Radiative Lifetime of a Bound Excited State of Te^-

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We report on the first experimental study of the lifetime of a bound excited state of a negative ion. A new experimental technique was developed and used to measure the radiative lifetime of the $5p^5\,^2P_{1/2}$ level of Te^-. The experiment was performed in a magnetic storage ring, where a laser beam was applied along one of the straight sections. In the experiment the population of the excited $J = 1/2$ level was probed each time the Te^- ions passed through the laser field. A decay curve was built up by sampling the population of the excited level of the Te^- ions as a function of time after injection into the ring. A multiconfiguration Dirac-Hartree-Fock calculation was performed in conjunction with the experiment. The calculation yielded a radiative lifetime of 0.45 s, in excellent agreement with the measured value of 0.42(5) s.

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There is a strong fundamental interest in negative ions since electron correlation plays an important role in determining their structure and dynamics. Correlation effects are generally more enhanced in negative ions than in atoms or positive ions as a consequence of the more efficient screening of the nucleus by the core electrons. The structure of a negative ion differs intrinsically from that of atoms or positive ions due to the short-range nature of the force that binds the outermost electron. The potential well associated with the induced dipole force is sufficiently shallow that it can typically support no more than a single bound state of a given electronic configuration. However, the possibility of the existence of bound excited states of negative ions was discussed more than three decades ago by Massey [1]. To date, with one possible exception [2], only excited states with the same electronic configuration as the ground state have been observed. Consequently, traditional spectroscopic studies involving transitions between bound states are not possible in the case of negative ions. The metastability of bound states of negative ions accounts for the lack of emission spectra.

The standard method to gain high precision information on negative ions involves the use of the photodetachment process. In photodetachment, transitions are induced between a bound state and the continuum. The energies of several bound excited states of negative ions have been determined by studying the threshold of the photodetachment cross section [3]. The small binding energies of the bound excited states of negative ions generally necessitate the use of a source of tunable infrared radiation to study threshold behavior. Haugen and co-workers have recently generated such radiation by Raman shifting the output from a tunable dye laser and have used it to measure the binding energies of excited states and fine structure splittings in the ground states of several negative ions [4]. It would, however, be of interest to study transitions between bound excited states directly. The simplest example of a metastable bound state is that of a level within a fine structure multiplet. Such a transition would predominantly occur via the emission of $M1$ radiation, with $E2$ radiation being negligible.

The measurement of a long radiative lifetime poses a challenge to the experimentalist. The most successful method to date involves the use of an ion storage ring. Mannervik and his co-workers [5], for example, have developed a laser probing technique in order to measure the radiative lifetimes of metastable states of atomic positive ions. Radiation from a laser is directed along one straight arm of the storage ring. The ions periodically traverse the photon field as they circulate in the ring. In such experiments, the laser is used to excite the ions from a metastable state to a short-lived, more highly excited state. The prompt fluorescence emitted in the decay of the latter state is used as a monitor of the time dependence of the population of the metastable state. A decay curve for the metastable state is accumulated by measuring the prompt fluorescence as a function of time after the ions are injected into the ring. This method has been used to measure lifetimes of metastable positive ions ranging from 15 ms [6] to 28 s [7].

Negative ions, however, differ from positive ions in that they are more readily neutralized in collisions with particles of the residual gas in the ring. In fact, the collisional detachment rate frequently determines how long negative ions can be stored in a ring. In some ions, a metastable state is not bound but rather it is embedded in a detachment continuum. In this case, the preferred mode of decay is autodetachment, which results in the production of neutral particles. The lifetime of the metastable state can be determined by counting the number of neutral particles detected as a function of time after the ions are injected into the ring. This technique has been applied, for example, to the study of the lifetimes of the metastable atomic negative ions Be^- [8] and He^- [9]. In the latter case, Pedersen *et al.* measured the autodetaching lifetimes of the three metastable $1s2s2p\ ^4P_j$ levels in the He^- ion. In other ions, radiative $E1$ transitions have been observed between doubly excited states in the continuum that are metastable against autodetachment. Such transitions have been reported in Li^- [10,11], Be^- [12,13], and Ca^- [14].

