

Experimental observation of an atomic hydrogen material with H–H bond distance of 150 pm suggesting metallic hydrogen

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 7017

(<http://iopscience.iop.org/0953-8984/16/39/034>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 17:59

Please note that [terms and conditions apply](#).

# Experimental observation of an atomic hydrogen material with H–H bond distance of 150 pm suggesting metallic hydrogen

Shahriar Badiei and Leif Holmlid<sup>1</sup>

Atmospheric Science, Department of Chemistry, Göteborg University, SE-412 96 Göteborg, Sweden

E-mail: holmlid@chem.gu.se

Received 15 January 2004, in final form 4 August 2004

Published 17 September 2004

Online at [stacks.iop.org/JPhysCM/16/7017](http://stacks.iop.org/JPhysCM/16/7017)

doi:10.1088/0953-8984/16/39/034

## Abstract

A phase of hydrogen Rydberg matter (RM) is formed in ultra-high vacuum by desorption of hydrogen from an alkali promoted RM emitter (Holmlid 2002 *J. Phys.: Condens. Matter* **14** 13469). The RM phase is studied by pulsed laser-induced Coulomb explosions which is the best method for detailed studies of the RM clusters. This method gives direct information about the bonding distances in RM from the kinetic energy release in the explosions. At pressures  $> 10^{-6}$  mbar hydrogen, H\* Rydberg atoms are released with an energy of 9.4 eV. This gives a bonding distance of  $150 \pm 8$  pm which corresponds to a metallic phase of atomic hydrogen using the results by Chau *et al* (2003 *Phys. Rev. Lett.* **90** 245501). The results indicate that a partial 3D structure is formed.

It should be possible to form solid metallic hydrogen from H atoms since hydrogen may be considered to be the lightest alkali metal [1]. In metallic hydrogen, the electrons from the H atoms become delocalized in the solid material and form a conduction band. The main obstacle to forming metallic hydrogen from hydrogen atoms is that covalent bonds are easily formed and molecular hydrogen results. Several groups have applied extremely high static pressures to molecular hydrogen phases [2–4], in some cases apparently in the search for metallic hydrogen. This method has not yet been successful in creating metallic hydrogen. The H–H bond distance is in fact required to *increase* from 74 to 150 pm during compression to form metallic hydrogen from H<sub>2</sub> molecules. Positive results using dynamic compression are reported [5–7]; however, in these experiments the temperature is so high that partial dissociation to atoms takes place [7]. The metallic transformation may be inhibited at low temperature,

<sup>1</sup> Author to whom any correspondence should be addressed.

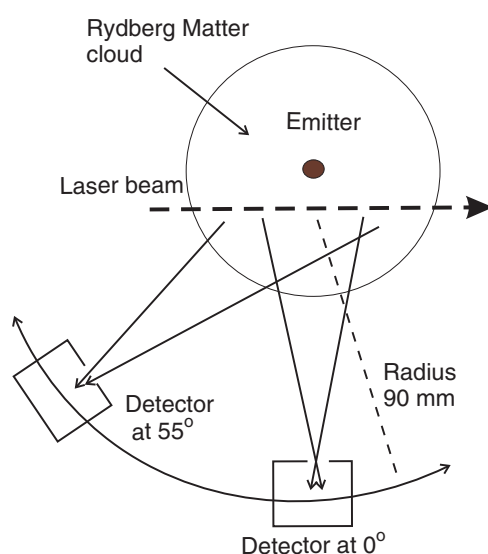
where thermal dissociation is low. Recent experiments show that H<sub>2</sub> molecules are still intact at high static pressures [8] (metallization above 450 GPa is anyway predicted). Thus, one may conclude that molecules still dominate at the pressures studied so far. This is also supported by a theoretical study of molecular hydrogen in a hcp lattice using quantum Monte Carlo methods [9].

