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Photodetachment spectroscopy of stored H^- ions

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Abstract. Threshold photodetachment of negative hydrogen ions stored in a Penning trap has been studied. The electron affinity of hydrogen is determined to 6082.8(7) cm^{-1} in good agreement with previous experiments. The Wigner law has been found to be valid in a region of 400 cm^{-1} above the threshold.

1. Introduction

Most chemical elements form stable negative ions which play an important role in the quantitative understanding of electron–electron correlations [1]. The H^- ion is the most fundamental among these.

The three-body system is isoelectronic with the He atom but has only one bound state. In the 1950s the first theoretical interest arose from the understanding that the photoeffect in H^- ions is the most important cause of opacity in the atmosphere of the sun and of stars in the wavelength region of $\lambda = 0.6$–1.6 μm [2]. The electron affinity (EA) of the hydrogen atom or, alternatively, the binding energy of the H^- ion can be determined from *ab initio* calculations with high accuracy. Pekeris [3] obtained a value of $\mathrm{EA} := E(\mathrm{H}^-) - E(\mathrm{H}_{F=0}) = 6083.06(1)$ cm^{-1} by performing extended Hylleraas-type variational calculations, Drake [4] confirmed these results including radiative corrections in 1988.

The most direct method of measuring binding energies of a negative ion A^- is to determine the threshold of the photodetachment process

$$\mathrm{A}^- + h\nu \rightarrow \mathrm{A} + \mathrm{e}^-. \tag{1}$$

Wigner [5] derived the photodetachment cross section σ for small kinetic energies of the departing electron:

$$\sigma \sim \Delta E^{l+1/2} \tag{2}$$

where l is the orbital angular momentum of the free electron in the centre-of-mass frame of the negative ion, $\Delta E = h\nu - \mathrm{EA}$ is the energy above threshold. In the case of H^- an s-electron is detached into an outgoing p-wave electron ($l = 1$) and thus

$$\sigma \sim \Delta E^{3/2}. \tag{3}$$

In 1991 Lykke *et al* [6] measured the EA of the H^- ion using collinear laser spectroscopy of an ion beam. They merged 2.5 keV H^- ions with the laser beam along a 30 cm interaction region. The measured EA value of 6082.99(15) cm^{-1} was a 20-fold improvement over previous experiments, but the accuracy of theoretical predictions from the early 1960s has not beaten been by experiment yet.

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The main experimental difficulty arises from the fact that at the p-wave photodetachment threshold, both the cross section and its slope are zero and therefore one has to measure very small effects. For example, at $\Delta E = 0.01$ cm^{-1} above the threshold one obtains a photodetachment cross section of the order of 10^{-24} cm^2 [7].

An alternative to measurements on an ion beam is to store the ions in an ion trap in order to increase the interaction time between ions and the detaching laser radiation. Various atomic and molecular negative ions, most of them showing s-wave photodetachment, have been investigated in a Penning trap [1]. Such experiments can also provide new information about photodetachment in the presence of a strong static magnetic field (see the discussion later in this paper).

In this paper, we report about experimental steps we have taken to overcome difficulties connected with the measurement of the EA of the hydrogen atom in a Penning trap and present initial results. Because of the large experimental effort necessary to load a Penning trap from an external ion source [8] or to produce the ions via electron exchange near Cs monolayers [9], respectively, we decided to produce the ions directly inside the trap volume by resonant dissociative attachment from NH_3. A new experimental difficulty, however, is due to the unfavourable ratio of H^- production to H^- destruction.

In a first series of experiments we have obtained a value of 6082.8(7) cm^{-1} for the electron affinity of hydrogen, which is in good agreement with the experiment by Lykke *et al* [6].

2. Experimental set-up

To determine the electron affinity of hydrogen we measure the spectral shape of the relative H^- photodetachment cross section and extrapolate it to the threshold according to the Wigner law (3). The experimental set-up shown in figure 1 consists of two main parts, the ion container and a tunable radiation source.

H^- ions are stored in a permanent magnet Penning trap described in detail by Gomer *et al* [10]. The magnetic field of 0.7 T, with a homogeneity of better than 10^{-2} in a volume of 1 cm^3, is produced by NdFeB magnetic rings. The electrical quadrupole field is generated by a cylindrical ring electrode of 3 mm radius and two flat end caps. One of the caps has a central bore, the other one consists of a copper net in order to be penetrable by electrons and ions, respectively. A trapping voltage of typically 2 V is used. The trap and the permanent magnets are cooled to 77 K to achieve a background pressure of 10^{-9} T.

