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Highly excited Rydberg states of hydrogen from a high-temperature diffusion source

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Abstract. The methods used for formation and observation of HR (highly excited Rydberg) states of alkali are here adopted for the study of hydrogen HR states. Electronically highly excited states are formed in a hydrogen-filled diffusion source with a graphite foil as emitter at high temperature. The excited states are detected by electrostatic methods, mainly by their interaction with a well shielded collector. Excited negative hydrogen and/or alkali ions are formed at the first grid in the analysing device, and give emission of electrons at the collector. The flux from the source can be cut off instantaneously with a beam flag, which reveals time constants of the order of minutes in the signal. It is concluded that surface layers of excited states are formed on the electrode surfaces. A condensed phase of electronically excited so-called Rydberg matter was predicted by Manykin *et al* and reported by Åman *et al* and Svensson *et al*. Åman *et al* later reported on non-alkali Rydberg matter. A similar type of matter appears to be found in the present study.

1. Introduction

We have recently reported on the observations of excited negative Cs ions [1-4], and on doubly excited states of Cs [4] and their chemical reactions [5]. We have also reported on condensed matter of Rydberg states, so-called Rydberg matter [6-9]. The lifetime for singly excited Rydberg states increases rapidly with the principal quantum number n , at least as n^3 [10, 11], and in the case of nearly circular orbits as n^5 . Doubly excited Rydberg states may have quite long radiative lifetimes due to strong correlation effects between the excited electrons.

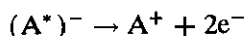
The simplest molecular systems where long-lived excited Rydberg states should be observed are the H_2 molecule and the H_2^- ion. It is known that doubly excited states of H_2 can be formed by electron impact excitation [12], and they have been studied by laser methods [13]. We have recently reported on Rydberg states of H_2 from a simple diffusion source [14]. In other excited state experiments, H_2^- is observed by mass spectrometry to be formed at a grid covered with a layer of excited states [15]. It is of great interest to investigate further whether excited states of hydrogen can be found in the desorbing flux from improved high-temperature diffusion sources, employing carbon foils as emitters. The detection of excited states is also of great interest for the combustion of solids such as coal and coke, as well as for astrochemistry.

In the present experiments, an excited state signal is detected with H_2 in the source. Part of the signal is probably due to excited negative ions $(H_2^*)^-$, but

a contribution due to negative ions of alkali metal from impurities in the source material also exists. The experimental results can be explained if both the first grid and the collector in the analysing device are covered by excited matter, of the type predicted by Manykin *et al* [16, 17] and recently observed experimentally in our group [6–9].

2. Excited states at surfaces

In recent experiments, it was shown that Rydberg states can be formed at high-temperature surfaces [1–9, 14, 15]. This effect is taken advantage of in the source used in the present study. A carbon foil is used as emitter here, but a fair amount of information also exists about the formation of Rydberg states at other surfaces. At present, however, little is known about the behaviour of Rydberg states during *impact* on surfaces at or below room temperature. Examples of experiments with impact of Rydberg states against surfaces are grid transmission experiments [18–22]. There also exists one study in which ionization of K^* at a gold surface is observed [23], and in another study condensation of excited states on 80 K surfaces is reported [8]. A few studies are also published which conclude that excited negative ions, e.g. $(Cs^*)^-$, interact with surfaces in Auger-like processes which may give emission of two electrons from the excited ion [3, 4]. The current measured to a surface on which such excited negative ions impact depends on the electric field outside the surface. When the field is retarding for electrons, a negative current is measured to the surface, but with an accelerating field the following process takes place:



and the electrons can be emitted from the surface, giving a positive net current to the collector.

