Conditions for forming Rydberg matter: condensation of Rydberg states in the gas phase versus at surfaces

Leif Holmlid

Reaction Dynamics Group, Physical Chemistry, Department of Chemistry, Göteborg University, SE-412 96 Göteborg, Sweden

E-mail: holmlid@phc.gu.se

Abstract
The recent experiments on processes in cold Rydberg gases produced by laser excitation have so far only a weak relation to Rydberg matter (RM) and its formation, despite some attempts to make such a connection. The problems of forming RM from cold Rydberg gases are severe and due to at least five obvious factors: the condensation energy, the non-circular states formed, the spatial and temporal incoherence of the electronic motion, the low density of Rydberg states formed and the too large interionic distance. Evidence on why these factors are important is given. It is furthermore not obvious that formation of RM would have been detected in the laser excitation experiments since no suitable diagnostics methods were employed. The methods of forming RM using condensation in the boundary layer at surfaces are discussed for comparison. Better designed experiments seem necessary to achieve true condensation to RM in cold Rydberg gases, since large differences exist between Bose–Einstein and Rydberg condensation.

1. Introduction

The formation of so-called Rydberg matter (RM) has been described in several publications over the last ten years, using different methods involving the condensation of Rydberg species close to solid surfaces. The recent interest in forming RM in other types of experiments, especially involving cold Rydberg gases, necessitates a thorough discussion of the drawbacks of the different methods available.

The existence of RM was predicted by Manykin, Ozhovan and Poluéktov [1, 2] 20 years ago. Improved quantum mechanical (QM) calculations of the macroscopic properties of RM built up by Cs Rydberg states were also published later [3, 4], matching the experimental results from our group. Further developments of the theoretical approach from the same group have also been published recently [5]. A quasi-classical theory for RM [6], including electron correlation by a simple scheme, gives atom binding energies and work function values in

reasonable agreement with the QM calculations. The work function used here has its normal meaning for the metallic RM. Jellium theory [7] gives similar values of the work function of RM. Thus, three different theoretical approaches give similar results, which confirms the RM concept.

The RM concept is defined theoretically by the requirement of a bonding interaction between the condensing Rydberg species. The form of RM described theoretically by Manykin *et al* and also recently by Manykin [8] consists of spherically symmetric high-n Rydbergs states which interact to form two- or three-dimensional clusters. The radiative lifetime of an s state is, however, several orders of magnitude shorter than for a high-l (almost circular) state. Thus, it is probably easier to form and observe RM formed from such long-lived states with lifetimes of the order of seconds. It is also likely that the bonding interaction will be strong for such a case, as described in [6]. A strong bonding interaction between circular states is possible if all the interacting Rydberg species have the same excitation state, i.e. principal quantum number n [6], and if the electronic motion is coherent. It is possible that similar conditions must also be fulfilled for the case of s-state bonding, especially if it is taken into account that the Born–Oppenheimer approximation is not valid. The experimental results on RM clusters indicate that the RM observed is in the form of condensed circular states which form two-dimensional clusters, but a formation of RM from s-states could possibly exist under dynamic and short-lived conditions.

Experimentally, the observation of RM can be confirmed either by a substantial broadening or shifting of the energy levels of the interacting Rydberg species [9, 10], or better by an observation of a bonding energy [11–13]. Macroscopical parameters, such as the work function, have also proved to be valid indicators of RM formation [14]. Of course, an observation of clusters with magic numbers corresponding to the six-fold symmetric planar RM clusters can also be considered as definitive proof [11]. It should be pointed out once more that the experiments only give proof for the two-dimensional form of RM which is composed of circular Rydberg species. Thus, the discussion here is limited to the formation of this type of RM, which is the only type known to exist at present.

Stable RM is formed experimentally by condensation of circular, long-lived Rydberg states [15, 16] of atoms and small molecules at surfaces. Long-lived Rydberg states of alkali atoms in the form of RM clusters are formed directly in desorption from nonmetallic surfaces [17]. Condensation of the Rydberg states to RM clusters in the surface boundary layer of the emitter has been observed directly by molecular beam scattering [18]. Experimental results on the desorption of Rydberg atoms and small electronically excited clusters of alkali atoms can be found in numerous publications: see [19] for a partial review and [20] for a recent example from another laboratory. The efficient desorption of Rydberg species and a decreased desorption of the ground state is a kinetic effect. It seems to be related to the low population of the ionically bound state on the surface, i.e. the surface alkali atom state that correlates with the ground state outside the surface. Thus, the desorption of ground state atoms is strongly inhibited, instead giving desorption of excited states. This is a process resembling selective catalysis. In the detailed kinetic studies of K and Cs desorption from graphite [17, 21] the extremely large pre-exponential factors of 10^{20}–10^{25} s^{-1} (normal value 10^{12} s^{-1}) prove directly that a switch to electronically excited states takes place. A potential energy diagram for the case of K on an iron oxide surface is shown in figure 1. The data on which this diagram is based are described in [19] and in references given there. The corresponding more detailed diagram for K on graphite is presented in [17].

