Electronic Raman Processes in Rydberg Matter of Cs: Circular Rydberg States in Cs and Cs$^+$

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We report the first Raman study of the Rydberg matter form of Cs, using a ns pulsed dye laser. Electronic Raman anti-Stokes and mixed Stokes processes are detected in the range 290–920 nm after nonresonant excitation at 564 nm. No fluorescence is observed. The anti-Stokes transitions are from a high circular Rydberg state to a low circular state $8J$ in Cs$^+$, close to $4F$ in Cs. The Stokes transitions are mixed in one more step with the laser radiation, and go from low circular states to Rydberg matter states. The transitions observed agree well with transitions in Cs$^+$.

Since the first experimental observations of Rydberg matter (RM) in cesium metal plasmas [1,2], spectroscopic studies of this highly excited form of condensed matter have been needed. A few such studies have been made, such as an emission spectroscopy study in the visible of Cs(RM) [3], and an emission study of the light emitted during the explosion of this energetic matter [4]. Recently, the first laser induced fragmentation study of RM clusters (small particles of RM) was published [5], giving the first microscopic proof of the existence of this special form of matter. We now report a new type of study, which gives unique information about the electronic processes in RM.

The prediction of RM, i.e., a condensed phase of excited atoms or molecules, was made in the 1980s by Manykin *et al.* [6,7]. Quite complete quantum mechanical calculations were performed to predict a range of properties [8,9], and the lifetime of RM was shown to be years for rather low excitation levels. This is not unlikely considering the long radiative lifetimes of even isolated circular Rydberg atoms. The lifetime averaged over the angular momentum quantum numbers is 0.18 s at $n = 40$ and 17 s for $n = 100$ [10]. The main deexcitation processes were found to be Auger processes [9], involving two electrons which simultaneously change their energy and orbital angular momentum.

The RM is proposed to take part in many natural phenomena both on earth [11] and in interstellar space [12]. It is on the borderline between the classical and quantum mechanical descriptions of matter, and thus of large fundamental importance. Because of the low surface work function of RM, predicted and also verified experimentally [2,13,14] to be in the range 0.2–0.8 eV, many applications seem possible within power electronics, energy conversion, and optoelectronics.

By considering the dynamics of the electrons in the RM, a better understanding has recently been found [15].

The very high quantum numbers involved mean that a classical description of the electron motion should be possible. If a bonding shall exist, all of the highly excited electrons have to move in one plane [15]. Thus, RM, at least in its highly excited states, has the form of planar monolayers of atoms. The correlation forces keep the electrons as far apart as possible.

We report here on Raman processes in Rydberg atomic states within RM. While Rydberg atoms and molecules are widely studied, the use of Raman scattering to study their properties seems to be seldom employed. For example, in the otherwise excellent book by Gallagher from 1994 [16] Raman scattering is not mentioned at all. Stimulated electronic Raman scattering has been studied in K vapor, using ps pulses to form tunable IR pulsed radiation [17]. The vapor of In was employed to give stimulated electronic Raman scattering after resonance excitation [18]. Vacuum ultraviolet emission was studied in Na vapor under two-photon resonance excitation followed by hyper-electronic Raman scattering [19]. No previous publications exist on the non-resonant Raman observation of Rydberg-Rydberg transitions in alkali metal plasmas or vapors, probably since these Raman processes can only be observed in an RM medium.

The experiments are carried out in a high vacuum (HV) apparatus with a base pressure of 1×10^{-5} mbar. It has been fully described previously [1,20]. The principle of the experiment is shown in Fig. 1. Cesium vapor leaves the multi-hole array in the front of the source, forms Rydberg states at the graphite covered electrode surfaces, and condenses to Rydberg matter in the interelectrode space. The Cs reservoir is held at 600 K, giving a vapor pressure of 2 mbar, and the vapor is superheated to 800 K in the front part of the source. Thus, the ground state Cs$_2$ dimer content is negligible. The Mo emitter in contact with the vapor is heated to a temperature in the range of 1200–2000 K, which means that the dimer content is

decreased even further. The desorption of Cs atoms from graphite covered surfaces gives Rydberg states, since no Cs state on the surface correlates with the ground state outside the surface [21–23].