The negative ions are created by resonant dissociative attachment of slow electrons on NH_3. A leak valve is used to regulate the ammonia pressure in the vacuum system to 1.5×10^{-7} T. The pressure values are readings from a Bayard–Alpert gauge without any corrections. An electron beam of some 100 nA with a kinetic energy of about 5 eV is sent into the trap volume generating H^- and NH_2^- with approximately equal cross sections of 1.4×10^{-18} cm^2 [11]. H_2O shows the 5-fold cross section for this process [11], but is difficult to pump out of the vacuum chamber.

The main difference in H^- storage compared to that of other negative ions investigated in Penning traps is that the electron energy required for the attachment is large compared to the binding energy of the generated ion. For example, S^- ions are produced by 1.4 eV electrons [12]. This energy is less than the binding energy of the ions (2 eV) and therefore S^- production is not limited by electron detachment. In the case of H^-, the kinetic energy of the attaching electrons is far above the detachment threshold. The cross section for electron detachment of H^- is three orders of magnitude larger than for resonant attachment [13].

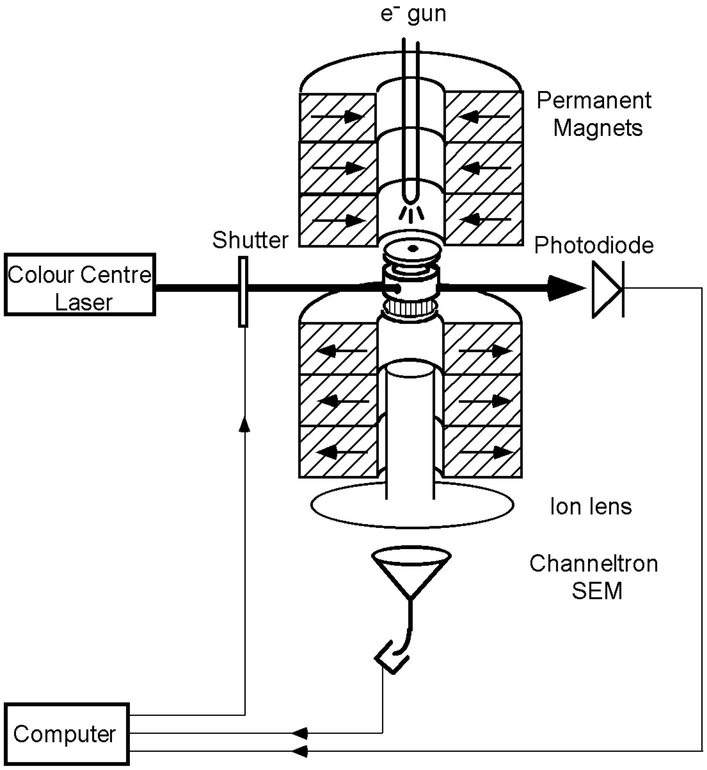

Figure 1. Experimental set-up. The vacuum system is filled with ammonia up to a pressure of 1.5×10^{-7} T. An electron source above the trap allows injected electron currents of a few 100 nA into the trap volume.

For that reason the equilibrium number of stored negative hydrogen ions saturates with increasing electron current. For high electron flux the number of ions is proportional to the ammonia pressure. Figure 2 shows the number of trapped H^- ions versus the kinetic energy of the electrons. The creation time is 500 ms. The maximum in the attachment at about 5 eV is in good agreement with values given in the literature [11]. The storage time of H^- ions at a pressure of 10^{-7} T is about 1 s.

For detection the stored ions were mass selectively extracted from the trap by applying an RF voltage resonant with the axial motion of the ions. An additional DC voltage applied to one cap electrode ensured that most of the ions escaped from the trap in only one direction. The extracted ions are accelerated by the field of an ion lens and detected by a channeltron SEM. The typical number of detected H^- ions is about 100.

The light is generated by a CW NaCl:F_2^+-colour centre laser pumped by a 6 W commercial Nd:YAG laser with 6 W output power. An argon ion laser (200 mW at $\lambda = 468$ nm) serves as an auxiliary light source reorientating the colour centres. The ring laser is tunable from $\nu = 6060$ to 6500 cm^{-1} with a single-mode output power of 50 mW.

The wavelength is determined by a travelling Michelson wavemeter. The wavemeter accuracy was tested by performing absorption spectroscopy on the methane $2\nu_3$ overtone transition, and was found to be better than 0.02 cm^{-1}.