Studies by laser fragmentation time-of-flight mass spectrometry [22] have identified the special planar cluster shapes predicted by RM theory [6]. It is also possible to form clusters with the same hexagonal planar shape from hydrogen and nitrogen molecules [11, 23]. In
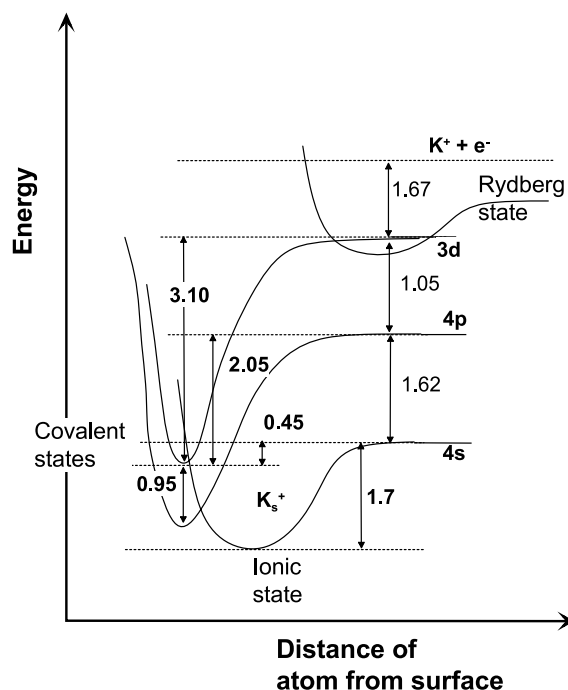
Figure 1. A partial potential energy diagram for a K atom at a surface used for formation of RM in desorption, a K-impregnated iron oxide material. All energies are given in eV and the bold values are experimentally found, see further [19].

the laser fragmentation experiments, neutral RM clusters are released with a quantized kinetic energy corresponding to repulsion between ions in the RM. The time-of-flight spectra change strongly when the polarization plane of the laser is rotated [11, 24], which indicates that the clusters are non-spherical and even oriented in space.

From our group, several methods of forming RM and RM clusters have been described, all involving surfaces from which efficient desorption of Rydberg states and RM clusters takes place. They cover different pressure and temperature regimes, and also different types of Rydberg species. Table 1 is provided with a few key references. The main species used are alkali metals. It is apparent from these studies that the function of the surface is as crucial for the formation of RM as the catalyst in an ordinary catalytic process. For example, it is not possible to form RM in experiments of the type in [10, 14, 25] without the application of a layer of colloidal graphite on the cold electrode: using a fresh emitter and no carbon addition does not give any observable formation of RM.

From a purely physical point of view, it may seem tempting to form RM by direct laser excitation of atoms to Rydberg states in a gas. The observations of line broadening and line splitting in 'frozen' Rydberg gases [26, 27] were interpreted as due to many-body effects between the large Rydberg atoms, at Rydberg densities of 10^{10} cm^{-3}. This seemed encouraging and is probably one reason for the recent interest in methods of forming RM, as observed in the recent conference session discussing RM [28]. However, at the beginning of the 1980s a similar type of system had already been shown by Haroche *et al* not to give condensation of the Rydberg states formed at densities of 10^{12}–10^{13} cm^{-3} [29, 30]; such a result is certainly expected from the facts given below. This early result has been considered as proof of the nonexistence of RM, instead of giving evidence that this special approach to the formation of

Table 1. The various methods of forming RM and clusters of RM described in the literature. The last method in the table has only been shown to form Rydberg states. Under 'Feed dir.' cf means counter-flow feed, i.e. the RM flows in the direction opposite to the feed material, while cl means collinear feed, with the RM formed flowing in the same direction as the feed material.