A Nd:YAG laser with a maximum power of 1 W at 532 nm wavelength and 7 ns pulses with a 10 Hz repetition rate is used to pump a dye laser (Lambda-Physik). Rhodamine 6G in the dye laser gives a radiation at 564 nm in 5 ns pulses at a maximum power at the HV chamber of 200 mW. The linewidth of the laser is 0.15 cm^{-1}, which corresponds to 5×10^{-3} nm. Since the laser beam diameter is approximately 3 mm without focusing, the power density is less than 3 W cm^{-2} without focusing. A single lens with a focal length of 0.6–0.8 m is used to focus the laser beam in most experiments. The laser beam enters through a BK7 glass window in the vacuum chamber and passes between the two electrodes. Its plane of polarization is in the vertical direction, perpendicular to the plane of the cut through the apparatus in Fig. 1. The light from the interelectrode space is taken out either through a quartz fiber looking down in the vertical direction or through a quartz fiber outside the vacuum, behind the dichroic mirror deflecting the laser beam into the chamber. The spectroscopic analysis is done by a Spex 500M equipped with a Hamamatsu R928 multiplier, which has a sensitivity range 185–900 nm. The resolution of the spectrometer is low, of the order of 1 nm. The laser induced peaks are observed on a 200 MHz oscilloscope with no further amplification.

We report now on the spectroscopy of the fast peaks created by the laser pulses, which decay with the time constant of the measuring circuit. The experimental results are obtained under various conditions such as Cs pressure (approximately 1 mbar), interelectrode spacing (0.5–6 mm), emitter temperature (typically, 1500 K), and quartz fiber position. One important parameter is the direction of the electric field [1,3] giving two modes of operation: the ion mode, with the hot emitter at a

negative voltage of 2–5 V emitting electrons onto the RM surface; and the RM mode, with the emitter at a similar positive voltage and the large electron current to the emitter supported by the relatively cold source (collector) due to the extremely low work function of the RM which covers it [2,14]. In both modes, Rydberg atoms are formed in contact with the graphite covered electrode surfaces and condensation takes place, but in the ion mode there is no complete condensation of RM over all of the interelectrode space.

Two types of observed lines are summarized in Tables I and II. The probable error in the line positions is ±0.4 nm. In the following, a level named nR means a high Rydberg state with principal quantum number n. The R stands for F and higher term values. Only two lines which may be due to fluorescence have been observed, namely, the transitions $7P_{1/2} \rightarrow 6S_{1/2}$ and $6P_{3/2} \rightarrow 6S_{1/2}$. Raman scattering, together with mixing processes of the type described below, may, however, also give rise to these lines. The observed continuous Raman bands are probably due to the continuum states in the conduction band of the RM and to RM cluster [5] deexcitation processes. Here, we will report only on the line (narrow band) part of the observations.

Most of the observed anti-Stokes transitions are from intermediate Rydberg levels down to $8J$ in Cs$^+$, or alternatively to $4F$ in Cs. A set of such lines is shown in Table I, giving good agreement with the calculated values, but with a common shift relative to the calculations (see below). In the calculations for Cs$^+$, the Rydberg energy levels are taken to be 4 times lower than for Cs (levels encircling Cs^{2+} instead of Cs$^+$), but otherwise standard data are used. The lowest transition in Table I cannot be a transition in Cs, but has to be a transition in Cs$^+$ to $8J$. The higher transitions may belong both to Cs, in the form of free Rydberg atoms, and to Cs$^+$, in the form of core ions in RM. However, the agreement with the theoretical values turns out to be considerably better for transitions in Cs$^+$.

