Observation of the $^2S_{1/2}$ metastable state in Pt^-

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We have experimentally investigated the structure of the Pt^- ion using laser photodetachment threshold spectroscopy. The experiment was conducted using a collinear laser-ion beam apparatus, in which the residual atoms created in the photodetachment process were detected. A *p*-wave threshold was observed in the photodetachment spectrum at an energy of 6851(13) cm^{-1}. We conclude that this onset originates from a photodetachment transition in which the initial state of Pt^- is the previously unobserved $5d^{10}6s\ ^2S_{1/2}$ state and the final state of Pt is the $5d^96s\ ^3D_3$ ground state. The excitation energy of the $^2S_{1/2}$ state is determined to be 10 289(13) cm^{-1}. This value can be compared with a multiconfiguration Dirac-Fock calculation performed by Thøgersen *et al.* [Phys. Rev. Lett. **76**, 2870 (1996)], which yielded an excitation energy of 11 301 cm^{-1}. Our data show no indication of the presence of any other state of Pt^-. We conclude that the structure of the Pt^- ion is now fully known.

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INTRODUCTION

The structure of negative ions is intrinsically different from that of atoms or positive ions. This is due to the nature of the force that binds the outermost electron. The long-range Coulomb force characteristic of atoms and positive ions becomes a short-range polarization force in the case of negative ions. Typically, this potential supports only a few, if any, excited states, in contrast to the infinite spectrum of bound states associated with the long-range Coulomb potential. In most negative ions, the only bound excited states are those with the same electronic configuration as the ground state [1]. In a few cases, in particular among the transition metals and the lanthanides, bound excited states with an electron configuration that differs from the ground states have been observed [2]. With two exceptions, these excited states are of the same parity as the ground state and are hence metastable due to their inability to decay via an E1 process. Only in the cases of osmium [3] and cerium [4] have dipole-allowed transitions been observed.

One negative ion that has attracted a lot of interest is Pt^-. Figure 1 is an energy-level diagram that shows previously observed and predicted bound states of Pt^- and the lowest states of Pt. Most experimental investigations of Pt^- have focused on determining the binding energy of the $5d^96s^2\ ^2D_{5/2}$ ground state, i.e., the electron affinity of Pt. All these experiments involved a measurement of the threshold energy for photodetachment of an electron from the ground-state ion. The earliest experiment was that of Hotop and Lineberger [5], who determined an electron affinity of 17 163(16) cm^{-1}. Subsequent experiments by Gibson *et al.* [6], Thøgersen *et al.* [7], and Bilodeau *et al.* [8] yielding values of 17 125(9) cm^{-1}, 17 141(6) cm^{-1}, and 17 140.1(4) cm^{-1}, respectively. The result of Bilodeau *et al.* is now the value recommended by Andersen, Haugen, and Hotop [1].

The excitation energy of the $5d^96s^2\ ^2D_{3/2}$ state was estimated by Zollweg [9] to be 9760 cm^{-1} using an isoelectronic extrapolation. Later, a multiconfiguration Dirac-Fock (MCDF) calculation by Thøgersen *et al.* [10] yielded an energy of 9535 cm^{-1}. The excitation energy was measured by the same group to be 9740.9(5) cm^{-1} using laser radiation to drive an M1 transition between the $^2D_{5/2}$ ground state and the $^2D_{3/2}$ excited state [10].

In the present paper we report on a search for the $5d^{10}6s\ ^2S_{1/2}$ metastable state in the Pt^- ion. Zollweg [9] predicted the stability of this state, with an estimated excitation energy of 12 847 cm^{-1}. The MCDF calculation by Thøgersen *et al.* [10] yielded a value of 11 301 cm^{-1}. Prior to the present experiment there was no experimental evidence of the existence of this state.

EXPERIMENTAL PROCEDURE

The technique of laser photodetachment threshold spectroscopy [11] has been used in the present search for metastable states of Pt^-. The apparatus, which will be described in detail in a subsequent paper [12], is shown in Fig. 2. The Pt^- ions are produced in a caesium sputter ion source using a piece of solid platinum mounted in an aluminum cathode. The ions extracted from the ion source are accelerated to 6 keV, focused to form a beam, mass selected in a 90° sector magnet, and then guided by several electrostatic elements into the interaction chamber. The ion beam is bent by an electrostatic quadrupole deflector into the interaction region, and measured in a Faraday cup situated at the end of the ion beam path. Ion beam currents were typically 1–3 nA. The solid line in Fig. 3 shows a mass spectrum of ions recorded with this cup. The range of the scan is 191–200 u The mass resolution $M/\Delta M$ of the apparatus is approximately 350. We chose to perform the experiment on the ^{194}Pt isotope since this mass is least likely to be contaminated by molecular interferences, as will be discussed later.