| Emitter material	Emitter temp. (K)	Feed type	Feed dir.	Vapour press. (mbar)	Feed temp. (K)	No. of publications	References
C on Mo	1200–2000	Cs	cf	0.1	500–600	12	[10, 14, 25, 45]
C foil	1000–1500	Cs	cl	10^{-3}	400	4	[46–48]
C foil	1100–1400	H_2, C_2H_4	cl	30–1000	Emitter	2	[49]
C nozzle	1100–1400	H_2	cl	10–30	Emitter	1	[50]
C on Ir	1350–1700	Cs	cl	10^{-3}–10^{-1}	450–700	6	[51]
Fe–O, K doped	300–1000	K, H_2	cl	—	500 or emitter	11	[11, 23, 42]
Fe, K doped	900–1100	K	cl	—	Emitter	5	[32]
C	300–1500	K	cf	$< 10^{-7}$	500 or emitter	6	[22, 33]
ZrO_2	1000–1500	K	cf	$< 10^{-7}$	500	2	[18]
C on Ir	1500	Cs, K	cf	10^{-9}	500	3	[17]

RM is not well conceived. I now proceed to a discussion of the problems making this approach unlikely to be successful if the experimental design is not improved considerably.

2. Condensation energy

The theoretical predictions of the condensation energy due to Manykin *et al* are based on functional density calculations. They agree reasonably well with those found from quasi-classical theory including electron correlation in [6]. The predictions of the work function of RM from both theories agree quite well with the one from jellium calculations [7]. Thus, the calculated bond energies or condensation energies should be quite accurate. For the highest quantum number $n = 20$ used in the calculations, the bond energy per Rydberg state is 200 K (17 meV) classically, and 600 K (52 meV) from QM calculations. In many of the RM cluster studies, $n = 3$–6 is observed [11, 12]. For a strongly bound experimental case of $n = 5$, one finds an extrapolated bond energy close to 0.2 eV.

During condensation of a gas of Rydberg states, this binding energy must be removed. If not, it is likely that the condensation energy is used to release electrons from the RM clusters. In general, the electron binding energy (work function) is more than a factor of 2 larger than the atom binding energy in RM, but thermal energy of the atoms or nearby moving charged particles may contribute the energy remaining for the release of an electron, destroying the condensation to RM clusters. Thus, the condensation energy has to be removed quickly before ionization starts and before the Rydberg states separate again. As soon as even small stable clusters are formed, consecutive addition of Rydberg states is more probable since the degrees of freedom in the cluster become more numerous and the time period for safe removal of the condensation energy becomes longer. However, in a gas where there is no energy sink available, ionization may certainly take place, giving a plasma and no RM formation, as apparently observed from the laser excitation experiments.

In the various schemes for forming RM that have been shown to work, the condensation energy for the formation of small clusters is normally removed already in the boundary layer of the emitter surface. The formation of small and large clusters in desorption has been studied in several cases [31–33]. It has even been possible to directly observe the addition of ground state alkali atoms to an RM cluster in the boundary layer [18]. The angular scattering distribution in
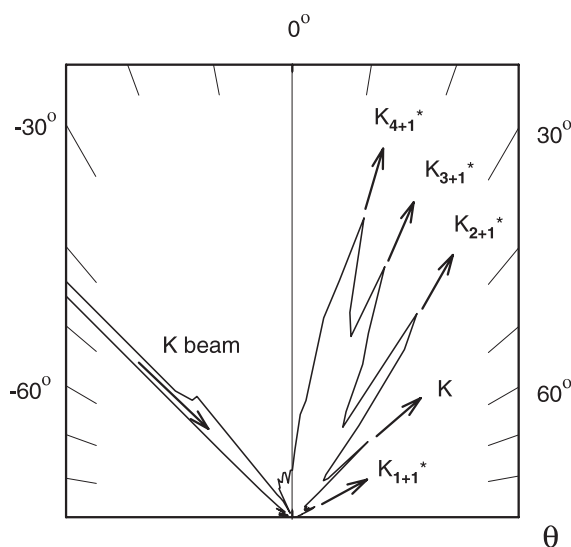
Figure 2. Angular distribution of K flux from a zirconia surface with a K molecular beam at −45°. The peaks shown are due to clusters formed in the surface boundary layer by addition of K atoms from the beam to the RM clusters desorbing thermally from the surface at 1100 K. Zero degrees is in the direction of the surface normal.

this case (figure 2) shows sharp peaks at the positions of the centroids for the scattering of a K atom from the molecular beam against a small cluster $(K)_N^*$ moving out from the metal oxide surface close to the direction of the surface normal. Since the intensity of scattering is peaked at the centroid, it can be concluded that clusters $(K)_{N+1}^*$ have been formed by a condensation reaction [18].