Thus far, however, there have been no reported measurements of the forbidden radiative decay of bound excited states of negative ions. The present paper describes a new method that has been developed to measure the radiative lifetimes of such states for the first time. We have applied the technique to the Te^- ion, which has a ground state configuration of $5p^5\ ^2P_{3/2}$. This state is bound by 1.970 876(7) eV relative to the ground state of the parent Te atom [15]. The excited $J = 1/2$ level of the same ^2P term lies 0.620 586 eV [16] above the $J = 3/2$ level. The only radiative decay channel for the $J = 1/2$ level is to the $J = 3/2$ level, which takes place primarily via $M1$ transitions. An energy level diagram is shown in Fig. 1. In this paper an experimental determination of the radiative lifetime of the $J = 1/2$ state is presented. The experimental value is then compared with a theoretical prediction using a multiconfiguration Dirac-Hartree-Fock (MCDHF) calculation.

The experiment was performed at the heavy ion magnetic storage ring CRYRING at The Manne Siegbahn Laboratory in Stockholm [17]. Negative ions of Te were produced in a cesium sputter ion source. The cathode material was ZnTe. After acceleration to an energy of 30 keV, the ions were injected into the ring, which has a circumference of 52 m. A laser beam was directed along one arm of the storage ring so that it merged collinearly with the ion beam, as shown in Fig. 2. A neutral particle detector [18] was placed in the tangential arm of the ring just after the laser-ion interaction section. This detector was used to monitor the number of neutral atoms produced in interactions with both the laser (the signal) and the residual gas particles in the ring (the background). The fast neutral atoms impinged on the glass plate which was coated with a thin layer of In_2O_3:Sn. Secondary electrons emitted from the coating were detected with a channel electron multiplier (CEM). The coating served to prevent the glass plate from becoming electrically charged.

The Te^- ions were produced in the ion source in both the $J = 3/2$ and $1/2$ levels. The photon energy was chosen to selectively detach ions in the upper $J = 1/2$ level, while leaving those in the lower $J = 3/2$ level unaffected. This technique allowed us to probe the time-varying population of the $J = 1/2$ level by detecting the neutralized Te atoms as a function of the time after injection of the ions into the ring. This selective detachment scheme required that the Doppler-shifted photon energy has to be less than the 1.97 eV required for detachment of the $J = 3/2$ state. The laser radiation was produced using a dye laser that was pumped by an argon ion laser. The laser power in the interaction region was approximately 200 mW, and the cross section of the laser beam was typically 1 cm^2.

The experiment was straightforward. For each ring injection, the laser beam was turned on at different times after injection ($t = 0$) to track the evolution of the population of the $J = 1/2$ level. A generic timing diagram is shown in Fig. 3. The signal in this experiment was the number of neutral Te atoms reaching the detector when the laser was on for a fixed time period. In order to obtain data of high statistical quality at each pressure, the signal

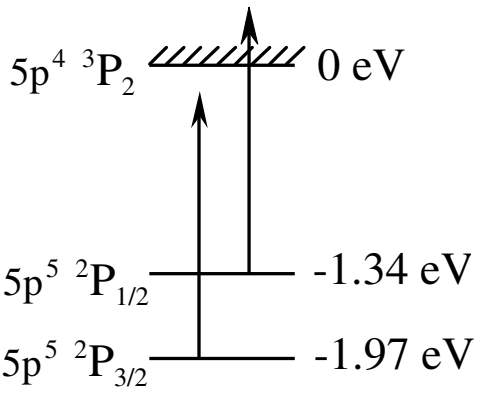

FIG. 1. An energy level diagram of Te^- showing the fine structure levels associated with the $5p^5\ ^2P$ state. The vertical arrows indicate the laser-induced transitions used in the experiment.