The large number of anti-Stokes lines shows that the Cs atoms in the interelectrode space are highly excited, probably since they are surrounded by RM fragments. Similar transitions are not observed in emission, which means that the Raman transitions have a high probability due to their connection with the polarizability. In Rydberg atoms, the polarizability α increases as the principal quantum number n^7, while the dipole moment only increases as n^2. Thus, it is better to probe for Rydberg atoms by Raman techniques than by other laser spectroscopic methods.

It is appropriate to ask how the intermediate Rydberg states probed by the anti-Stokes Raman have become excited. One can immediately discard laser excitation, due to the very short lifetimes of intermediate excited states. We conclude that the reason for the high excitation levels is the thermal excitation of Rydberg states and the condensation of them to form RM. The fact that the
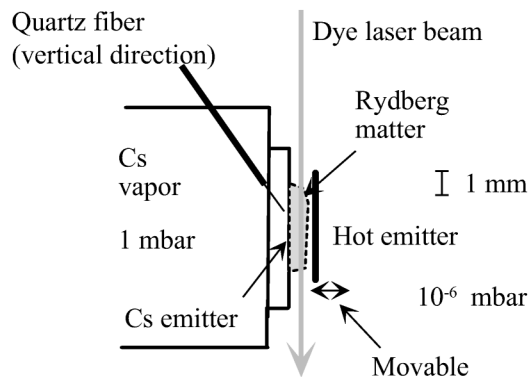

FIG. 1. Experiment in a horizontal view, with vacuum walls left out. The quartz fiber approaches the RM region from the vertical direction. The hot emitter can be moved out to 6 mm distance during the experiment. See also Ref. [20].

TABLE I. Anti-Stokes Raman lines observed in ion mode, with a negative voltage applied to the hot emitter. Laser line at 17 730 cm^{-1}. The nR indicates a high Rydberg state. Typical uncertainty in λ is ±0.4 nm, corresponding to approximately ±20 cm^{-1}.

Observed λ (nm)	Anti-Stokes (cm^{-1})	Transition in Cs	Calc. (cm^{-1})	Transition in Cs$^+$	Calc. (cm^{-1})
418.4	6170	$13R \rightarrow 4F$	6290	$26R \rightarrow 8J$	6210
426.6	5710	$10R \rightarrow 4F$	5840	$20R \rightarrow 8J$	5760
438.2	5090	$8R \rightarrow 4F$	5220	$16R \rightarrow 8J$	5140
449.0	4540	$7I \rightarrow 4F$	4700	$14R \rightarrow 8J$	4620
496.0	2430	$5G \rightarrow 4F$	2550	$10R \rightarrow 8J$	2470
522.6	1410	$\cdots$	$\cdots$	$9R \rightarrow 8J$	1440

anti-Stokes lines are observed in the so-called ion mode indicates that the RM is decomposed slightly by the thermal electrons from the emitter, which impact on the RM with a few eV energy. In this way, the deexcitation by Raman transitions becomes possible, while such a process is not observed for the RM mode without electron impact on the RM.

In Table I it is shown that the observed transitions in general are 40 cm^{-1} smaller than the calculated Raman transitions for Cs$^+$. The most likely reason for this is that the observed lines are caused by two-electron transitions, with an electron being promoted from a low RM state to a high RM state simultaneously with the electron deexcitation shown in Table I. Such an effect will be caused by a strict angular momentum conservation, but the size of this effect is not known. Therefore, this would give a smaller value of the observed transition, and with an excitation from $n = 50$ to $n = 80$ the shift would be 27 cm^{-1}.

Just a few Stokes lines can be observed, mainly in the RM mode. The most prominent one is at 911 nm, which corresponds to a Stokes transition of 6750 cm^{-1}. It is at the start of a more or less continuous region at even longer wavelengths. This line is interpreted as a transition to an RM level, RM $\leftarrow 4F$ in Cs, or, more likely, RM $\leftarrow 8J$ in Cs$^+$. That so few Stokes lines are observed is expected since all Cs atoms are part of the RM phase, and thus their outermost electrons are already in highly excited states. Since $4F$ in Cs is the lowest Rydberg level, it functions as the lowest state of the Cs atoms in the RM.