Here, we present experimental results with a different approach in which a condensed phase of H atoms is formed from an electronically highly excited metallic state known as Rydberg matter (RM) [10–15]. An atomic hydrogen phase with a short interatomic distance is formed by de-excitation to the lowest state  $n = 1$  of RM, mainly from the state  $n = 3$ . The bond distance in the final H atomic state is observed from laser induced Coulomb explosions, giving the distance between the H atoms as  $150 \pm 8$  pm. The method chosen seems to overcome several obstacles. For example, the initial atomic H RM phase at  $n = 3$  is metallic (from RM theory) which should simplify the de-excitation to a metallic  $n = 1$  phase. Further, the polarizability of the H atoms in the initial state  $n = 3$  is large according to theory, of the order of that of Na; the transition to a metallic state seems to be easier for atoms with large polarizability [7]. Since the observed H atom phase is monatomic, it should resemble an alkali metal more than a hydrogen molecule gas at high pressures. From the recent dynamic compression results by Chau *et al* [7] a metallic state should exist at the scaled density  $D^{-1/3} a^* = 0.35$  that is obtained in our experiments, where  $D^{-1/3}$  is the average interatomic distance and  $a^* = 52.9$  pm.

The state of the outermost electrons in a free atom is described by a few quantum numbers, of which the principal quantum number  $n$  and the angular momentum quantum number  $l$  give the main form of the orbital in which the electron moves. High  $n$  values for any atom describe so called Rydberg states where the outermost electron is not influenced by the inner electrons, and if the  $l$  value approaches  $n$ , with the limit  $l = n - 1$ , the electron or atom state is a circular Rydberg state. Such states are very long lived, with the radiative lifetime increasing as  $n^5$ , reaching 1 ms at about  $n = 40$ . Circular Rydberg states exist for all atoms, and for H atoms they will have rather simple properties since no inner electrons exist. The energy of the circular Rydberg states below the ionization limit is given accurately by the Bohr formula  $W = -R/n^2$ , which is valid exactly in the limit of large quantum numbers.  $R$  is the Rydberg constant equal to 13.6 eV. For hydrogen atoms, different  $l$  states are degenerate. Thus, the energy of all H states is given by the Bohr formula, and since there are no inner electrons in the case of hydrogen atoms all states of the H atom are similar to Rydberg states. The more or less classical description by Bohr gives the energy of all the hydrogen atomic states with good accuracy.

The properties of Rydberg atoms are most easily studied for the alkali atoms, since the unpaired electron in their outermost  $ns$  orbital is not strongly coupled to the inner electrons, and thus easy to excite to high Rydberg states. It is possible to form a condensed phase of circular Rydberg species which is called Rydberg matter (RM) [11–18]. This material, which is almost metallic, can be formed in a vacuum by desorbing alkali atoms at emitter temperatures of the order of a few hundred degrees celsius. Formation of a metallic RM phase was recently independently confirmed [12]. The desorption of Rydberg species (RM clusters) from typical emitters is also independently confirmed [19–21]. A cloud of RM, mainly in one quantum state, is formed in the experiments. Small clusters released from the RM cloud by laser pulses usually have the form of planar monolayers with sixfold symmetry. This means that the most stable RM clusters with large values of  $n$  consist of 7, 19, 37, 61 or 91 atoms in a plane [14, 16]. These numbers are the so-called magic numbers  $N$  for such clusters.

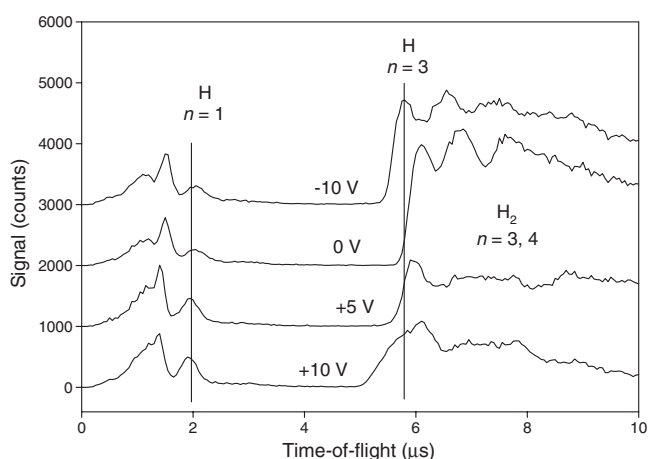
The intent of this study is to observe the formation of H RM clusters in high vacuum. The layout of the central part of the experiment is shown in figure 1. The apparatus has a base pressure of  $10^{-8}$  mbar, and hydrogen gas can be admitted at pressures up to  $10^{-4}$  mbar.