A similar process was recently studied in the gas phase by Peng *et al* [34], confirming this type of addition reaction. In this study, a Rydberg dimer Na_2^* formed an excited trimer by addition of Na in a beam. The Rydberg trimer was field ionized after <0.3 μs and observed as an ion. As described below, this time is too short to give gas phase Rydberg condensation at low temperatures and low Rydberg densities. Furthermore, the condensation is not by Rydberg species addition. Thus, the excitation energy per atom decreases in such a process, which prevents further condensation to RM if this process takes place in a cold Rydberg gas.

A recent discovery provides an alternative method to remove the condensation energy from the RM clusters. In RM laser fragmentation experiments, strong self-cooling of the clusters released from the RM cloud is observed. The temperature measured by the velocity spread of the clusters is down to 20 K even for small K_N clusters with $N < 7$ [13]. For large clusters of hydrogen $(H_2)_N$ with $N = 37, 61$ and 91 the kinetic temperature was found to be as low as a few K [11]. This effect was attributed to electron evaporation from the RM cloud, which is not radiatively coupled to the laboratory surroundings due to its very long radiative lifetime. Another possibility is stimulated emission in the IR which has recently been observed to be efficient in RM [35]. If such self-cooling processes can be initiated and supported, it could simplify the condensation of a cold Rydberg gas to RM.

3. Circular states

The theoretical description of RM in the quasi-classical model [6] employs circularly symmetric electron orbits. Only small departures from such a form of electron orbits can

be accommodated. In a circular Rydberg state, the value of the angular quantum number l is close to the limiting value $n - 1$. This is the most long-lived type of Rydberg state (0.1 s at $n = 100$), which means that in a randomly created distribution of l, these states survive the states with lower values of l (typical lifetime 100 μs). It has been demonstrated in many experiments, for example related to ZEKE studies [36, 37] but also with cold Rydberg gases [38], that collisions between Rydberg states and surrounding ions and other collision partners give an effective increase in the l quantum number (l-changing collisions). Thus, in many experimental situations, the long-lived circular states are formed more or less automatically. This is apparently the case in the methods that have been shown to work for formation of RM. There is no indication from experiments that a condensation of non-circular states (low-l states) is possible.

In the various laser excitation experiments, the allowed transitions, often from an S state as in the case of alkali atoms, leads to a P state which is far from circular, independent of which n value is reached. By two-photon schemes it is at best possible to reach a D state (mixed with S states). The state 3 ^{2}D in, for example, H would meet the requirement of $l = n - 1$, but this is still far from a long-lived circular state. In the cases where $n = 3$ is observed in Coulomb explosions in RM [11], the state 3 ^{2}D may be involved (together with other states) in the bonding in condensed matter, but this does not mean that 3 ^{2}D states fill the requirements for condensation to RM. Higher states than this are probably required for condensation. However, such higher circular states cannot easily be reached by laser excitation.

The remaining possibility to use laser excitation is then to form a gas of low-l Rydberg states and wait for a spontaneous, at least partial development into a high-l Rydberg gas. Even if such a process may be possible under suitable conditions [38], the resulting distribution will not easily give condensation, if not all the other requirements discussed here can be fulfilled.

4. Coherent coplanar electronic motion

The quasi-classical calculations of the RM structure give the most detailed information about the planar structure expected for RM clusters [6]. The experimental verification of the magic numbers for the clusters is clear evidence of the planar structure of the RM clusters [11, 24]. In the quasi-classical model [6], the electrons are assumed to move coherently and in one plane that coincides with the plane of the clusters. Without such regular motion, the binding is decreased and vanishes. To form an RM cluster, several circular Rydberg states should become aligned and polarized and bring their electrons into coherent motion in identical electronic states nlm_l. Certainly, the mutual interaction between the Rydberg states will influence their electronic motion considerably, but it appears unlikely that such alignment and polarization processes can take place rapidly enough relative to deexcitation in a gas. The chaotic structure concerning the direction of the circular states that are formed by collisions will, for example, be a major problem.

