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Electric dissociation of negative ions – II

#13

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As an alternative to naturally occurring negative ion discrimination, we have used electric dissociation to discriminate between isobars, by destroying the weaker negative ion of a pair. This technique also permits the determination of the properties of the quantum states and the binding energy of some weakly bound negative ions (Ca, Tm, Dy and Yb), some of which had not been studied previously (Tm, Dy, Yb). During the course of this study, it was also established that some very weakly bound negative ions (Dy and Yb) are destroyed by weak electric fields such as those in tandem accelerators. This fact was used to verify the theory of electric dissociation by the comparison of the dissociation probability under different field configurations and gradients. The results regarding the lanthanide elements indicate that in all three cases the extra electron occupies a p orbital which does not follow the "natural" filling of the periodic table. The study of Ca^- concluded that the lowest states are the $4s^2 4p\ ^2P\ J = 1/2, 3/2$ states with binding energy of 21.0 ± 2.5 meV and a spin-orbit splitting in the range 0.4–.5 meV with a maximum probability at 0.75 meV. The ordering of the levels has not yet been established.

1. Introduction

Three years ago, at the AMS-5 conference, electric dissociation was proposed as a method both to study weakly bound negative ions and a way to discriminate against the more weakly bound negative ion of a pair of isobars [1]. The goal of this article is to report the results of this work and to discuss the problems encountered.

The original objective of this experiment was to dissociate the negative ion of calcium in order to measure with a different technique the quantum numbers (l,j) and the binding energy of the extra electron in Ca^-, which had been measured previously by laser photodetachment methods, and to destroy $^{44,48}Ca^-$ thus making possible the analysis of $^{44,48}Ti$. The reasons justifying the analysis of ^{48}Ti were given in ref. [1]. Both these goals were achieved, the first more completely than the second. The extra electron of Ca^- was measured to be bound by $E_b = 21 \pm 2.5$ meV in an $l = 1$ orbital. It was also demonstrated that the $^{48}Ca^-$ beam could be destroyed completely and the residual ^{48}Ti was observed. A sample preparation technique and a protocol for analysis still need to be developed to make the analysis of ^{48}Ti or ^{44}Ti useful.

For the electric dissociation experiments, an apparatus, called a dissociator, was designed. The particularities of the design were presented at AMS-5 [1]. It consists of a set of six axially symmetric electrodes arranged so that they form a zoom lens for a specific voltage relationship. This particular arrangement was designed to keep a unit magnification and constant object–mage distance over a range of voltages broad enough to cover the destruction of the negative calcium ions with a binding energy of 43 meV [2]. Unfortunately, the ion optical properties of the zoom lens were never tested, mainly because the negative calcium ions were found to be less strongly bound (21 ± 2.5 meV) than had been reported in an earlier publication (43 ± 7 meV [2]) and did not survive the minimum electric gradient required by the zoom lens. It also proved difficult to maintain a total voltage higher than 22 kV in the presence of an ion current. As a result of these problems, the dissociator was operated as a single einzel lens.

2. Theory

The presence of an external field causes the potential well of the negative ion to tilt in the direction of the gradient. As a result, the most loosely bound electron can be transferred to the energy continuum by tunneling through the barrier created by the external

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220

field. The tunneling probability depends on the field intensity, the binding energy and the quantum numbers (l,m) of the electron and the time spent in the field, [1,3–5].

The theory was originally developed by Smirnov and Chibisov [3] and is described for this application elsewhere [1,5]. The reader is referred to these publications for further details.

3. Experimental considerations

Several technical problems had to be addressed in the fabrication of the dissociator. The need for a high electric gradient (up to 10 MV/m) and an acceptable transmission over a range of voltages covering the destruction of the negative ions were the prime concerns.

The electrodes were made of stainless steel and the areas submitted to the highest field were mirror polished. During tests prior to the experiment, a voltage of 30 kV was applied successfully across the electrodes separated by 1 mm.