Most of the ions emerging from the source were in the ground state but a small fraction, depending on source con-

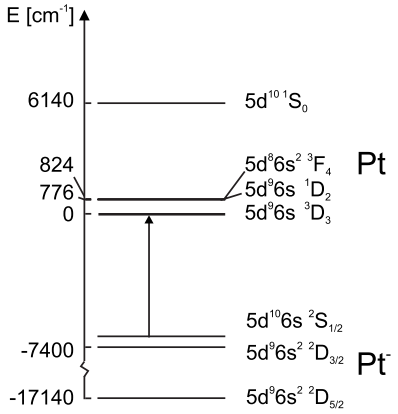

FIG. 1. Energy-level diagram showing the observed and predicted bound states of the Pt^- ion and the lowest-energy states of the Pt atom. The vertical arrow indicates the photodetachment transition studied in the present experiment.

ditions, was produced in metastable states. This fraction remained effectively constant during the collection of a data set. The $5d^{10}6s\ ^2S_{1/2}$ state decays primarily by an E2 process and has an estimated lifetime in the millisecond range. As a consequence, metastable ions emerging from the ion source travel to the region where they interact with photons from the laser with essentially no radiative decay occurring in flight.

In the interaction region the ion beam is merged collinearly along a field-free 60-cm-long path with a pulsed beam of infrared radiation generated by a tunable laser system. The laser system consists of a 10 Hz Nd:YAG laser pumping an optical parametric oscillator followed by an optical parametric amplifier. This system produces 6-ns-long pulses with typical pulse energies ranging between 5 and 12 mJ. For normalization purposes the laser light is measured by a laser energy meter after passing through the interaction region. Here the energy ranged between 0.5 and 1.2 mJ.

The signal in the present experiment consists of neutral Pt atoms produced by photodetachment in the interaction region. In the neutral atom detector, secondary electrons, arising from the impact of the residual atoms on a glass plate, are counted by a channel electron multiplier (CEM). The transparent glass plate is coated with a conducting layer to prevent the plate from charging up. The detector has been described in detail in an earlier publication [13]. The detection system was gated to coincide with the arrival of the residual atoms after they have traveled from the interaction region. The gate width was 6 μs, a duration determined by the range of transit times of the atoms from the interaction region to the detector. A second detection gate of the same length was opened at a time between the laser pulses when no photon-induced signal was present. This gate measured the background arising from ions detached by collisions with the residual gas. The difference in yields of neutrals from the two gates represented the photodetachment signal. The count rate was carefully controlled to avoid saturation of the neutral particle detector.

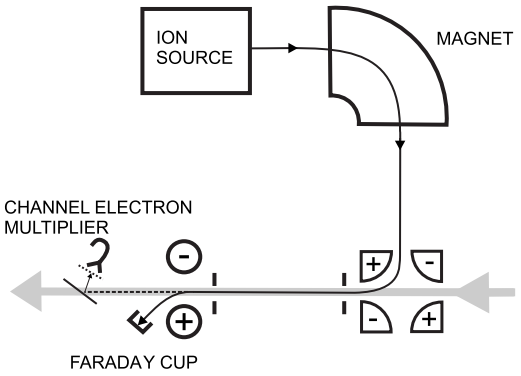

FIG. 2. Schematic drawing of the collinear laser and ion beam apparatus used in the experiment. The solid black line represents the ion beam trajectory, the dotted line represents the path of the neutral fragments, the small solid arrow represents secondary electrons, and the gray arrow indicates the path of the laser light.