In the case of the experimental approaches that are demonstrated to give RM, the Rydberg states are bound to the emitter surface by long-range forces due to the extremely large polarizability of the Rydberg states. This means that they have a large volume for their motion outside the actual emitter surface, the so-called boundary layer. In this bound surface phase, there are continuous excitation, deexcitation and collision processes involving Rydberg species and other states. If several Rydberg species combine to form an RM cluster, the interaction with the surface is decreased markedly since the bonding between the Rydberg states in the cluster leads to a smaller effective volume for the electrons and thus a smaller polarizability. This in turn gives a weaker interaction with the surface. Such a cluster formed by Rydberg states moving out from the surface can thus decrease its collective binding energy to the surface so that

it can become free and move out from the surface. This kind of cluster formation is observed from the angular distributions of desorption [31, 32] and from the scattering of molecular beams from the clusters [18, 33] (see figure 2). Of course, most collisional attempts to form such clusters in the boundary layer are unsuccessful due to unsuitable directions of the electron orbits, no matching of the electron states, etc, but only the successful events are observed in desorption. It should be noted as well that the collisional systems are in close contact with a heat bath (the surface) within a strong adsorption potential. This means that energy can easily flow between the surface and the Rydberg species, before the cluster decouples from the potential. In this way, the condensation energy is likely to be successfully transferred to the surface.

It appears unlikely that anything similar to this selective desorption process can operate in a gas of Rydberg states.

5. Density of circular Rydberg states

Close interaction between Rydberg species is necessary if electronically excited clusters, for example RM clusters, should be formed in the gas phase. The first step in the condensation is probably an excited dimer. Whether this dimer is a Rydberg state dimer $(A_2)^*$ or an RM dimer A^*A^* is not known. An RM dimer does not appear to be stable, at least not in the classical limit. This is supported by several experimental facts, for example the much smaller peak for the cluster K_2^* (or K_{1+1}^*) in figure 2. The dimers observed in many experiments, together with formation of large RM clusters, are probably some type of Rydberg dimers. Thus, direct formation of trimers or even quadrumers may be required if RM clusters should be formed in a gas condensation process. Collisions of this type, involving three or four particles, have a very low probability in a gas, which means that spontaneous formation of such clusters are rare events. In principle, a collision between a circular Rydberg state and a ground state may give a dimer in an electronically excited state. A polar Rydberg dimer of the form proposed to exist by Greene *et al* [39] may be a possible intermediate form which can give a reaction pathway that will not involve multiple particle collisions. However, such a dimer has not yet been observed and its radiative lifetime is not known accurately but it is probably rather short, considerably less than the corresponding lifetime for a circular atomic Rydberg state. Another form of Rydberg state dimer which could be involved in the formation of RM under some conditions are the macrodimers proposed by Boisseau *et al* [40]. Their bond distances are very large, of the order of 10 nm, comparable to the bonding distances observed in laser fragmentation of RM clusters. However, the bond is very weak, at a fraction of one K, several orders of magnitude smaller than in RM.

If several Rydberg species have to interact simultaneously to form RM clusters, the density of such states must be large in the laser excitation experiments if they are to be successful. Since collisions with lower excited states may give energy transfer from the Rydberg species, the density of such low states must be small in comparison so that the quenching rate is not too high. This means that the ratio of Rydberg state species relative to other species should be as high as possible. In many cases with cold Rydberg gases, the thermal velocity is so low that the displacement of the atoms during a few microseconds (time of the experiment) [27] is too small to allow any multiple collisions to take place. Thus, a condensation is very unlikely in such cases. In the laser excitation experiments at high temperatures [29, 30] with a considerably higher density, multiple collision processes may take place. However, the other factors discussed here still indicate that RM cannot be formed under such conditions.

6. Interionic distances

The quasi-classical theory with electron correlation [6] gives a clear minimum of the potential energy for the interacting circular states at an interionic distance of 2.9 times the electron radius of circular motion. This value is verified experimentally in the laser induced Coulomb explosions, where the interionic distances are given directly by the repulsion energy between the fragments [11, 12]. There exists a shallow region around the minimum in which the energy is negative relative to the zero at infinite distance. However, the binding energy is lower at larger interionic distances, so the condensation of the Rydberg states is most easily performed if the average interionic distance is close to the value given by theory. For a typical value of $n = 40$, the interionic distance should be as close to 250 nm as possible. This corresponds to a density of 6×10^{13} cm^{-3}, which is a factor of 10^2–10^5 higher than those reached in experiments with cold Rydberg gases (10^9–10^{10} cm^{-3} [26, 38, 41]). Thus, the Rydberg densities in these experiments are much too low to meet this condition. However, in the early experiments with high temperature gas [29, 30] Rydberg densities of 10^{12}–10^{13} cm^{-3} were indeed reached, but only plasma formation was reported.