The dissociator was installed between the electric analyzer and the injection magnet [1,5,6]. It would have been preferable to install the dissociator between the magnet and the accelerator since the voltage holding capacity of the insulator-electrode assembly is sensitive to the amount of current passing through the plates, but this was not possible. The necessity of adequate steering and focusing both before and after the dissociator to counteract misalignment and construction defects prevented it.

The electrodes were put in series with high impedance resistors (285 MΩ total) to suppress electrical arcs between the plates. These proved to be useful for monitoring the leakage current that developed during the experiments. The insulating properties of the ceramic balls separating the electrodes degraded after several hours of experiment and needed to be cleaned periodically. The measured leakage current was also used to calculate the exact voltage across the electrodes in the analysis of the data.

Even if precautions were taken in the construction of the electrodes in order to avoid wedges and misalignments between the plates resulting in voltage dependent steering, some residual steering effects were observed. This, coupled to a voltage dependent transmission due to the changes in magnification in the einzel lens, demanded the use of normalization beams which were used as a reference during the analysis of the data. The voltage dependent steering effect was observed to be less than 0.5 mrad.

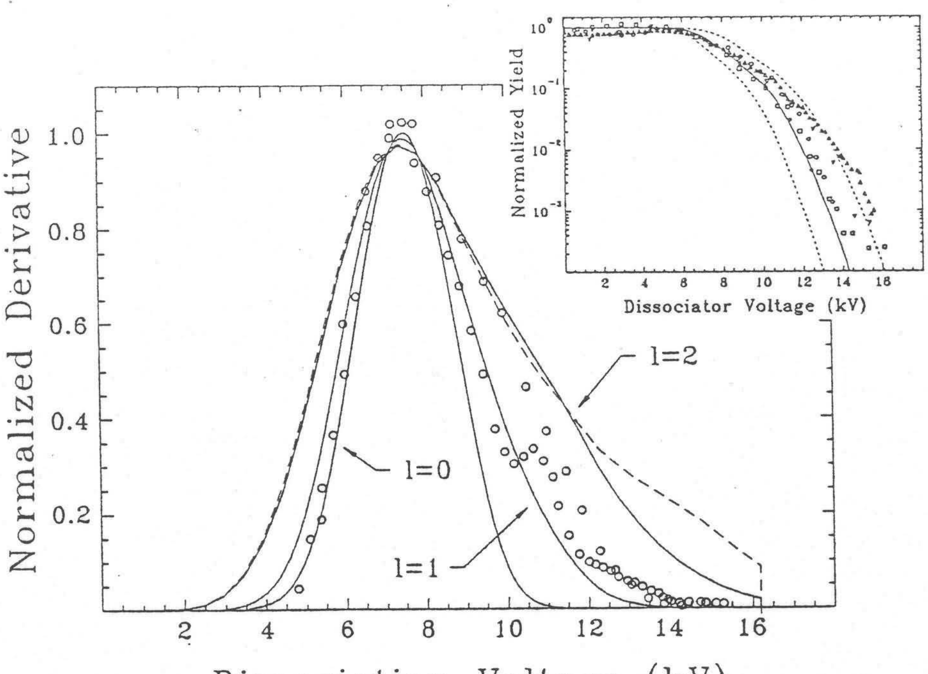

Fig. 1. Dissociation of Ca^- in the field of the dissociator. The binding energy used for the calculations was 24.75 and 13 meV for the $l=0$ and $l=2$ states and $E_b1/2 = 21.5$ meV and $E_{b3/2} = 20.75$ meV for the $l=1$ states. The solid curve of the $l=2$ states represents the $^2D_{3/2}$ state and the dashed curve the $^2D_{5/2}$ state. The insert shows the yield of Ca^- vs. dissociator voltage. The solid curve is the theoretical prediction for $E_{b1/2} = E_{b3/2} = 21.0$ meV. The dashed curves are the estimates for 19.0 and 23.0 meV. The symbols represent different experiments.