3. Experimental details

For the experiments, a vacuum chamber with a base pressure of 1×10^{-6} mbar is used. The apparatus is shown in schematic form in figure 1. The hot emitter part of the source is made from carbon foil (Goodfellows, Cambridge, UK) with a thickness of 0.125 mm. The foil is held between high-purity graphite rings in a quartz tube as shown in the inset in figure 1. It is heated to a temperature of approximately 1100 K by a low voltage AC current through the separately heated coil of Ta wire wound around the quartz tube, and by the outer cylindrical resistive heater of Ta foil. The other high-temperature parts in contact with hydrogen are made from quartz. Hydrogen was admitted to the source through a needle valve at a pressure up to 30 mbar, measured with a capacitive manometer. The gas is fed into the source through a central tube and is pumped out from the source with a forevacuum pump. In this way, the gas in the source is of constant composition. The graphite emitters had to be replaced after approximately 50 h when they were destroyed, probably by reaction with hydrogen. The flux from the source was analysed with an electrostatic device used in the previous experiments on Cs, consisting of two plane grids held at

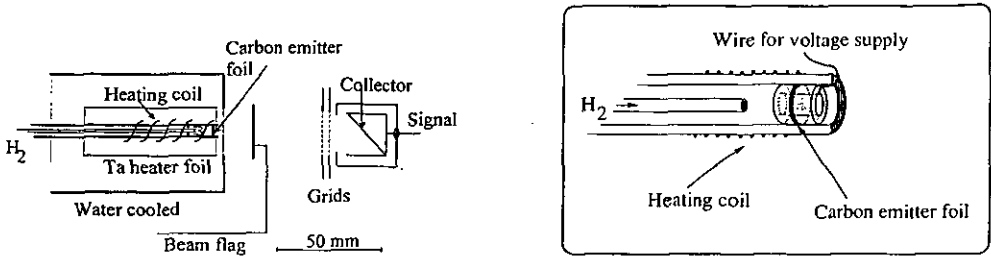


Figure 1. Schematic of the apparatus. The lower part shows the carbon foil and its graphite holders in the central quartz tube. The Ta foil cylinder and the heating coil are heated by separate AC current supplies.

various potentials (U_1 and U_2) up to 400 V and a well shielded and guarded Faraday cage-type collector.

The experiments are done with the first grid negative and the second grid positive, or conversely, such that ions or electrons from the emitter will not be able to reach the collector. This design has been used successfully in several previous studies on Rydberg states.

4. Results

Most experiments have been performed as described above with hydrogen admission to the source. In some cases, however, the graphite parts were removed and no hydrogen gas was admitted. Only the excited alkali atom signal from the heaters is observed. An example is shown in the upper curve in figure 2, where a large positive signal from the source can be flagged. With the beam flag closed and the collector at -100 V, the current is 50 pA, while with the flag open it is approximately 600 pA. The behaviour in the lower curve in the same figure is measured shortly afterwards, but with the collector at $+100$ V. The signal has changed its polarity, and its absolute value is somewhat lower, about -400 pA. The small maxima in the signals after the flag opens are observed in both cases, and the two signals mirror each other almost identically, except for a factor of 1.5 in the signal level. The signal cannot be due to positive ions from the emitter, since the grid at 200 V blocks such ions. This type of behaviour, where the signal changes sign with the collector voltage, has been reported previously in experiments with alkali Rydberg states [3, 4]. The signal is interpreted as being due to excited negative alkali ions, which in the present case are formed at the first negative grid, as will be shown below (see also the discussion section).

With hydrogen in the source, somewhat different results are found, but they still show the effects of excited state formation in the source. The excited states may interact with the collector, and emit up to two electrons on impact. If on average only one of the electrons from each excited negative ion can leave the collector due to a blocking field outside the collector, no net signal change at flagging will be observed. An example of such behaviour is shown in figure 3 for the case of $U_c = 84$ V. The signal observed when the beam is flagged varies directly with the collector voltage, and at a relation $U_c/U_2 = 0.42$, the signal change with flagging vanishes. This condition is due to the balance of the charge carriers entering and leaving the collector, as described above.

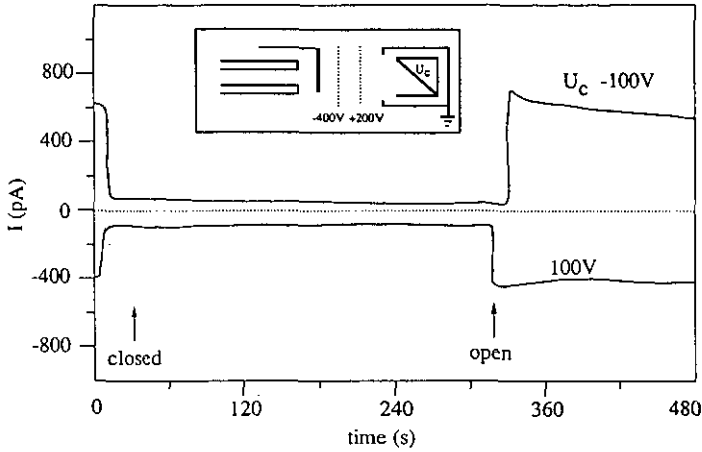


Figure 2. Time variation of signal with only alkali impurities from the source, with the first grid negative. Open and closed refers to the beam flag at the source. The time of flag movement is indicated only approximately by the arrow. See also the inset with voltages.