A fast condensation should be obtained if the Rydberg density matches the binding distance in the RM. For higher states of excitation, the binding distance increases and the binding energy decreases [6]. Thus the densities of 10^9–10^{10} cm^{-3} reached in experiments with cold Rydberg gases are better matched if the laser excitation reaches states with $n \approx 160$. For such an excitation level, the density in the RM is the same as that reached in the experiments.

If cluster formation starts spontaneously at some point in the Rydberg gas, an accumulation of other Rydberg states to the cluster is certainly possible. However, such a process will take some time. The typical interionic distance from the experimental densities cited above is 5 μm, which is covered by an atom at 300 K in typically 10 ns. However, if the temperature is 50 μK [38] the motion is much slower and the typical time to move this distance is 24 μs. This is not long, but adding the times required for subsequent additions at longer distances, the typical time to form a cluster with $N = 37$ is of the order of 1 ms. (This does not include the time needed to remove the condensation energy.) Thus, it might seem better to start with a warmer Rydberg gas. Since the condensation energy is of the order of 10–50 meV per atom for $n \approx 20$, a kinetic energy for the atoms less than this will not be important. Thus a temperature of 10–50 K is probably tolerable from this point of view. In fact, the experiments give plasma formation much faster than the 1 ms time probably required to form even an intermediately sized cluster. In most experiments, the signals are followed only up to 200 μs. In one case [38] a much slower time variation was indeed observed, giving long-lasting electron emission at times up to 20 ms. Such results are in agreement with what is expected in the case of RM formation.

In the cases shown in table 1 the surface densities of the adsorbate vary strongly due to the large variation in vapour density. Assuming a carbon covered emitter surface, the rate constants for desorption are accurately known from [17]. This means that the surface densities and average interatomic distances on the surfaces can be calculated. With a pressure of 0.1 mbar, the surface density is more than one monolayer at 1500 K. At a flux density corresponding to 10^{-9} mbar, the surface density is 10^{-6} of a monolayer. Assuming a thickness of the boundary layer at the surface of <100 μm [31], the average adsorbate density in this layer is $>10^{13}$ cm^{-3} in all cases with pressure $>10^{-7}$ mbar. Since most alkali atoms are transferred into Rydberg-like states during the desorption process, the Rydberg density is more than required for immediate condensation in all cases but the last one in table 1. In that case, no cluster desorption has been observed in agreement with this calculation. As shown here, it is much easier to reach a high Rydberg state density at a surface than in a gas phase experiment.

7. Detection of Rydberg matter

One further important point to discuss is the detection of RM formation in the various experiments using laser excitation. Since undisturbed RM does not absorb or emit radiation easily, the problem of detection is not straightforward. Due to the low work function of RM and the coupling between the Rydberg states in RM, intense electron emission may be observed when RM is formed. In the experiments from our laboratory, intense electron emission from RM in contact with electrodes was one of the first signatures of RM formation [14]. However, the geometry of the laser excitation experiments usually does not allow the conduction of very high electron current densities through open space. Some space charge compensating ions must also be allowed to exist between the actual location of laser excitation and the electron current collector if large currents could be conducted. Further, since the RM which may be formed in such experiments is not connected to any metallic support, a voltage to give a sustained electron current cannot be applied.

Other possibilities for observing formation of RM exist, such as current conduction due to the low resistivity of RM [14]. Methods such as voltage probing have also been applied successfully [25]. Both these methods have the same problem as the work function measurements, and they are furthermore hardly selective enough to be the sole diagnostic means. The identification methods developed in our group, such as stimulated Raman [9, 10, 42, 43] and cluster observation by neutral time-of-flight or TOF–MS [11, 12, 22–25], are of course available. An example of the neutral time-of-flight results is shown in figure 3. Such a fingerprint spectrum from the exploding RM in a laser excitation experiment may be the best signature of RM formation.

The early studies with laser excitation [29, 30] certainly lacked any means of detection to identify the formation of RM. Despite this, it has often been stated (private communications, various anonymous referees) that these studies show that RM was not formed. The correct statement would be that no condensation could be observed due to the lack of diagnostic methods. In [30] the main point of discussion was a Mott transition, not the formation of RM. In this experiment, the threshold density for apparent plasma formation was studied and found to vary with the effective principal quantum number n^* as $(n^*)^{-4}$. This may be different from the expected behaviour for a Mott transition, but it is certainly what is expected for an ordinary condensation, since the geometrical cross section for the Rydberg states varies in this way. Thus, the experiment shows that a collision process is responsible for the formation of the numerous free electrons observed, but no conclusion as to the nature of this process seems possible, being either initial condensation or ionization due to hot electrons.