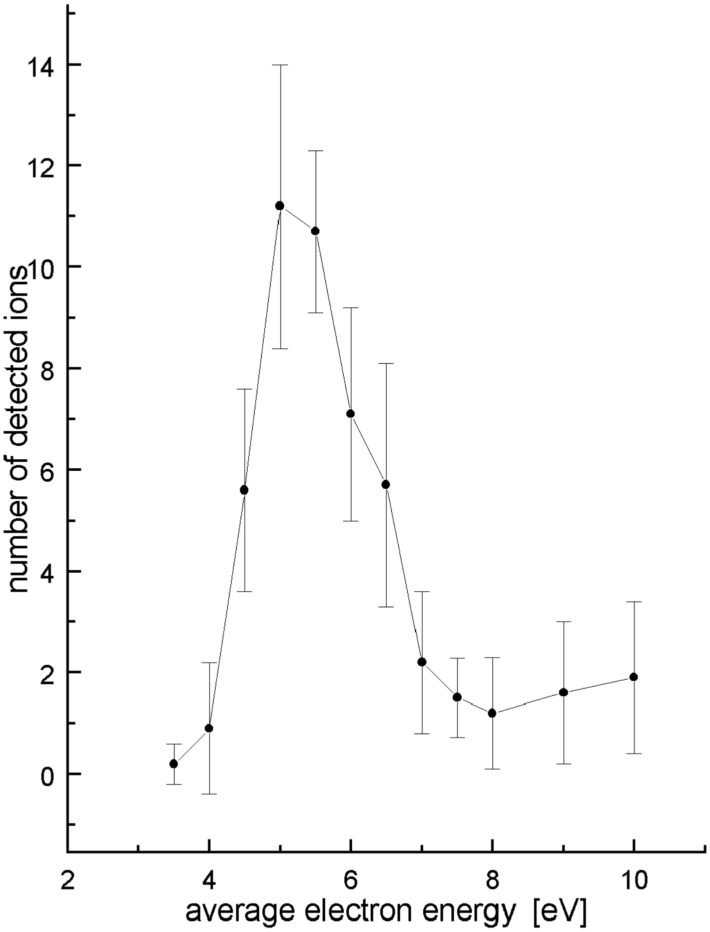

Figure 2. Resonant electron attachment on NH_3. Shown is the number of stored H^- ions versus the kinetic energy of the electrons $E_{\mathrm{kin}} = e(U + \Delta U_{\mathrm{Fil}}/2 + U_{\mathrm{trap}}/2)$ in the centre of the trap, where U is the electron acceleration voltage, U_{Fil} is the voltage across the glow cathode and U_{trap} the trapping voltage. The spread of the energy distribution is $eU_{\mathrm{Fil}} = 2$ eV. The absolute number of ions is a factor of 10 larger. The line joining the points is only to guide the eye.

The laser beam is focused into the trap by an $f = 200$ mm lens through a 1 mm diameter bore in the ring electrode. In order to determine the photodetachment cross section, one has to relate the number of ions destroyed by the radiation to the number of photons interacting with the ion cloud. Therefore the transmitted power is detected by a germanium photodiode and integrated by a resetable analogue integrator. A shutter allows us to control the irradiation time.

After loading the trap, the ions are irradiated with laser light for 500 ms. After that the ions are driven out of the trap and counted. In order to distinguish the destruction by the radiation from other loss mechanisms the identical process is performed alternately with the shutter opened and closed. This measurement cycle is repeated a few hundred times for each wavelength, resulting in three averaged values: the number of ions N and N', which survived the measurement time with and without laser irradiation, respectively, and the time integrated light power W.

By using the equation

$$N' = N \exp[-\alpha\sigma(\nu)W] \tag{4}$$

for additional ion losses due to photodetachment, the value for $\alpha\sigma(\nu)$ is extracted from the data. The coefficient α describes the geometrical overlap of the laser mode with the ion cloud and is constant because the periods of ion motion are short compared to the measurement time. The error is dominated by the fluctuations of the number N of detected ions due to statistical fluctuations in the creation process and the detection efficiency. The ion number distribution was measured to be Poissonian. Therefore these fluctuations do not affect the result systematically.

3. Analysis and discussion

Figure 3 shows the experimental results for the light polarization parallel to the magnetic field of the trap (π-polarization). The inset graph in figure 3 shows that the Wigner law describes the photodetachment process well for frequencies up to 400 cm^{-1} above threshold. The data points were a least-squares fit to the one-threshold Wigner function $\sigma(\nu) = A(\nu - \nu_{\text{thr}})^{3/2}$, where the scaling factor A and the threshold frequency ν_{thr} are the only fit parameters.

For interpretation of the data two effects have to be taken into account.