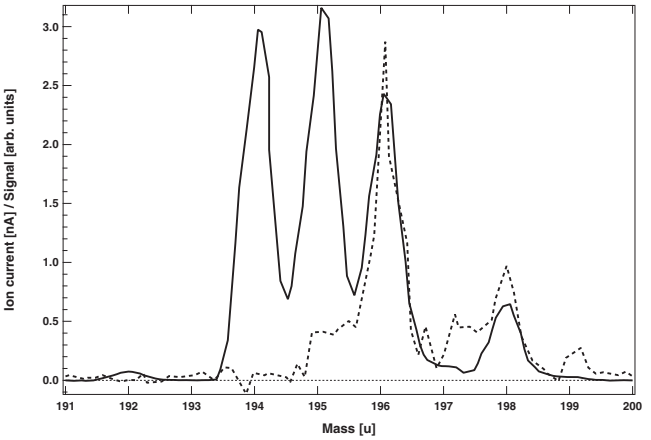

FIG. 3. The solid line represents the ion beam current as measured in a Faraday cup at the end of the ion beam path. The dashed line shows the number of detected neutral atoms that have been produced via the photodetachment process at 6400 cm^{-1}.

RESULTS

Figure 4 shows the result of a study of the photodetachment spectrum made over a range of photon energies 6400–7500 cm^{-1}. The spectrum shows a zero cross section below 6851 cm^{-1}, after which a gradual increase in the cross section can be seen. This is the typical behavior for the opening of a new photodetachment channel. Wigner [14] described the near threshold cross section for the breakup of a system bound by a short-range potential. An operational form of the Wigner law can be expressed as

$$\sigma = a + c(\varepsilon - \varepsilon_0)^{l+1/2} \quad \text{for } \varepsilon \geqslant \varepsilon_0,$$

$$\sigma = a \quad \text{for } \varepsilon \leqslant \varepsilon_0. \tag{1}$$

In this formula ε is the photon energy, ε_0 is the threshold energy, and l is the angular momentum of the detached electron. The quantity c is the fitting parameter that describes the strength of the photodetachment process, and a is a param-

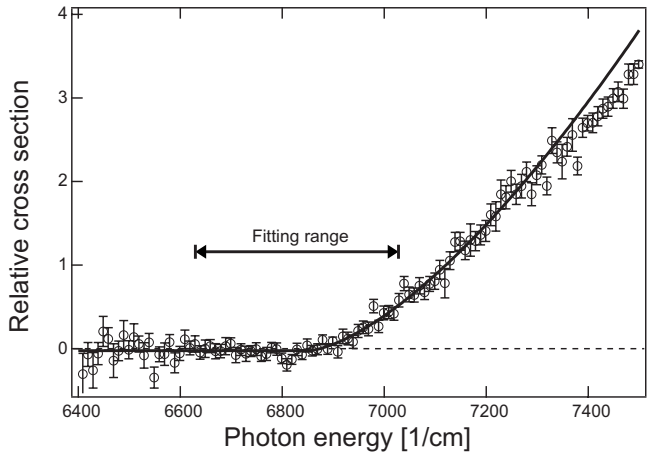

FIG. 4. The measured photodetachment cross section in the photon energy range 6400–7500 cm^{-1}. The solid line represents a fit of Eq. (1) using data points in the range 6640–7040 cm^{-1}. The fit range is indicated in the figure by the horizontal bar. This fit has been extrapolated to 7500 cm^{-1} in order to display the deviation of the data from the Wigner law as the photon energy increase above threshold.

eter that takes into account the possible presence of a constant background associated with a photodetachment channel that has opened at a lower photon energy. Initially, a, c, ε_o, and l were treated as free parameters when the above formula was fitted to the experimental data. This revealed a value of l close to 1.5. It was hence concluded that the observed threshold is caused by the opening of a channel leading to the emission of a p-wave electron. In the final fitting of the parameters, l was therefore fixed to the value of 1.5. The range of validity of the Wigner law is expected to be quite small. In order to fit the Wigner threshold law to the data we had to make sure we were within the range of validity of the law. Therefore, we decided to fit the data in the range 6640–7040 cm^{-1}, a range that extends to about 200 cm^{-1} above the measured threshold. The solid line in Fig. 4 represents a fit of the background and the Wigner law to the data over this range. The fit determined that parameter a, associated with a possible background, was zero within the statistical uncertainty. When this fit is extrapolated over the whole data range a deviation from the Wigner law can be seen to occur around 7300 cm^{-1}. Thus it appears that the range of validity of the Wigner law in this case is approximately 450 cm^{-1}. This value is comparable to the value of about 400 cm^{-1} observed by Hotop and Lineberger [5] in the case of detachment from the ground state of Pt^- to the ground state of Pt.