In recent studies with cold Rydberg gases, the experimental results are quite similar. Strong electron emission is observed, often delayed and with long decay times [38], but no other information is found. It is often concluded [41, 44] that the electrons formed in ionizing collisions are trapped by the remaining ions, giving further ionization and plasma formation. Since the process observed may as well be due to initial condensation, improved diagnostics is needed. In one case, it is also concluded [44] that condensation of the Rydberg states could have taken place.

8. Conclusions

It is shown that it is not likely that large amounts of RM can be formed by laser excitation in a gas, due to several problems that can only be removed by ingenious experimental designs. Otherwise, several well-documented approaches for forming RM at surfaces are already available to the scientific community.
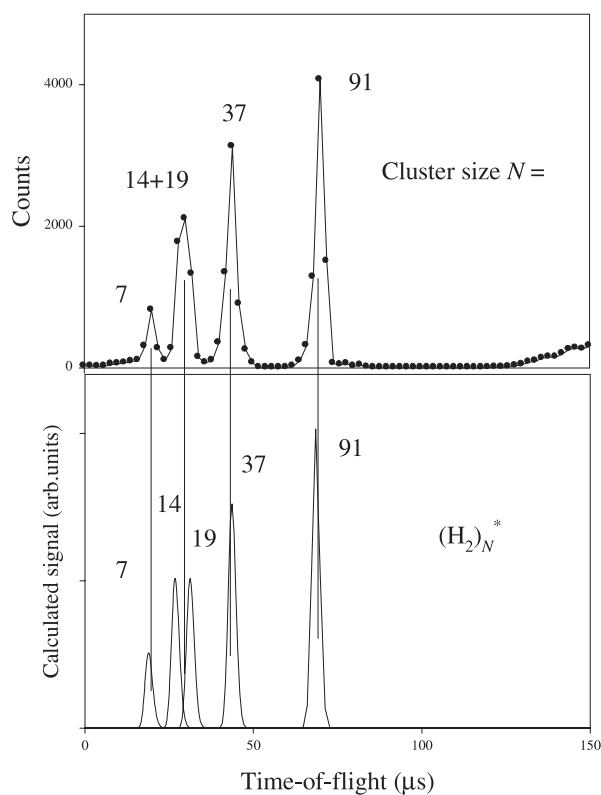
Figure 3. A neutral time-of-flight experiment showing different peaks due to hydrogen molecule clusters with sizes as shown. The lower panel shows the calculated spectrum. The kinetic energy release is 1.0 eV, corresponding to a principal quantum number $n = 3$ in the ion–ion Coulomb repulsion.

Acknowledgments

References

[1] Manykin É A, Ozhovan M I and Poluéktov P P 1980 *Sov. Phys. Tech. Phys. Lett.* **6** 95
[2] Manykin É A, Ozhovan M I and Poluéktov P P 1981 *Sov. Phys.–Dokl.* **26** 974
[3] Manykin É A, Ozhovan M I and Poluéktov P P 1992 *Sov. Phys.–JETP* **75** 440
[4] Manykin É A, Ozhovan M I and Poluéktov P P 1992 *Sov. Phys.–JETP* **75** 602
[5] Manykin É A, Ozhovan M I and Poluéktov P P 2000 *J. Physique* IV **10** Pr5–333
[6] Holmlid L 1998 *Chem. Phys.* **237** 11
[7] Svanberg M and Holmlid L 1994 *Surf. Sci.* **315** L1003
[8] Manykin É A 2002 *Laser Phys.* **12** 435
[9] Holmlid L 2001 *Astrophys. J.* **548** L249
[10] Svensson R and Holmlid L 1999 *Phys. Rev. Lett.* **83** 1739
[11] Wang J and Holmlid L 2002 *Chem. Phys.* **277** 201
[12] Badiei S and Holmlid L 2002 *Int. J. Mass Spectrom.* **220** 127
[13] Badiei S and Holmlid L 2002 *Chem. Phys.* **282** 137
[14] Svensson R, Holmlid L and Lundgren L 1991 *J. Appl. Phys.* **70** 1489

