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The alkali metal atmospheres on the Moon and Mercury: Explaining the stable exospheres by heavy Rydberg Matter clusters

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Abstract

Despite recent progress in the modeling of alkali atmospheres like those around the Moon and Mercury, many problems still exist. It is proposed that Rydberg Matter (RM) clusters containing Na and K atoms are the main part of the alkali atmospheres of the Moon and Mercury, forming large clouds. RM clusters are studied in the laboratory with laser fragmentation and laser spectroscopy methods. Due to the very large collision cross sections of Rydberg atoms and RM clusters, the atmospheres are not collision free, as normally assumed based on the low densities of free alkali atoms. The non-escaping radial density variation for the Na atoms, observed, e.g., on the Moon, and the Maxwellian velocity distributions observed on Mercury are caused by a true atmosphere with collisional equilibration; this process is not possible in an exosphere. Fast alkali atoms are released from the RM clusters already at large heights by solar photons and charged particle impact. The kinetic temperatures derived for the atmospheres agree with the quantized energy release. The cluster model predicts that the rate of loss from the surface is much smaller than for a purely atomic model, since the transient storage is in the RM cluster form in the atmosphere and not at the surface. The conductance of the atmosphere is of the order of 100 S due to the facile collisional ionization of the RM clusters. The apparent depletion of K in the atmosphere of Mercury is explained.

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Keywords: Moon; Mercury; Atmospheres; Rydberg Matter; Cluster

1. Introduction

The alkali atom atmospheres (often considered to be exospheres) observed around the Moon and Mercury from the atomic resonance fluorescence are intriguing and pose several problems, that are discussed, e.g., by Stern (1999), Mendillo et al. (1999) and Madey et al. (2002). Some of the longstanding problems may have been solved by the quite complete Monte-Carlo simulation of the Mercury atmosphere by Leblanc and Johnson (2003). This simulation takes into account many of the boundary and throughput problems like the total amount of Na entering the atmosphere, the large number of emission processes contributing to form the atmosphere, the total loss from the atmosphere, etc. However, many of the more internal problems remain, e.g., (1) the origin of the high-velocity (non-thermal) component in the atmosphere, concluded to exist from the very large extension of the alkali atmospheres, (2) the origin of the high temperature (thermal) velocity distributions and high average velocity of the alkali gas, with no accommodation to the low surface temperature, (3) the origin of the unusual radial variation of the density at the Moon that corresponds to neither an escaping nor a stationary atmosphere, (4) the reason why the alkali atom density in the atmosphere depends directly and in a complex way on the sunlight. The questions about the thermal desorption and the surface accommodation have been covered by Leblanc and Johnson (2003), but with the more complex model of the atmosphere used here a few problems remain also in this area (to be published elsewhere).

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In this contribution, I want to draw the attention to a quite comprehensive solution to these problems, namely the formation of a collisional atmosphere of alkali Rydberg species, notably clusters of the so-called Rydberg Matter (RM) in the planetary (satellite) atmospheres. Due to the large collision cross sections involving Rydberg species and RM clusters, the alkali atmosphere is not collision free. The RM clusters provide a temporary storage of the alkali atoms, which are released as Rydberg atoms and small RM clusters with high kinetic energy by radiation. After collisional or radiative de-excitation to lower excited species, the alkali atoms become eventually thermalized in the atmosphere before they are again incorporated into RM clusters. The atmosphere has a higher temperature than the surface, as observed. The alkali atoms are detected by their D line emission, excited either as fluorescence (resonance) radiation from the sunlight, or from the de-excitation of Rydberg atoms released from the RM clusters. The heavy and slow clusters will give a more stable atmosphere due to the resulting smaller velocities and lower loss rate than possible if only atoms exist in the extended exosphere, and they will provide a temporary storage for the alkali atoms even far from the surface. This proposal is based on extensive experimental results concerning RM from our group. Our early results on RM and desorption of Rydberg species have been independently confirmed by experiments in other groups (Yarygin et al., 2003; Kotarba et al., 2000a, b, 2001).

RM was first proposed to exist by Manykin et al. (1980, 1981) and the theory has later been further developed (Manykin et al., 1992a, b, 2000; Holmlid, 1998a). The existence of RM in interstellar space is inferred from the interpretation of the so-called unidentified infrared bands (UIR) (Tokunaga, 1997; Geballe, 1997) as due to de-excitation processes in RM (Holmlid, 2000, 2001a). Recently, the stimulated emission from RM was studied in detail and shown to give good agreement with theory and with the UIR bands. A widely tunable IR laser has been constructed (Badiei and Holmlid, 2003) giving the same emission bands as seen in the UIR spectra. The stimulated emission from RM has been studied in the range 800–16,000 nm (Holmlid, 2004a). This confirms that RM is in an excited long-lived state. RM has been proposed to be at least part of the dark matter in the universe (Badiei and Holmlid, 2002a), and has been shown to explain the Faraday rotation results obtained for transmission of radiofrequency waves in intergalactic space (Badiei and Holmlid, 2002b). The studies of H_2 Rydberg molecules forming RM clusters (Wang and Holmlid, 2002) and of H atom RM (Badiei and Holmlid, 2004) are of direct relevance for RM processes in space, as are also the calculations of 60 diffuse interstellar bands from transitions in RM clusters (Holmlid, 2004c), and the interpretation of the quantized redshifts observed from galaxies in the local supercluster by stimulated Raman processes in RM clusters (Holmlid, 2004b).