Fits to several data sets yielded a mean threshold value of 6852.4(11.9) cm^{-1}. A small correction to the fitted value was made to account for the Doppler shift associated with the moving ions in the beam. This was determined to be -1.8 cm^{-1} in the present case, yielding a final Doppler-corrected threshold value of 6851(13) cm^{-1}. The quoted uncertainty in the threshold is essentially the standard deviation of the mean value obtained by fitting the Wigner law to a series of 11 data sets. The fitting error was the dominant source of uncertainty in the measurement. Other sources of error, negligible in comparison, include the finite laser bandwidth (0.2 cm^{-1}), the uncertainty in the calibration of the wavelength meter used to read the wavelength of each laser pulse (0.01 cm^{-1}), and the error in the Doppler shift correction caused by uncertainties in the speed of the ions and the overlap angle (less than 0.05 cm^{-1}).

DISCUSSION

Pt^- is efficiently produced in a sputter source using a piece of solid platinum mounted in an aluminum cathode. The output of the source yields a mass spectrum in which the isotopes of atomic Pt^- are the dominating mass peaks. In the current experiment, however, special care was taken to exclude the possibility that we were observing a photodetachment signal from contaminant ions in the beam. The importance of excluding contaminants is twofold. First, a metastable state is under investigation and one can expect a population of only a few percent of that of the ground state. Second, photodetachment cross sections involving p-wave detachment are very small just above threshold. An interfering molecular negative ion could have an electron affinity that is substantially smaller than the photon energy used in this experiment. In this case the photon energy would be far above threshold, giving rise to a cross section that could be orders of magnitude larger than the cross section of the excited Pt^- ion near its threshold. Considering these two effects, we are led to conclude that contaminants in the beam, even with abundances as small as 10^{-4} times that of Pt^- could give rise to signals of comparable strength to that arising from the photodetachment of excited Pt^-.

To investigate potential contamination problems the experiment began with a careful analysis of the mass spectra of the ions exiting the ion source. In this work it was essential to have sufficient mass resolution to clearly separate the different masses in the range of interest. The solid line in Fig. 3 shows the ion current measured with a Faraday cup placed at the end of the interaction region. The relative heights of the peaks correspond to the natural abundances of the Pt isotopes. Hence, we can conclude that the mass peaks in the range shown in Fig. 3 arise predominantly from the production of Pt^- ions. As an additional test we measured the photodetachment signal at 6400 cm^{-1} as a function of the mass of the ions. This scan is represented by the dashed line in Fig. 3. From this data we can draw the conclusion that the signal produced by photodetachment does not originate from Pt^-, since one would then expect a contribution at the mass 194 u. The signal instead shows larger peaks at mass 196 and 198 u and minor peaks at mass 195, 197, and 199 u. This mass spectrum can be explained by the presence of a combination of PtH^- and $CuCs^-$ contaminant ions. It is a well known fact that sputter sources produce hydrides of most elements. Contaminants from Cu and Cs can be expected since copper has previously been extensively used as the cathode material in this source and caesium ions are used for sputtering. In a final test a full mass spectrum from zero to 200 u was acquired. No elements were observed that could form a molecular ion with the mass 194 u. Our conclusion is that the only contributor to the peak at mass 194 u is the

$^{194}Pt^-$ ion. As a result this isotope was chosen in the photodetachment threshold measurements presented in this paper.

In the following section we will discuss in more detail the origin of the onset that was observed at 6851 cm^{-1}. The *p*-wave shape of the photodetachment cross section close to the threshold indicates that either an *s* or a *d* electron is ejected in the detachment process. As described in the Introduction, previous theoretical work has shown that there are three bound states in Pt^- [9,10]. The observed onset cannot be caused by photodetachment from the $5d^96s^2\ ^2D_{5/2}$ ground state or the $5d^96s^2\ ^2D_{3/2}$ excited state since the photon energy used in this experiment is too small to detach these states. Based on the calculations, the initial state for the observed onset must be the $5d^{10}6s\ ^2S_{1/2}$ state. Thøgersen *et al.* [10] predict that this state lies about 1800 cm^{-1} above the $5d^96s^2\ ^2D_{3/2}$ state.