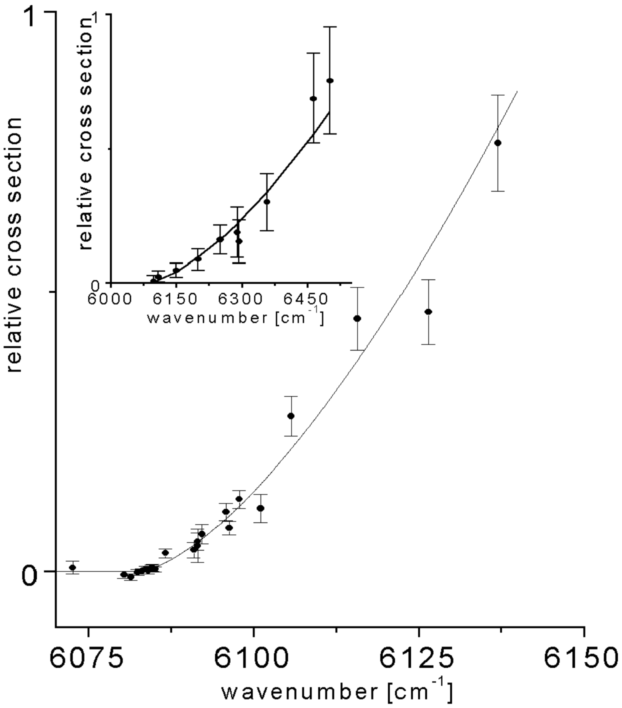

Figure 3. The measured relative photodetachment cross section with π-polarized light. The full curve is a least-squares fit to the one-threshold Wigner law. From this data the threshold frequency of 6082.8(6) cm^{-1} was determined. Inset, a rough measurement shows that the Wigner law describes the photodetachment process well for frequencies up to 400 cm^{-1} above threshold.

First, the Doppler effect due to the velocity distribution of the ions modifies the Wigner law and tends to shift the photodetachment threshold to values below the electron affinity. The effective cross section $\bar{\sigma}(\nu)$ is determined by

$$\begin{aligned} \bar{\sigma}(\nu) &= \frac{1}{\pi v_0^2}\int_0^{2\pi} \mathrm{d}\theta \int_0^{\infty} \sigma\left(\nu\left(1-\frac{v}{c}\cos(\theta)\right)\right)\rho(v)\,\mathrm{d}v \\ \rho(v) &= v\exp\left(-\frac{v^2}{v_0^2}\right) \\ v_0 &= \sqrt{2k_\mathrm{B}T/M_\mathrm{H}} \end{aligned} \tag{5}$$

where M_H denotes the mass of the ions, v_0 is the mean velocity and k_B is the Boltzmann constant.

In our case, numerical integrations of equation (5) show that even for a thermal energy of $k_\mathrm{B}T = 1$ eV the additional uncertainty in determining the threshold frequency due to the Doppler effect is less than 0.1 cm^{-1}.

The second source of deviation from the Wigner law is the strong magnetical field. First of all, it causes a decoupling of the spins. The two hyperfine levels of the hydrogen atom ground state split into four sublevels according to the Breit–Rabi formula. The electric dipole photodetachment transition conserves the spin and one gets four threshold energies, which differ by less than 0.05 cm^{-1} and are beyond the experimental resolution.

Furthermore, the magnetic field modifies the density of the final states of the detached electron and one expects polarization-dependent deviations from the Wigner law [14–16]. These effects have been observed experimentally on S^- ions stored in a Penning trap by Blumberg *et al* [12]. In the case of light H^- ions with a temperature far above room temperature the Landau resonances in the photodetachment cross section are easily washed out due to Doppler and motional Stark effect [12, 17]. Even in the case of σ-polarization, in which the effect is expected to be much stronger than for π-polarization, no such deviation from the Wigner law was observed in our experimental data.

The final result for the EA of hydrogen is 6082.8(7) cm^{-1}. The uncertainties due to the Doppler effect and magnetic substructure have been estimated to be negligible. This value is in good agreement with the value of 6082.99(15) cm^{-1} measured by Lykke and is consistent with the *ab initio* calculations performed by Drake [4] and Pekeris [3].

In order to improve the experimental resolution, plans are under way to apply a quadrupolar excitation to axialize the ions and enlarge the geometrical interaction factor α. This RF excitation allows us to work at higher ammonia pressures and therefore increase the number of stored H^- ions. Secondly, the temperature of the ions will be reduced. In addition, the laser power in the trap centre will be increased by incorporating a build-up resonator. Extrapolating the results given in this work to an experiment with two orders of magnitude more ions with a temperature of 200 K and an increase in available laser power by a factor of 50 leads to an accuracy of 0.01 cm^{-1}.

With these parameters it will be possible to resolve the hyperfine splitting and Landau resonance structure in the H^- photodetachment cross section in a magnetic field and to test the corresponding theory. Furthermore, the experimental value of the EA of hydrogen will be improved to test the *ab initio* calculations.

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