4. Results

Three negative ions have been successfully studied with the dissociator, Ca^-, Tm^- and Dy^-. In the latter case, Dy^-, it was also possible to monitor the destruction of the negative ions in the electric field of the accelerator.

4.1. Calcium

Even though the existence of calcium negative ions has been established for more than 20 years [7], the actual stability, as opposed to metastability, of the negative ions of atoms with closed subshells such as Ca, Sr, Ba, and Ra has long been questioned. Theoretical calculations using both density functional theory and multi-configuration Hartree–Fock theory have shown that the extra electron of the ground state should fill an np orbital instead of the expected $(n-1)$d orbital [8]. In measuring the electron affinity of calcium via electric dissociation [5], it was possible to verify this prediction. Unfortunately, the remaining members of group IIA have larger binding energies which proved beyond the capability of the present dissociator.

In the last few years, several publications have addressed the negative ion properties of calcium. Theoretical estimates of its electron affinity range from 0 to 89 meV; c.f. ref. [5] for a discussion of the different theoretical results. The theoretical work of Froese Fisher et al. [8], first to predict the stability of the $4s^24p\ ^2P$ states, estimated its binding energy to be 45 meV.

Two experimental results regarding Ca^- were published prior to our measurement, both involving laser photodetachment methods leading to two irreconcilable results. Pegg et al. [2] have observed $E_b = 43 \pm 7$ meV, while Walter and Peterson [9] obtained $E_b = 18 \pm 2.5$ meV. More recent work by McLaughlin and Duquette [10] using the interaction between laser excited calcium atoms in Rydberg 4snd states and ground state calcium atoms obtained a value of $E_b = 24 \pm 1.5$ meV.

Our results support the theoretical prediction of Froese Fischer et al. [8] that the extra electron occupies a p orbital with a binding energy of 21 ± 2.5 meV. The derivative of the Ca^- yield vs. the dissociation field also provides a measurement of the $J = 1/2$, $3/2$ spin-orbit splitting of the ^2P states. From the width of the distribution, we deduce that $-3.0 \leq \Delta_{so} \leq +3.0$ meV with the exclusion of the region $-0.4 \leq \Delta_{so} \leq +0.4$ meV with a most probable value at $+0.75$ meV leading to $E_b(1/2) = 21.5 \pm 2.5$ meV and $E_b(3/2) = 20.75 \pm 2.5$ meV [5,11]. The spin orbit splitting, Δ_{so}, is defined positive for $E_b(1/2) > E_b(3/2)$. The width of the derivative of the Ca^- yield vs. the dissociation field does not readily support the possibility that the extra electron occupies an s or a d orbital. Fig. 1 shows the derivative of the yield of $^{44}Ca^-$ vs. dissociator voltage.

It is still possible that the spin-orbit splitting, Δ_{so}, of Ca^- is much larger, ~ 9 meV. In that case, the first excited state, $^2P_{3/2}$, with a binding energy around 12 meV, would be destroyed by the electric fields of the ion source and the accelerator, leaving the $^2P_{1/2}$ state alone to be destroyed by the electric field of the dissociator. This is only a possibility, however, plans have been made to verify its likelihood.

Calcium metallic targets were used for most of the experiments. Targets made of CaF_2 mixed with other salts such as NaCl and KI and Nb metallic powder were also used. In both cases, it was impossible to predict whether the Ca^- current would be stable since it varied from target to target without apparent reason. Beams of Cl^- K^- and Ti^- were used as normalization beams.

4.2. Thulium

Very recently, Chevary and Vosko [12] predicted a bound state of Tm^- in the $[Xe]4f^{13}6s^26p$ state. Our results point in the same direction, the extra electron being bound in a p orbital by 32 ± 7 meV. Another state was observed with the same angular momentum, bound by 27 ± 7 meV. A study of the isoelectronic YbI shows that these could be the $J = 3$ and $J = 4$ states, respectively [13].