**Figure 1.** The central part of the apparatus, showing that many fragments originating from the outer parts of the RM cloud may have shorter times of flight, as seen in figures 2 and 3.

The RM emitter is a small piece of a commercial catalyst used for the production of styrene from ethyl benzene [22, 23]. It is used for hydrogen atom transfer reactions in catalysis. It is mainly porous iron oxide with various additives, notably K at an initial amount of 8 wt%. This emitter is mounted in a Ta foil holder, and heated to a temperature of 500–900 K by a 50 Hz AC current through the foil. The emitter desorbs highly excited RM clusters of  $H_2$  and H, which then form a cloud of RM around the emitter [23]. It is necessary to introduce a small amount of carbon on the surface of the emitter to increase the rate of RM cluster desorption [24]. In the present case, this is done by covering the inside of the laser dump in the chamber with a layer of Aquadag (Acheson Colloid). The laser is a Nd:YAG pumped dye laser (Lambda-Physik) at 564 nm, at the peak efficiency of the R6G dye used. The laser pulse length is 7 ns and its repetition rate is 10 Hz. The laser beam passes through the RM cloud in front of the RM emitter, at a distance of 5–15 mm from the emitter front. A lens with focal length 40 cm is used to focus the laser beam in front of the emitter. The diameter of the beam waist is approximately  $100 \mu\text{m}$ , and the intensity there is  $<1.5 \times 10^{10} \text{ W cm}^{-2}$  during the pulse. The detector can be rotated around the centre of the apparatus. Each ion initially formed by the laser pulse in the Coulomb explosion process captures an electron from the RM phase in a charge transfer process. The result is a high Rydberg state which is finally field ionized in the detector. Inside the detector box, the Rydberg species are ionized at a field strength of a few hundred  $\text{V cm}^{-1}$ , and the ions are accelerated to a voltage of 6 kV and impinge on a Cu–Be dynode. The same high voltage accelerates the secondary electrons ejected from the dynode to a plastic scintillator, and the light pulse from the scintillator is measured by a photomultiplier. These individual RM fragment counts are collected in a fast multi-channel scaler (EG&G Ortec Turbo MCS) that is triggered by a photodiode. The detector can only measure Rydberg species (including RM fragments) and ions. Ions can be identified and/or rejected through acceleration or deceleration by applying a voltage to the emitter. As seen in figure 2, the peaks observed at  $2 \mu\text{s}$  and shorter are due to neutral Rydberg species.

Several different techniques have been reported for producing RM [15]. We have studied RM especially with spectroscopic techniques like stimulated Raman spectroscopy, and also



**Figure 2.** Time-of-flight spectrum with a time resolution of 50 ns, showing the H and H<sub>2</sub> kinetic energy release from the laser induced Coulomb explosions. The curves are shifted upwards to increase visibility. Most fragments observed are neutral, since their times of flight do not change appreciably with the voltage of the emitter. H ( $n = 1$ ) has a kinetic energy of 9.4 eV. The fragments from states  $n = 3$  have a kinetic energy of 1.0 eV while  $n = 4$  gives 0.59 eV. Such fragments would not reach the detector at all in the case of negative emitter voltage if they were in ionic form. The base line between the H atom peaks from  $n = 1$  and 3 shows that very little intensity comes from  $n = 2$ .

with the technique used here with an intense pulsed laser releasing charged or neutral fragments from the cloud. The fragments released by the laser pulse from the RM cloud often receive a large excess energy. This is due to Coulombic repulsion in the RM cloud between neighbouring ions (ion pairs) induced by the laser pulse. It is enough to excite two electrons encircling two adjacent atomic cores into other orbits for a very short time, so that one of the naked ions is exposed to the other charge with the same sign. The ions are repelled from each other, breaking the RM cluster into two parts, which is called a Coulomb explosion. In most cases, the breaking up of the RM cluster is asymmetric, which means that the smaller fragment is sent away with practically all the repulsion energy. This energy is (with  $e$  the unit charge) [17, 18]

$$W_R = \frac{1}{4\pi\epsilon_0} \frac{e^2}{d}. \quad (1)$$

The distance  $d$  between two atoms in RM can thus be determined from the kinetic energy of the emitted fragment that is equal to  $W_R$ . If the Rydberg orbits were to just touch, the distance  $d$  would be twice the Rydberg radius for the electron motion  $n^2 a_0$  (the Bohr radius  $a_0 = 52.9$  pm). Stability calculations show [16] that the distance  $d$  is a factor of 2.9 larger than the Rydberg radii, thus the distance is