2. Properties of RM

A short summary of the most pertinent properties of RM is given here. For a more complete view, see other publications from our group. In Holmlid (2002), a short review of the methods used to form RM in the laboratory is given.

RM is an almost metallic phase of low density, built up by planar clusters with a thickness of one atomic layer at the densities of interest in the atmospheres. These planar clusters have six-fold symmetry in their most stable form, and contain a number N of 7, 19, 37, 61 or 91 atoms (Holmlid, 1998a; Wang and Holmlid, 1998, 2000, 2002) (see Fig. 1). These numbers are the so-called magic numbers for planar clusters. RM can contain any kind of atom or small molecule initially in a circular Rydberg state, and the clusters are easily formed in desorption of alkali atoms from non-metal surfaces. Circular Rydberg states with large principal quantum number n and also large angular momentum quantum number l slightly less than n are very long lived. The Rydberg electrons in the clusters are delocalized as in a metal, but retain their large angular momentum. An RM cluster can only be stable for a long time if all species in the cluster have the same value of n; the bonding in an RM cluster requires strict electron correlation (Holmlid, 1998a). This condition is met primarily by sharing of excitation energy between the species incorporated in the cluster so that they all receive the same excitation level. Different clusters have different n values, and a distribution of n values exists in the atmospheres.

Quantum mechanical calculations were performed to predict a range of properties of RM (Manykin et al., 1992a, b). RM can be produced in various total pressure regimes, and over-dense RM has been produced at alkali pressures of 1 mbar and at high temperatures in a large number of experiments during the last 10 years. Methods

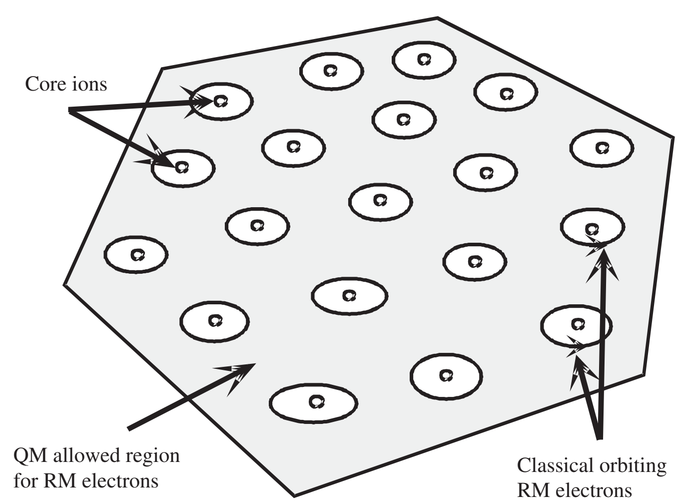

Fig. 1. A cluster of Rydberg Matter with 19 atoms (or molecules). This type of six-fold symmetry cluster is one of the main types found in experiments on Rydberg Matter clusters in ultra-high vacuum.

to produce RM in cluster form at low total pressure (down to 10^{-9} mbar) and low temperatures have been developed somewhat later (Wang and Holmlid, 1998, 2000). The alkali atom pressure in these experiments is 10^{-12} mbar and lower.

The bonding distances between the atoms and molecules in the clusters at an excitation level of $n = 100$ are around 1 μm, and the diameters of the clusters are a few μm.

Manykin et al. calculated the radiative lifetime of RM in various excitation levels, and found it to be long, of the order of 100 years at an excitation level of $n = 16$. The main de-excitation processes for RM were found to be Auger processes (Manykin et al., 1992b), involving two electrons which simultaneously change their energy and orbital angular momentum. At $n = 80$ which is a probable value for the atmospheres discussed, the radiative lifetime would be extremely large (order of 1 Gy) from a simple extrapolation of this calculation. In the laboratory with collisional quenching as well, the lifetime of RM is of the order of 1 min–1 h (Svensson and Holmlid, 1999, Holmlid, 2001b), depending on the pressure and temperature.

The question of the stability of RM and RM clusters is often posed. It should be observed that Rydberg states are formed by recombination of electrons and ions, e.g., after ionization of ground-state species by ionizing radiation, and that RM can be thought of as being formed by condensation of circular Rydberg states. Thus, one of the sources of the excitation energy in RM is energetic ionizing radiation. In the laboratory, the RM clusters survive intense focused laser light in the form of nanosecond pulses. Multiphoton processes appear to be most important for the fragmentation processes observed (Wang and Holmlid, 1998, 2000). One reason for this may be that the RM electrons are delocalized, which will give collective excitation and not just ionization and bond destabilization through the removal of a single electron. Arguments based on the small size of the cavities surrounding the core ions in RM have further been used to explain the very small coupling between RM and electromagnetic radiation (Badiei and Holmlid, 2002b).