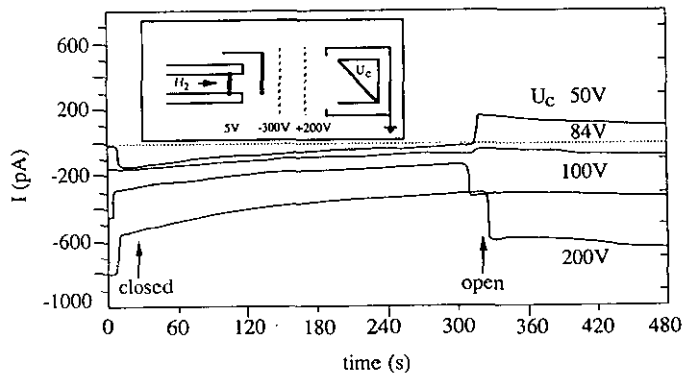


Figure 3. Time variation of signal during hydrogen admission with a negative first grid and the collector positive. Open and closed refers to the beam flag at the source. The time of flag movement is indicated only approximately by the arrow. See also the inset with voltages.

In previous studies, it was concluded that the negative alkali ions were formed at the first negative grid from excited neutrals [4, 15]. In figure 4, results are shown that lead to the same conclusion in the present case with hydrogen in the source. The signal steps at flagging almost disappear when the collector is more negative than the first grid. Thus, part of the signal is due to excited negative ions formed at the first grid. That the signal changes when the collector has the same voltage as the first grid is also shown in figure 5.

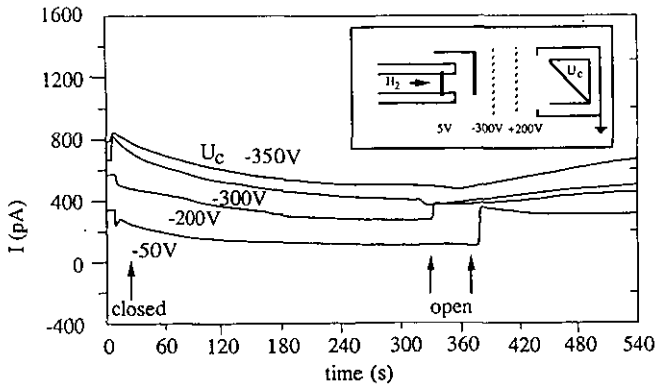


Figure 4. Time variation of signal during hydrogen admission with a negative first grid and the collector negative. Open and closed refers to the beam flag at the source. The time of flag movement is indicated only approximately by the arrow. See also the inset with voltages.

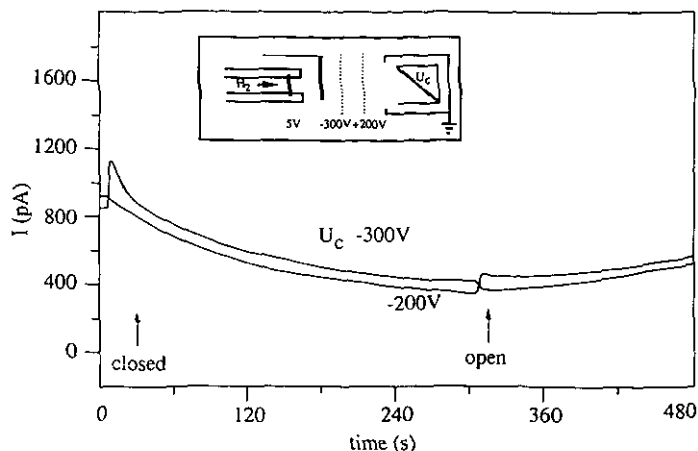


Figure 5. Time variation of signal during hydrogen admission with a negative first grid and the collector negative. Open and closed refers to the beam flag at the source. See also the inset with voltages.