$$d = 2.9n^2 a_0. \quad (2)$$

Experiments show that the energy released in Coulomb explosions in RM is indeed quantized in good agreement with these formulae [14, 17, 18], for example in RM formed from H<sub>2</sub>. The principal quantum number observed in RM formed from K or H<sub>2</sub> is in the range  $n = 3$ –7. Higher  $n$  values give large bonding distances  $d$ , and thus small energy release. This means that the fragments released by the laser pulse from states with  $n > 7$  move so slowly that they cannot be distinguished from RM clusters moving with thermal velocity. Lower values of  $n$ , i.e.  $n = 1$  or 2, are not expected for RM formed even from small molecules like H<sub>2</sub> [14] since the inner electrons occupy the space where the low level Rydberg electrons would move. The

situation is different for RM formed by H atoms, since there are no inner electrons in this case to prevent the formation of a condensed phase with  $n = 1$  or 2. For  $n = 1$ , the interatomic distance  $d$  is 153 pm and the repulsion energy 9.38 eV from equations (1) and (2). Since  $n = 1$  is the lowest state, it is likely that an RM phase formed from H atoms will de-excite down to this state while  $n = 2$  is rather short lived.

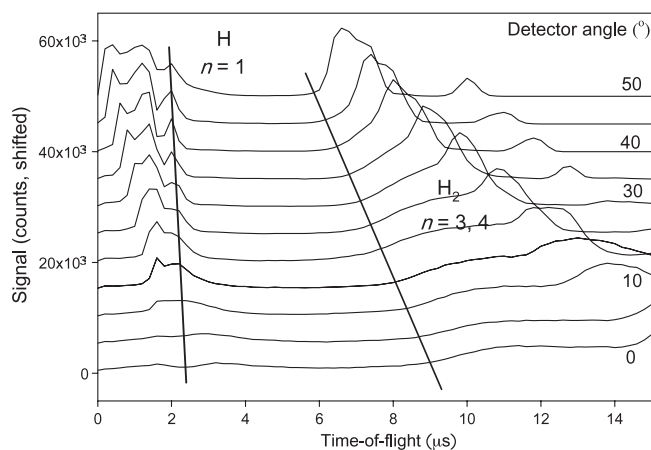
We now report formation of a condensed phase of H atoms together with a H<sub>2</sub>(RM) phase. We concentrate on the H atomic phase with typical experimental results in figure 2. There, fast H atoms from RM structures with  $n = 1$  and 3 are seen. H<sub>2</sub> molecules from planar RM clusters at  $n = 3$  and 4 are observed at flight times longer than 6  $\mu$ s. The particles giving the observed signal are neutral, which is shown by applying a voltage to the RM emitter in the centre of the chamber: this does not change the time of flight of the particles as it would if they were ions. The kinetic energy release calculated from the flight time of the H atoms observed in the time-of-flight peak at 1.9–2.0  $\mu$ s is approximately 9.4 eV per mass unit. The broader peaks at 1.40–1.45 and 1.1–1.2  $\mu$ s are due to multiple Coulomb explosions, by repulsion from two and three charges respectively. The width of the peaks can be used to derive typical temperatures of initial motion of the atoms before the Coulomb explosions. The temperatures derived are 9000 K (first peak), 3000 K (second peak) and 1500 K (third peak, at 2  $\mu$ s) respectively. The corresponding bond length is  $150 \pm 8$  pm ( $2.83 \pm 0.15$  au) in the H phase from the peak at 1.9–2.0  $\mu$ s. The scaled density  $D^{-1/3}a^*$  defined by Chau *et al* [7], where  $D^{-1/3}$  is the average interatomic distance and  $a^* = 52.9$  pm, is  $0.353 \pm 0.019$  using this result. This gives a conductivity of  $10^3 \Omega^{-1} \text{cm}^{-1}$  for a monatomic material according to [7].