4.3. Dysprosium

The accelerator, which is normally operated at 2 MV, was set at 1.25 MV during the dissociator tests with Dy^- in order to maximize the counting rate. As can be appreciated from Fig. 2, a higher voltage would have reduced the ion yield considerably. Because of the tight constraints imposed on the ion optics by the dissociator, it was not possible to operate the ion source at a voltage lower than the 20 kV for which it has been designed. This caused the destruction of the first excited state of Dy which was observed later.

The measurements are consistent with the detachment of a $p_{1/2}$ electron with a binding energy of 15.5 ± 2.5 meV. By analogy with the isoelectronic HoI, we deduce that the ground state should be the $[Xe]4f^{10}6s^26p$ $J = 15/2$ state.

5. Dissociation in the accelerator field

For weakly bound negative ions, the electric field of the tandem accelerator (up to 1 MV/m over 2 m) could be used as a dissociating field. This requires extreme care since the high energy analyzers had to be

220

re-optimized for each data point since the energy of the ions was different. Several parameters had to be taken into consideration in order to make the experiment successful. The negative ion yield studied was compared to a few more strongly bound beams of similar mass and atomic number in order to minimize the differences in transmission through the accelerator. The targets had to deliver stable currents over several hours, this experiment being longer than other studies.

Three elements (Dy, Yb and Ca) were studied with this method and only in the case of dysprosium were the results entirely satisfactory. Dy and Yb were studied with the IsoTrace Tandetron while Ca was studied with the MP tandem at AECL Chalk River with the collaboration of Drs. H.R. Andrews and V. Koslowski.

5.1. Dysprosium

Dysprosium was an excellent candidate for such an experiment. Its electron affinity is such that it does not survive the electric field of the accelerator when operated at 2 MV. More strongly bound lanthanide elements (Gd, Tb and Lu) were used as pilot beams. Metallic targets of these elements also provided stable currents for several hours.

The accelerator tests were performed after the dissociator had been removed from the path of the ions and, free of this constraint, it was found possible to lower the ion source voltage to 7.5 kV. The accelerator voltage was varied from 0.6 to 2.0 MV, the maximum range for which the accelerator maintains the stability necessary for this experiment. The field of the accelerator is 2 m in length.

Due to a lower ion source voltage (7.5 kV instead of 20 keV), the electric dissociation of Dy vs. accelerator voltage shows the effect of two states. The excited state was destroyed in the field of the ion source in the experiment involving the dissociator.

The relatively large size of the experimental errors is due to the variations introduced by the optimization of the post-acceleration analyzers for each data point. Some variations are also caused by the erosion of the targets with time. This is usually not a problem, however in this case the delays due to the re-optimization of the system for each accelerator voltage are exceptionally long.

No ions were detected at a terminal voltage of 2 MV, defining upper limits for the binding energy of the ground state depending on the assumed angular momentum quantum numbers, l and m. $E_b = 15.5$, 15.2, 7.0 and 4.3 meV for $l = 0$, 1, 2 and 3, respectively.

A fit through the data suits the data points best for the detachment of two $6p_{1/2}$ electron states with $E_b = 15 \pm 3$ and 11 ± 4 meV. Fig. 2 also shows the best fits for $l = 0$, 2 and 3. The first criterion considered for the fits was that there should be no detectable yield at 2 MV. The second criterion was the closeness to the data points. As a result of the emission of $6p_{1/2}$ electrons only, each state of Dy^- corresponds to only one step in Fig. 2. The $6p_{3/2}$ states of Dy^- are expected to be much higher in excitation, as they are in HoI, and the size of the spin-orbit splitting supports the emission of only the $6p_{1/2}$ electron from the ground state.