Experiments with a positive first grid have also been performed to demonstrate that not only the negative ions formed at the first grid, but also the neutral excited flux directly from the source influence the signal obtained. In figure 6, the signal variation is shown with the collector at both 300 and -300 V, and with the first grid at 200 V. Any negative ions formed at the second (negative) grid will reach the collector when its voltage is 300 V, but they will be repelled when the collector voltage is -300 V. The signal changes sign when the collector voltage changes sign, and there appears to be no large negative ion signal from the second grid. (An ordinary negative ion signal from this grid would also be interrupted by the flag, which is not observed.) It can be observed that the signal variation is almost exponential when the flux from the source is cut off, and almost linear when the flag is opened again. This points to a deposition process as the source of the signal in figure 6.

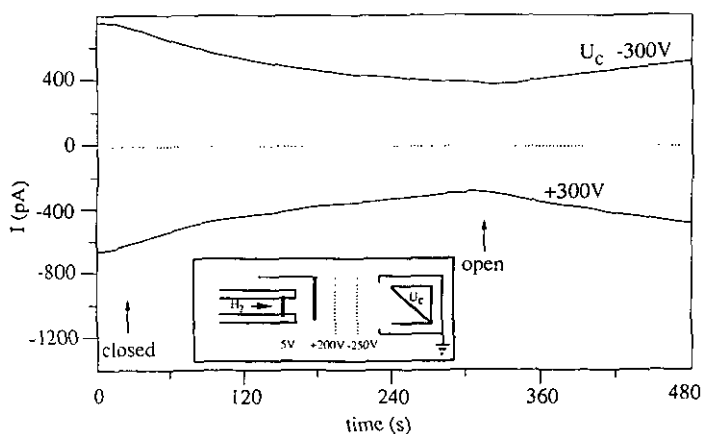


Figure 6. Time variation of signal during hydrogen admission with a positive first grid. Open and closed refers to the beam flag at the source. The time of flag movement is indicated only approximately by the arrow. See also the inset with voltages.

Other interesting results can also be found with a positive first grid, as shown in figure 7. In this case, as in figure 2, no hydrogen is admitted to the source, and only excited alkali atoms from the heaters of the source contribute to the signal. When the flag is closed, the signal shows a large negative peak, and a large positive peak is found when the flag is opened again. There are no slow processes, in contrast to

the case with a hydrogen-filled source. This measurement is taken immediately after that in figure 2, and the peaks are approximately twice as large as the steps observed in figure 2. These results probably indicate that a surface layer with very special properties is destroyed when the beam flag is closed, and replenished when the flag is opened again.

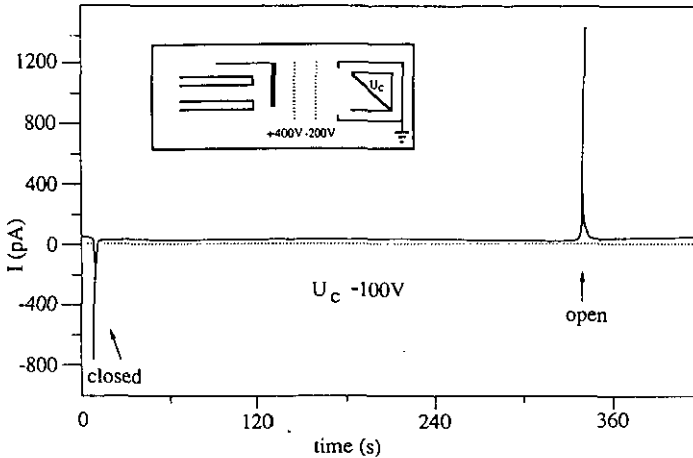


Figure 7. Time variation of alkali impurity signal with a positive first grid and the collector negative. Open and closed refers to the beam flag at the source. See also the inset with voltages.

5. Discussion

5.1. Composition of the flux from the source

Many properties of highly excited Rydberg states will be determined by the excited electrons. This means that it may be quite difficult to determine the chemical composition of the flux from the source, employing techniques which are sensitive mainly to the Rydberg nature of the flux. Of course, ions formed can always be studied by mass spectrometry, but the short lifetime of excited ions may prevent their detection and correct identification, as observed in the studies leading to [5]. Spectroscopic methods would work in principle, but the likely species (H_2^-) and (K^+) do not appear to be well known spectroscopically. Besides, the flux densities are quite low and many different states are likely to exist.