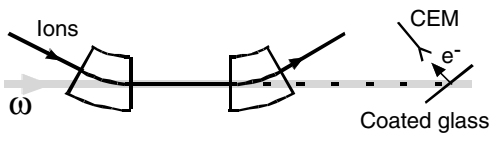

FIG. 2. A schematic of the interaction and detection regions. Fast moving neutralized atoms, denoted by the dashed line, impinge on the coated glass plate. The secondary electrons that are subsequently emitted are detected with the CEM.

FIG. 3. A timing diagram of the experiment. The light grey area represents the collisional detachment contribution. The dark grey areas show the contribution due to the photodetachment of the excited state for three separate ring cycles.

was accumulated for about 1 h and involved many ring cycles. As a result it was necessary to normalize the signal with respect to the number of excited ions injected into the ring in each cycle. This was achieved by applying a short (10 ms) duration laser pulse in the beginning of each cycle. The increase in the signal during this pulse is proportional to the initial population in the upper fine structure level. The pulse was made sufficiently short to ensure that the population of the upper level was not depleted appreciably during the time the probe pulse was applied.

Figure 4 shows a decay curve obtained by sampling the population of the $J = 1/2$ level at different delay times following the injection of the ions into the ring. In order to obtain the curve shown in Fig. 4 the data were collected during 1500 ring cycles. The points are the number of detected neutrals, corrected for the collisional detachment contribution, which correspond to the dark grey areas in Fig. 3. They therefore represent the number of the photodetached ions, which, in turn, is proportional to the population of the excited $J = 1/2$ level at a given time after injection. The solid line shown in Fig. 4 is a fit of the data which represents the decay of the excited $J = 1/2$ state, with a lifetime of about half a second. The background is due to a process in which the $J = 1/2$ level is populated via collisions that redistribute the populations

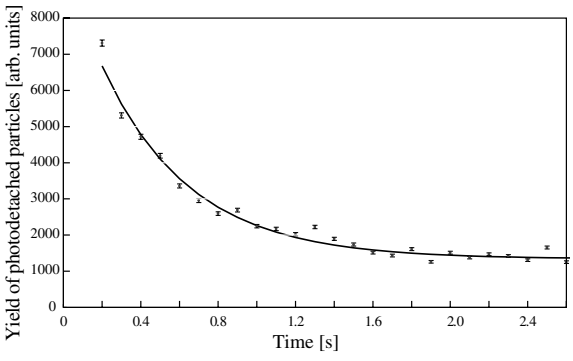

FIG. 4. The figure shows the number of photodetached Te^- ions that were detected as a function of the time after injection into the ring. This curve was recorded at the base pressure. The points are the experimental data, where the error bars represent the statistical uncertainty. The solid line is a curve fit, as described in the text.

of the $J = 3/2$ and $J = 1/2$ levels. As the ion beam circulates around the ring, Te^- ions in both the $J = 1/2$ and $3/2$ levels are neutralized in collisions with particles of the residual gas in the ring. In addition to causing detachment, the collisions are also able to redistribute the populations between the lower and the upper levels. This repopulation of the $J = 1/2$ level gives rise to the relatively flat contribution seen at large times after injection. The decay constant of this contribution is the same as that arising from collisional detachment of the beam ions, which is of the order of 1 min. We therefore approximate the function used in the fit to a single exponential plus a constant. The rate for both collisional detachment and repopulation of the $J = 1/2$ level is proportional to the background gas pressure in the ring.

In order to investigate how the collisional effects change the lifetime of the $J = 1/2$ level, we measured decay curves at several different pressures and extrapolated the best linear fit to the data points to the zero-pressure limit. The measured rate for collisional destruction of the ion at each pressure was used to establish a relative pressure scale. At the zero-pressure limit, the decay is entirely due to the radiative process and the lifetime of the $J = 1/2$ level can be extracted from the data. The base pressure in the ring was below 10^{-11} mbar. The extracted lifetime of the $J = 1/2$ level of the ^2P state of Te^- changed by only a few percent when the pressure was increased by a factor of 4. The value of the radiative lifetime of the $5p^5\,{}^2P_{1/2}$ level in Te^- was determined to be 0.42(5) s. The uncertainty in the result is primarily associated with the linear fit to the pressure-dependent lifetime data.