The structure of higher states with  $n \geq 3$  of RM is determined by the planar orbits of the circular Rydberg electrons giving planar clusters [16]. However, it is not likely that the lower states  $n = 1$  and 2 have the same planar structure since the electron orbitals will not be strictly planar. Since the orbitals merge into the conduction band in RM, they are neither atomic s nor p orbitals. Thus, the structure at  $n = 1$  is expected to be three dimensional. Direct evidence for this is found in the peaks at 1.40–1.45 and 1.1–1.2  $\mu$ s. Such effects have not been observed in other RM systems with their planar cluster structure, and this is good evidence for the 3D structure of the  $n = 1$  material.

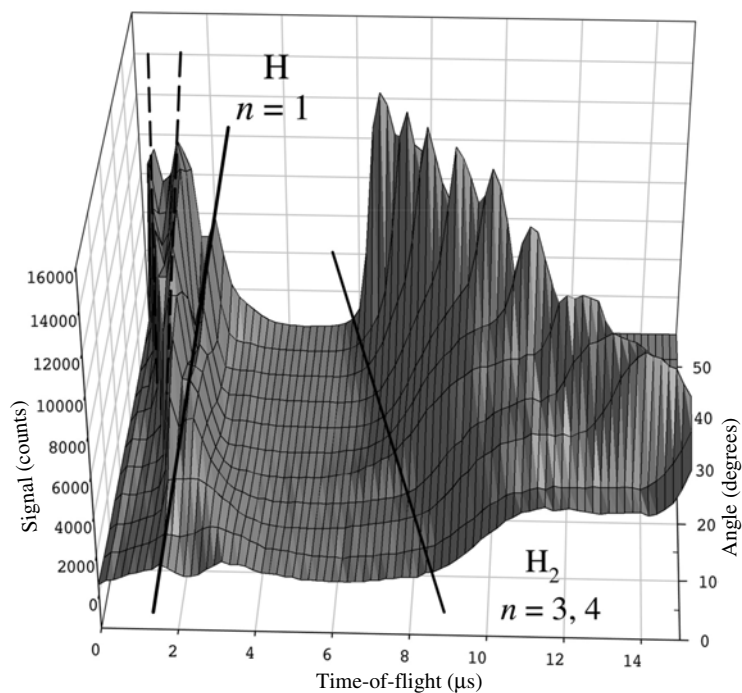
The peak at 1.9–2.0  $\mu$ s shows a spatial anisotropy. In figures 3 and 4, it is observed that the intensity and shape of this peak change with detector angle. This is strong evidence that other origins of the H atoms, like free highly excited molecular states of H<sub>2</sub> formed by the laser pulses, are excluded. The direction of the H<sub>2</sub> rotation axes of molecules in a gas is isotropic in space, and the molecules will rotate several thousand turns during the 7 ns long laser pulse. This means that fragmentation of H<sub>2</sub> gas molecules must be isotropic, at variance with the experiments. fs pulses and much higher laser intensities than used here are in fact required to dissociate H<sub>2</sub> molecules to H ions [25]. If the fragments observed at 1.9–2.0  $\mu$ s were H<sub>2</sub> molecules instead of H atoms, their kinetic energy from the TOF would be close to 19 eV. A source giving such a high energy release for H<sub>2</sub> cannot be envisaged.

In other studies of RM with the same method as used here, a strong self-cooling of the kinetic temperature of the fragments is observed [14, 17, 18]. The H atoms from the ordinary RM structure at  $n = 3$  have a temperature of 30 K, as derived from the steep rise of the peak at 0 V emitter voltage in figure 2. This self-cooling is virtually absent in the  $n = 1$  state, as seen from the high temperatures reported above. Thus, it seems that the H RM phase has not been able to cool down efficiently after its formation e.g. by de-excitation from the state  $n = 3$ .

To conclude, the interatomic distance at low pressure is found experimentally to be  $150 \pm 8$  pm. We predict a distance of 153 pm from RM theory which is expected to be valid also at  $n = 1$  for H atoms. A monatomic phase will be a metal at the interatomic distance measured, according to the dynamic compression results compiled by Chau *et al* [7]. Thus,



**Figure 3.** Angular variation of the fragments from the Coulomb explosions, with zero voltage on the emitter. The different curves taken with  $5^\circ$  steps in angle are shifted upwards to increase visibility. Zero degrees means the direction of the surface normal, and positive angles are closer to the incoming laser beam. The H atoms that are even faster than H ( $n = 1$ ) are due to repulsion from two and three charges, indicating a three-dimensional structure of the material. See also figure 4.