[15] Stebbings R F and Dunning F B (ed) 1983 *Rydberg States of Atoms and Molecules* (Cambridge: Cambridge University Press)
[16] Gallagher T F 1994 *Rydberg Atoms* (Cambridge: Cambridge University Press)
[17] Holmlid L 1998 *J. Phys. Chem.* A **102** 10636
[18] Wang J, Engvall K and Holmlid L 1999 *J. Chem. Phys.* **110** 1212
[19] Holmlid L and Menon P G 2001 *Appl. Catal.* A **212** 247
[20] Kotarba A, Baranski A, Hodorowicz S, Sokolowski J, Szytula A and Holmlid L 2000 *Catal. Lett.* **67** 129
[21] Möller K and Holmlid L 1988 *Surf. Sci.* **204** 98
[22] Wang J and Holmlid L 1998 *Chem. Phys. Lett.* **295** 500
[23] Wang J and Holmlid L 2000 *Chem. Phys.* **261** 481
[24] Wang J and Holmlid L 2000 *Chem. Phys. Lett.* **325** 264
[25] Svensson R and Holmlid L 1992 *Proc. 27th Intersociety Energy Conversion Engineering Conf. (IECEC 1992, San Diego)* vol 3 (Warrendale, PA: Society of Automotive Engineers) p 537
[26] Anderson W R, Veale J R and Gallagher T F 1998 *Phys. Rev. Lett.* **80** 249
[27] Mourachko I, Comparat D, de Tomasi F, Fioretti A, Nosbaum P, Akulin V M and Pillet P 1998 *Phys. Rev. Lett.* **80** 253
[28] DAMOP 2000 Collective effects in Rydberg matter *Bull. Am. Phys. Soc.* **45** session J4
[29] Raimond J M, Vitrant G and Haroche S 1981 *J. Phys. B: At. Mol. Phys.* **14** L655
[30] Vitrant G, Raimond J M, Gross M and Haroche S 1982 *J. Phys. B: At. Mol. Phys.* **15** L49
[31] Kotarba A, Engvall K, Pettersson J B C, Svanberg M and Holmlid L 1995 *Surf. Sci.* **342** 327
[32] Engvall K, Kotarba A and Holmlid L 1994 *Catal. Lett.* **26** 101
[33] Wang J and Holmlid L 1999 *Surf. Sci.* **425** 81
[34] Peng X, Abbott J E and Kong W 2000 *J. Chem. Phys.* **113** 3020
[35] Holmlid L 2002 *Chem. Phys. Lett.* at press
[36] Vrakking M J J and Lee Y T 1995 *J. Chem. Phys.* **102** 8833
[37] Sun X and MacAdam K B 1993 *Phys. Rev.* A **47** 3913
[38] Dutta S K, Feldbaum D, Walz-Flannigan A, Guest J R and Raithel G 2001 *Phys. Rev. Lett.* **86** 3993
[39] Greene C H, Dickinson A S and Sadeghpour H R 2000 *Phys. Rev. Lett.* **85** 2458
[40] Boisseau C, Simbotin I and Côté R 2002 *Phys. Rev. Lett.* **88** 133004
[41] Killian T C, Kulin S, Bergeson S D, Orozco L A, Orzel C and Rolston S L 1999 *Phys. Rev. Lett.* **83** 4776
[42] Holmlid L 2001 *Phys. Rev.* A **63** 013817
[43] Holmlid L 2001 *Langmuir* **17** 268
[44] Robinson M P, Tolra B L, Noel M W, Gallagher T F and Pillet P 2000 *Phys. Rev. Lett.* **85** 4466
[45] Olsson B E R, Svensson R and Davidsson J 1995 *J. Phys. D: Appl. Phys.* **28** 479
[46] Åman C, Petterssson J B C, Lindroth H and Holmlid L 1992 *J. Mater. Res.* **7** 100
[47] Åman C, Petterssson J B C and Holmlid L 1990 *Chem. Phys.* **147** 189
[48] Holmlid L, Petterssson J B C, Åman C, Lönn B and Möller K 1992 *Rev. Sci. Instrum.* **63** 1966
[49] Wallin E, Hansson T and Holmlid L 1992 *J. Phys.: Condens. Matter* **4** 9803
[50] Wallin E and Holmlid L 1992 *Chem. Phys.* **159** 313
[51] Olsson B E R, Hansson T and Davidsson J 1997 *J. Phys. D: Appl. Phys.* **30** 1683