser power. This gives the radiative decay rate $\Gamma_0 = 0.0624 \pm 0.0017\ \mathrm{s}^{-1}$ corresponding to a lifetime of $\tau = \frac{1}{\Gamma_0} = 16.0 \pm 0.5$ s.

The measured lifetime of 16.0 ± 0.5 s is in excellent agreement with the previous calculation of 16.5 ± 0.7 s by Walter *et al.* [20]. In that study the computational method was based on a combination of configuration interaction and the coupled-cluster method. However, when the experimental value is compared to the transition energy-scaled lifetime of 24.05 s by Su *et al.* [8] there is a significant difference. Su *et al.* used a fully relativistic multiconfiguration Dirac-Hartree-Fock method to investigate structural effects for a series of negative ions homologous to N^-, including Bi^-. The two calculations were performed using different computational methods and different procedures and this illustrates the importance of experiments like the present in order to further understand these complex systems with strong correlation effects. Accurate lifetime measurements can be of assistance when comparing computational results in order to further improve the accuracy of the computational methods. In order to conclude if one computational method is preferred to the other, more similar strategic approaches would have to be applied in order to compare the two methods. We can, however, conclude that for this case the computational result of Walter *et al.* [20] gives better agreement with the experiment than the result of Su *et al.* [8].

The present result is an illustrative example of the importance of the exceptional temperature and pressure conditions obtained in a cryogenic experiment such as the DESIREE. These conditions are the decisive factor for measuring high precision lifetimes of the long-lived excited states in negative atomic ions.

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