**Figure 4.** Angular variation of the fragment signals in figure 3, shown as a mesh plot. The  $H_2$  molecules come from the outer parts of the RM cloud as seen in figure 1, thus they have shorter flight time to the detector at large angles. The H–H bond distance from the Coulomb explosions for  $n = 1$  is 150 pm.

it is possible that the H phase is metallic hydrogen formed by a transformation of the planar metallic RM structure existing at high quantum numbers down to the 3D ground state for the

condensed H atom material. Many applications for metallic hydrogen are expected to exist [1], and the ‘Rydberg detour’ process used here may be a good method for production of metallic hydrogen.

### Acknowledgments

The Swedish Research Council (VR) supports our research on Rydberg matter. Discussions with Édward A Manykin are gratefully acknowledged.

### References

- [1] Nellis W J 1999 *Phil. Mag.* B **79** 655
- [2] Mao H K and Hemley R J 1989 *Science* **244** 1462
- [3] Narayana C, Luo H, Orloff J and Ruoff A L 1998 *Nature* **393** 46
- [4] Loubeyre P, LeToullec R, Hausermann D, Hanfland M, Hemley R J, Mao H K and Finger L W 1996 *Nature* **383** 702
- [5] Weir S T, Mitchell A C and Nellis W J 1996 *Phys. Rev. Lett.* **76** 1860
- [6] Nellis W J, Weir S T and Mitchell A C 1999 *Phys. Rev. B* **59** 3434
- [7] Chau R, Mitchell A C, Minich R W and Nellis W J 2003 *Phys. Rev. Lett.* **90** 245501
- [8] Loubeyre P, Occelli F and LeToullec R 2002 *Nature* **416** 613
- [9] Natoli V, Martin R M and Ceperley D 1995 *Phys. Rev. Lett.* **74** 1601
- [10] Manykin Éd A, Ozhovan M I and Poluéktov P P 1980 *Pis. Zh. Tekh. Fiz.* **6** 218  
Manykin Éd A, Ozhovan M I and Poluéktov P P 1980 *Sov. Tech. Phys. Lett.* **6** 95 (Engl. Transl.)
- [11] Manykin Éd A, Ozhovan M I and Poluéktov P P 1992 *Zh. Eksp. Teor. Fiz.* **102** 804  
Manykin Éd A, Ozhovan M I and Poluéktov P P 1992 *Sov. Phys.—JETP* **75** 440 (Engl. Transl.)
- [12] Yarygin V I, Sidel’nikov V N, Kasikov I I, Mironov V S and Tulin S M 2003 *JETP Lett.* **77** 280
- [13] Svensson R and Holmlid L 1992 *Surf. Sci.* **269/270** 695
- [14] Wang J and Holmlid L 2002 *Chem. Phys.* **277** 201
- [15] Holmlid L 2002 *J. Phys.: Condens. Matter* **14** 13469
- [16] Holmlid L 1998 *Chem. Phys.* **237** 11
- [17] Badiei S and Holmlid L 2002 *Int. J. Mass Spectrom.* **220** 127
- [18] Badiei S and Holmlid L 2002 *Chem. Phys.* **282** 137
- [19] Kotarba A, Adamski G, Sojka Z, Witkowski S and Djega-Mariadassou G 2000 *Studies in Surface Science and Catalysis (International Congress on Catalysis, 2000, Part A vol 130A)* (Amsterdam: Elsevier) p 485
- [20] Kotarba A, Dmytrzyk J, Narkiewicz U and Baranski A 2001 *React. Kin. Catal. Lett.* **74** 143
- [21] Kotarba A, Baranski A, Hodorowicz S, Sokolowski J, Szytula A and Holmlid L 2000 *Catal. Lett.* **67** 129
- [22] Meima G and Menon P G 2001 *Appl. Catal. A* **212** 239
- [23] Holmlid L and Menon P G 2001 *Appl. Catal. A* **212** 247
- [24] Holmlid L 1998 *J. Phys. Chem. A* **102** 10636
- [25] Thompson M R, Thomas M K, Taday P F, Posthumus J H, Langley A J, Frasinski L J and Codling K 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 5755