TABLE II. Stokes Raman transitions mixed with the laser line at 17 730 cm^{-1}. Observed in RM mode, with a positive voltage applied to the hot emitter. The nR indicates a high Rydberg state. Typical uncertainty in λ is ±0.4 nm, corresponding to approximately ±20 cm^{-1}. ω_E is the experimental transition wave number, as given in the text.

Observed λ (nm)	Wave number (cm^{-1})	ω_E (cm^{-1})	Transition in Cs$^+$	Calc. (cm^{-1})
347.2	28 800	6660	$55R \leftarrow 8J$	6710
374.6	26 700	8770	$55R \leftarrow 7I$	8810
428.4	23 340	12 120	$55R \leftarrow 6H$	12 050

This 911 nm Stokes wave can mix with the laser light again, to give a line at 353 nm. It can also be observed antiparallel to the laser beam, with an optical fiber behind the laser mirror outside the chamber, and is thus likely to be due to a stimulated Raman effect. The wave number of the observed line is $\omega_{\text{obs}} = 2\omega_L - \omega_E$, where ω_L is the laser wave number and ω_E is the wave number of the electronic transition. This line is included in Table II together with a few other lines due to the same type kind of Stokes-laser mixing. The transitions observed probably involves two electrons, as discussed for the anti-Stokes transitions above. A common upper level corresponding to $n = 55$ is chosen for simplicity. The corresponding Stokes lines have not been observed since they lie outside the spectral sensitivity of the photomultiplier.

The observed transitions are transitions between circular Rydberg states, most likely in Cs$^+$. The two levels, Cs$^+$ $8J$ and Cs $4F$, have almost the same energy relative to the ionization limit for the Rydberg electron (see Fig. 2), but the transitions involving Cs$^+$ agree better with observations. Several other states, namely, Cs$^+$ $6H$, $7I$,
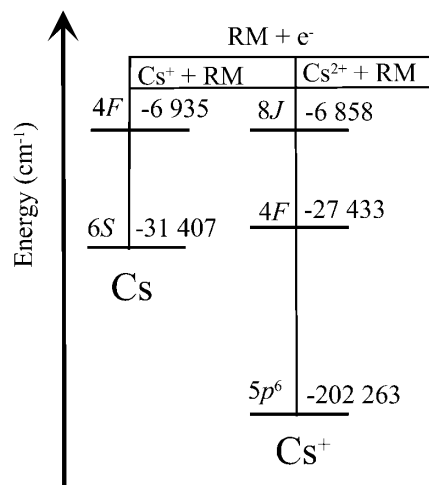

FIG. 2. Diagram of some levels of importance in Cs and Cs$^+$. The vertical axis is not to scale. Cs$^+$ + RM indicates that the electron is transferred into the delocalized RM electronic states.

and $9R$ have no counterpart in Cs. These states are involved in the observed transitions, and thus the conclusion that the transitions take place in Cs^+ has to be drawn. From the theoretical description of RM [6,7,15] it is clear that the outermost electron in each Cs atom is excited into the conduction band (the RM electrons). The only particles which exist in the RM besides the electrons are the Cs^+ ions. This supports the description of the phase under investigation as RM.

The origin of the considerable excitation energy in the Cs^+ states should also be discussed. To lift the second electron up to the high Rydberg states requires approximately 23 eV. We propose the following process, which is supported by mass spectrometric studies. In a 7-atom RM cluster, which is the smallest cluster observed in Ref. [5], the total excitation energy is close to 27 eV. If most of this energy can be pooled into one of the atoms by, e.g., the laser pulse, the excitation of Cs^+ is energetically possible. The energy pooling process is supported by other experiments. Molecular beam sampling mass spectrometric studies of the atomic and molecular flux from the RM region have been done previously [24]. Weak field ionization was used to ionize the flux at field strengths less than 600 V cm^{-1}. One of the largest mass peaks was Cs^{2+}, which is likely formed from cluster deexcitation. To prove that this considerable amount of energy was available in the flux from the RM, the excitation energy transfer was studied in Ar, N_2, O_2, and CO_2. The collision partners became ionized and dissociated as expected for an excitation energy transfer of $14-24$ eV. Thus, the available information supports a process involving the excitation energy in a Rydberg matter cluster.