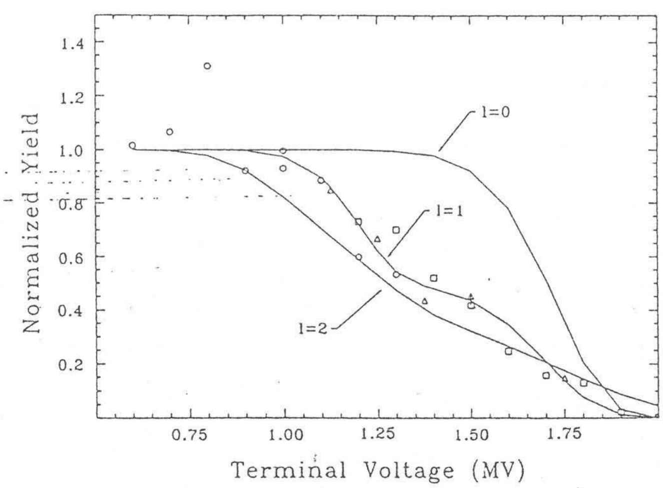

Fig. 2. Dissociation of Dy^- in the field of the accelerator. Comparison between the derivative of the dysprosium yield and theoretical prediction vs. dissociation potential for $l = 0$, 1, 2 states as indicated. The $l = 0$ an $l = 2$ states correspond to binding energies of 15.5 and 7.5 meV, respectively. The $l = 1$ curve was calculated for two states at 15 and 11 meV. The different symbols represent different sets of measurements obtained using different positive ion charge-states and system conditions.

The fact that both measurements on Dy^- resulted in very similar conclusions is also a test for the theory of electric dissociation itself. The fact that the results are the same for different electric field intensities proves that the asymptotic approximation used in the derivation of the theory does not limit its application and that its effects are much smaller than the experimental error.

5.2. Ytterbium

Due to its extreme fragility, ytterbium negative ions were difficult to observe even at the lowest voltage the system could function at. The ion source voltage was lowered to 10 kV and the accelerator was operated at 0.75 MV. It was not possible to bring the terminal voltage lower mainly because of the difficulty involved in the detection of such low energy ions and because of their decreasing positive ion charge-changing cross-section in the accelerator. The terminal voltage at which the ions were detected points to an electron affinity of 10 ± 3 meV, the electron occupying a p orbital. The results are not consistent with other angular momentum quantum numbers; c.f. ref. [13] for further details.

Vosko et al. had already predicted in their theoretical study [14] that the extra electron of Yb^- would occupy a p orbital.

5.3. Calcium

The results for the dissociation of Ca^- in the field of an MP tandem did agree with the fact that Ca^- is destroyed at higher fields. However, the instability of the calcium targets in the powerful ion source was such that no more could be extracted from the data. The AMS system proved to be suitable for such an experiment providing a more stable target or a more stable ion source could be used.

6. Conclusions

Electric dissociation of negative ions has proven to be a successful technique both to probe the structure of negative ions and to destroy the more weakly bound negative ion of a pair of isobars, thus making the analysis of the remaining isobar possible. The possible analyses of ^{44}Ti or ^{48}Ti are the first examples of this type of study.

It is important to note that for the four weakly bound negative ions studied, the extra electron occupies a p orbital and all of them do not follow the electron filling sequence of the periodic table. Although it is hazardous to generalize, it is reasonable to assume that the heavier group IIA elements (Sr, Ba and Ra) have configurations similar to Ca^- in binding a p electron.

It is also worth noting that for the three elements which had been studied recently by density functional theory [8,12,14], these studies were correct in predicting the binding of an np electron to the element.

The present equipment could not dissociate the more strongly bound negative ions of the remaining lanthanide elements. However, from the results obtained on Tm^-, an apparatus designed to hold a higher electric field (up to 15 MV/m) should be able to destroy the negative ions of the remaining lanthanide elements with the exception of La, Ce and Pr, which seem to be more strongly bound [13].

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020