The Te^- ion is relatively heavy and so calculations were performed using the MCDHF formalism. In this approach, the wave functions are expanded in jj-coupled configuration states and orbital optimization is performed using energy expressions from the Dirac-Coulomb Hamiltonian [19]. The finite size of the nucleus was modeled in the form of an extended Fermi distribution. The core orbitals ($1s$–$4d$, in nonrelativistic terminology) were determined from a multiconfiguration calculation that took into account some of the near degeneracy effects by including $5s^2 \rightarrow 5d^2$ and $5p^2 \rightarrow 5d^2$ excitations. The same orbitals were used for both the $J = 1/2$ and $J = 3/2$ levels. The correlation model was one in which the outer electrons were assumed to have a $5s^2 5p^5$ configuration. Both outer shell correlation from single and double excitations (SD) and core-polarization correlation from $4d^{10}$ were included. Since the principal quantum number has no specific meaning for correlation orbitals, it was convenient to omit the $4f$ orbital. Then an $n = 5$ calculation determined the $5s$–$5g$ orbitals by optimizing simultaneously on $J = 1/2$ and $J = 3/2$ states and keeping the core orbitals fixed. The generalized occupation number for the $5g$ orbital was about 0.002. Consequently, no other g orbitals were included. The

TABLE I. Calculated transition energies, ΔE, transition rates, A, and radiative lifetimes. l and v in column two denote the length and velocity forms, respectively.

N	ΔE (cm^{-1})	$A(E2)$ (s^{-1})	$A(M1)$ (s^{-1})	Lifetime (s)
6	4957.9	0.009 99 (l)	2.1805	0.4565
(SD)		0.011 55 (v)		
7	4966.2	0.010 35 (l)	2.1973	0.4537
(SD)		0.010 99 (v)		
7	4966.8	0.010 24 (l)	2.1926	0.4540
(SDTQ)		0.010 89 (v)		

$n = 6$ calculation determined the $6s$–$6f$ orbitals in a similar fashion. Finally, the $7s$–$7f$ orbitals were introduced, but these were optimized separately for $J = 1/2$ and $J = 3/2$. Once the orbitals were optimized, the frequency-dependent Breit and QED corrections were included using a configuration interaction calculation for the Dirac-Coulomb-Breit Hamiltonian. Finally, some triple and quadruple excitations (TQ) were added to the expansion, obtained as SD excitations from the $5s5p^5 5d$ and $5s^2 5p^3 5d^2$ configurations. These appeared to have a negligible effect on the decay rates. In Table I, the excellent stability of the results from the last three calculations is shown. The final value of the radiative lifetime of the $^2P_{1/2}$ level was determined to be 0.45 s, in excellent agreement with the experimental value of 0.42 ± 0.05 s.

To conclude, we have performed the first experimental investigation of a radiative lifetime of a bound metastable state in a negative ion. Our study of the radiative lifetime of the $5p^5\,^2P_{1/2}$ level in Te^- was found to be in excellent agreement with a theoretical value obtained using an *ab initio* MCDHF calculation. It is clear that the method has the potential for application to many other negative ions, as long as the lifetime of the excited state is of the order of 1 min or shorter. This upper limit is set by the storage time for negative ions in the ring, which is determined by the background pressure in the vacuum chamber. It is our intention to continue the investigation of forbidden radiative transitions in negative ions of other elements. Preliminary calculations have indicated a trend towards increasing lifetimes as one moves to the lighter np^5 negative ions (Se^-, S^-, and O^-). We plan to perform a systematic study of this group of elements.

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