The theoretical predicted states are the even parity $5d^96s^2\ ^2D_{5/2}$, $5d^96s^2\ ^2D_{3/2}$, and $5d^{10}6s\ ^2S_{1/2}$ states. In the isoelectronic Au atom, however, there are more even parity bound states. The three aforementioned states are the lowest lying states although their relative ordering is changed. The next higher energy state is the $5d^{10}7s\ ^2S_{1/2}$ state, which lies 54 485 cm^{-1} above the $5d^{10}6s\ ^2S_{1/2}$ state. This high level of excitation is associated with a change in the principle quantum number. In the case of Pt^- the $5d^{10}7s\ ^2S_{1/2}$ state appears to be sufficiently highly excited with respect to the $5d^{10}6s\ ^2S_{1/2}$ state to be no longer bound. This conclusion is strongly supported by the MCDF calculation and the fact that no photodetachment signal was observed beneath 6851 cm^{-1}. We conclude that the only possible candidate for the initial state in the photodetachment process is the $5d^{10}6s\ ^2S_{1/2}$ state.

In the photon energy range of the experiment, there are five allowed channels by which a Pt^- ion in the $^2S_{1/2}$ state could be photodetached. The five different final states, shown in the energy-level diagram in Fig. 1, all have an even parity. Photodetachment from the $5d^{10}6s\ ^2S_{1/2}$ state, which also has even parity, would in all five cases lead to *p*-wave detachment. Furthermore, in all five cases detachment is allowed according to the angular momentum selection rules. The final states also have similar electron configurations being various combinations of 5*d* and 6*s* orbitals. One therefore expects five *p*-wave detachment cross sections, each with its characteristic threshold energy. It also seems plausible that the cross sections for the five channels should not differ by orders of magnitude since the final states have similar electronic configurations. Our experimental data clearly demonstrate that the cross section below 6851 cm^{-1} is zero. From this evidence we are led to conclude that the onset observed in the present experiment is the lowest lying threshold of the five channels and arises from the process that leaves the residual Pt atom in its ground state. The photodetachment transition that we have observed is therefore

$$5d^{10}6s\ ^2S_{1/2} + h\nu \rightarrow 5d^96s\ ^3D_3 + \varepsilon p. \quad (2)$$

The difference between the binding energy of the ground state of 17 140.1(4) cm^{-1} and the observed photodetachment threshold energy of 6851(13) cm^{-1} yields an excitation energy for the $5d^{10}6s\ S_{1/2}$ state of 10 289(13) cm^{-1}. This measured excitation energy is about 1000 cm^{-1} lower than the prediction of the MCDF calculation by Thøgersen *et al.* [10]. In the case of the $5d^96s^2\ ^2D_{3/2}$ state the observed excitation energy is 205 cm^{-1} above the calculated value. One should note that the $5d^96s^2\ ^2D_{3/2}$ state is a member of a fine structure doublet that includes the ground state and therefore has the same electronic configuration as this state. The $5d^{10}6s\ ^2S_{1/2}$ state, on the other hand, has a different electron configuration than the ground state. In this case one might expect that the calculation would be more difficult. This could explain the larger discrepancy between the measured value and the calculated one.

The $^2D_{3/2}$-$^3D_3$ channel opens at 7400 cm^{-1}, but no evidence of this opening was observed in the present experiment. To gain more insight into the expected total cross-section shape, a simulation was made by adding two cross sections exhibiting *p*-wave threshold behavior. The separation of the thresholds was set to 548 cm^{-1}, the difference in energy between the $^2S_{1/2}$ and $^2D_{3/2}$ states. This simulation showed that even with a population ratio of 1:3 it would be very difficult to observe the opening of the $^2D_{3/2}$-$^3D_3$ channel in the presence of the $^2S_{1/2}$-$^3D_3$ channel at the level of statistics that we were able to attain. In addition, at 7400 cm^{-1} the situation becomes more complicated since the $^2S_{1/2}$-$^3D_3$ channel has already started to deviate from its *p*-wave behavior.

In summary we have observed the photodetachment cross section for the $^2S_{1/2}$-$^3D_3$ channel. The present measurement yields a threshold energy of 6851(13) cm^{-1}. Using this value and the measured electron affinity of Pt of 17 140.1(4) cm^{-1} [7] yields an excitation energy of a metastable state in Pt^- to be 10 289(13) cm^{-1}. We propose that this is the previously unobserved $5d^{10}6s\ ^2S_{1/2}$ state. The experiment showed no evidence for the presence of any other metastable states. We therefore conclude that the structure of the Pt^- ion is now fully known.

ACKNOWLEDGMENT

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