In conclusion, this study is the first optical spectroscopy study of Rydberg matter with a laser probe. It is concluded that the Raman process is very sensitive to excited high-l (circular) Rydberg states in the Rydberg matter, in a most useful way since very few alternative methods exist for such states within Rydberg matter or outside it. The transitions which are probed in the Rydberg matter are often Cs^+ core ion transitions. The lowest common level in the transitions is $4F$ for Cs and $8J$ for Cs^+. The observations of transitions in Cs^+ strongly support the theoretical description of Rydberg matter.

[1] R. Svensson, L. Holmlid, and L. Lundgren, J. Appl. Phys. **70**, 1489 (1991).
[2] R. Svensson and L. Holmlid, Surf. Sci. **269/270**, 695 (1992).
[3] B. E. R. Olsson, R. Svensson, and J. Davidsson, J. Phys. D **28**, 479 (1995).
[4] B. E. R. Olsson, R. Svensson, and J. Davidsson, *Proceedings of the 30th Intersociety Energy Conversion Engineering Conference (IECEC 1995)* (American Society of Mechanical Engineers, New York, 1995), Vol. 3, p. 137.
[5] J. Wang and L. Holmlid, Chem. Phys. Lett. **295**, 500 (1998).
[6] É. A. Manykin, M. I. Ozhovan, and P. P. Poluéktov, Sov. Phys. Tech. Phys. Lett. **6**, 95 (1980).
[7] É. A. Manykin, M. I. Ozhovan, and P. P. Poluéktov, Sov. Phys. Dokl. **26**, 974 (1981).
[8] É. A. Manykin, M. I. Ozhovan, and P. P. Poluéktov, Sov. Phys. JETP **75**, 440 (1992).
[9] É. A. Manykin, M. I. Ozhovan, and P. P. Poluéktov, Sov. Phys. JETP **75**, 602 (1992).
[10] I. L. Beigman and V. S. Lebedev, Phys. Rep. **250**, 95 (1995).
[11] É. A. Manykin, M. I. Ozhovan, and P. P. Poluéktov, J. Mosc. Phys. Soc. **8**, 19 (1998).
[12] L. Holmlid (to be published).
[13] R. Svensson, K. Engvall, L. Holmlid, J. Braun, and L. Lundgren, *Proceedings of the Eleventh International Conference on Magnetohydrodynamic Electrical Power Generation, Beijing, 1992* (International Academic Publishers, Beijing, 1992) Vol. 1, p. 248.
[14] L. Holmlid and E. A. Manykin, J. Exp. Theor. Phys. JETP **84**, 875 (1997).
[15] L. Holmlid, Chem. Phys. **237**, 11 (1998).
[16] T. F. Gallagher, *Rydberg Atoms* (Cambridge University Press, Cambridge, England,1994).
[17] H. Ohde, S. Lin, A. Minoh, F. O. Shimizu, M. Aono, and T. Suzuki, Appl. Phys. B **62**, 15 (1996).
[18] S. Chilukuri, Phys. Rev. A **54**, 908 (1996).
[19] T. S. Yih, B. J. Pong, W. T. Cheng, and C. C. Chu, Opt. Quantum Electron. **28**, 1463 (1996).
[20] R. Svensson, B. Lönn, and L. Holmlid, Rev. Sci. Instrum. **66**, 3244 (1995).
[21] L. Holmlid, Chem. Phys. **230**, 327 (1998).
[22] L. Holmlid, J. Phys. Chem. A **102**, 10 636 (1998).
[23] J. Wang, K. Engvall, and L. Holmlid, J. Chem. Phys. **110**, 1212 (1999).
[24] J. Lundin and L. Holmlid, J. Phys. Chem. **95**, 1029 (1991).