In the present experiments, the source is designed to give excited H_2 molecules, besides the unavoidable flux of ground state hydrogen molecules. A contribution to the signal due to excited alkali atoms, present as impurities in metal heaters, is also observed, and can be observed clearly in the experiments without hydrogen admission. In these cases, the signal is usually smaller and the signal behaviour is different. Thus, it is possible to distinguish between the pure alkali flux and the mixed alkali and hydrogen flux in the experiments with hydrogen in the source. The flux from the source thus contains excited hydrogen molecules and excited alkali atoms, probably mainly potassium K^+ .

5.2. Negative ions from the negative grid

In section 4 we showed that the observed signal is often due to negative ions from the first negative grid. These ions may emit up to two electrons at impact on the collector. The part of the signal which can be flagged rapidly is often connected with this type of flux, as seen in figure 3, where the signal steps at flagging have different signs depending on the voltage of the collector. However, in figure 4 the steps are positive when the flag is closed for a collector which is so negative that no negative ions can reach it. Thus, only neutrals can reach the collector in this case.

The negative ions H_2^- and K^- which are proposed to give rise to the signal are probably electronically excited. The negative hydrogen ion is not stable in its ground state [24], but it was recently observed by mass spectrometry [15].

5.3. Slow processes and Rydberg matter

A slow component of the signal, as in figures 3–6, is probably due to accumulation of the species giving rise to the signal somewhere on the surfaces in the analysing device. The first possibility to consider is of course accumulation of a conductive layer on the insulators carrying the collector, even if these insulators are well shielded. That the signal increases when the flag is closed, even in cases where no negative ions from the first grid contribute to the signal as in figures 4 and 5, excludes such an explanation. Further, the time constant of a few minutes excludes any coverage of a layer of a material with (a) a low vapour pressure such as ordinary alkali metal, since such an accumulation would decrease the insulation resistance irreversibly, or (b) with high vapour pressure such as ground state H_2 .

The results in figures 5 and 6 indicate an approximately exponential decay of the signal when the flag is closed, which agrees with the picture of decomposition of a material on the collector. When the flag is opened again, the signal change is approximately linear, with decreasing time derivative. This indicates that the material is renewed by deposition from the beam. We suggest that these changes are due to accumulation of excited states on the collector, presumably in the form of excited matter, so-called Rydberg matter [6–9, 16, 17].

More information on the behaviour of Rydberg matter can be found by analysing figures 4 and 5. In these two figures, cases are shown where the signal *increases* abruptly when the flag is closed. This behaviour is proposed to be due to decomposition of the excited matter on the collector. Electrons are probably emitted from the collector after the flag is closed, resulting in a net positive current to the collector. At collector voltages where negative ions from the first grid can reach the collector, a different steady-state coverage exists on the collector. The integrated signal in figures 5 and 6 is approximately 5×10^{-8} A s. Recalculating this to a surface monolayer with spacing r between the atoms or molecules on the surface, one finds $r = 100 \text{ \AA}$. This may be reasonable for an excited hydrogen layer or it may indicate island formation on the surface.

The results in figure 7, where only alkali gives the signal, can be interpreted in a similar way. The negative peak when the flag is closed corresponds to decomposition of a layer of excited alkali, with typical distance in a monolayer of $r = 2000 \text{ \AA}$. This value cannot correspond to a monolayer but to island formation on the surface. The positive peak when the flag is opened probably corresponds to the flux which decomposes on the surface before a stable surface layer can be formed.

6. Conclusions

We conclude that the observed signals have two causes: negative ions of hydrogen and alkali, formed at the negative grid in the same way as reported in previous studies [3, 15], and neutral excited states which form a condensed phase of excited matter, so-called Rydberg matter on the collector. Neutral excited states from the source form negative ions through interaction with the layer of excited states on the first grid. The excited negative ions interact with the collector surface by emitting up to two electrons. The long time constants and other transient phenomena observed in the signals are due to changes in the excited state layers.

Acknowledgments

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