The planetary atmospheres will probably be much calmer than the laboratory vacuum chamber with a laser intensity of 10^9 W cm^{-2} in the pulses, so the stability of RM is probably sufficient for it to survive for a very long time. The contact with ground-state atoms and molecules seems in the laboratory to mainly give incorporation of the ground-state species into the RM clusters with excitation energy sharing within the RM cluster. This is observed as the formation of clusters with masses corresponding to mixed clusters. Thus, collisions with slow particles do not destroy the RM clusters. The direct addition of Rydberg species to RM clusters was studied experimentally by Wang et al. (1999). Collisions with charged particles may give displacement of electrons in the same way as strong laser pulses do.

The main fragmentation process taking place in RM as a result of intense laser pulses and possibly also of collisions with charged particles takes the form of a Coulomb explosion. Such a process is well known to exist in cluster and molecule fragmentation. In RM, the electrons move coherently in circular orbits around the ion cores, which means that they shield the ion cores from their ion neighbors, giving a net bond energy (Holmlid, 1998a). This is similar to ordinary metal bonding, but in the RM the electrons are in orbits resembling high circular Rydberg orbits, giving the material a planar cluster form. When two electrons on neighboring atoms (or molecules) in the RM layer are excited, they move into localized orbitals. This means that they can no longer shield the ion cores from their repulsive interaction. This means that a repulsive Coulomb force breaks the cluster apart, usually giving emission of one small fragment from a larger cluster or cloud.

When such a repulsive Coulomb force breaks a cluster apart, the force is between two positive charges in the form of two alkali ions. The kinetic energy transferred to the relative motion between the two separating charges after reaching a large distance is equal to the Coulombic energy:

$$W = e^2\,(4\pi\varepsilon_0 d)^{-1}, \tag{1}$$

where d is the initial bonding distance between the two charges, e the elementary charge and ε_0 the vacuum permittivity. This equation is confirmed experimentally, even for K RM clusters (Badiei and Holmlid, 2002c, d, 2004). The time-of-flight (TOF) for the particles released by such Coulomb explosions is studied in many experiments. It is calculated with $d = 2.8n^2a_0$, where n is the principal quantum number and a_0 the Bohr radius. The factor 2.8 is found from the classical calculations of the minimum energy states of RM (Holmlid, 1998a). The TOF is then found from $t = s/v_0$, where s is the distance to the detector and $v_0 = (2W/M)^{1/2}$. The cluster mass M is equal to Nm, where m is the monomer mass and N the number of monomers in the cluster. The probability distribution of v (for the flux reaching a detector with a finite opening angle) is

$$P(v) \propto v_0^2 \exp(-Mv^2/(2kT)), \tag{2}$$

where T is the observed temperature from the TOF distribution. The factor v_0^2 means that a density velocity distribution is used. This type of analysis has been used in several experiments on laser fragmentation of RM. See, e.g., Wang and Holmlid (2000) and Badiei and Holmlid (2002c, d).

3. Results

3.1. Collisions in the atmosphere

It is usually believed that the alkali atmospheres of Mercury and the Moon are collision free, due to their assumed low densities. This is contrary to observations, e.g., of the radial density variation on the Moon studied in detail by Mendillo et al. (1999). They find that the Na atmosphere is neither simply escaping nor bound. The careful temperature measurement by Killen et al. (1999) at Mercury shows that the alkali gas temperature of the atmosphere is much higher than the surface temperature. This effect is likely due to the ionizing energy flux from the Sun to the atmosphere which excites the alkali atmosphere, while the surface may not be reached or reflects some of this influx. Killen et al. observe Maxwellian velocity distributions, which indicates an ordinary atmosphere with collisions thermalizing the initially fast alkali atoms in some way formed by the energetic radiation from the Sun (see further below). A high temperature (i.e., thermalized velocity components) cannot be maintained without collisions in the gas phase. Without collisions, a high translational energy may be obtained by energetic processes, e.g., in desorption, but Maxwellian velocity distributions would not exist, contrary to observations.

It is first of all necessary to determine whether a Rydberg-rich alkali atmosphere (Rydberg species, RM clusters) will be collision free or not. Rydberg species are well known to have extremely large collision cross sections σ, and this is probably true also for RM clusters. The physical dimensions can be considered as a first approximation, especially for Rydberg—ground-state collisions. Of course, the exact process must be specified for the collision, and if free electrons also exist in the Rydberg-rich atmosphere, electron—Rydberg collisions will also be important. Using the geometrical dimensions, a circular Rydberg atom in $n = 50$ has a collision cross section of the order of $5 \times 10^4\,\mathrm{nm}^2$, compared to typically $10^{-2}\,\mathrm{nm}^2$ for a ground-state atom. Absolute cross-section measurements for Rydberg metal atoms under relevant conditions are quite rare, but Kano et al. (1985) give $4.8\,\mathrm{nm}^2$ for the resonant charge transfer between Rb atoms in nP (not circular) Rydberg states at $n = 35-60$ in collisions with ground-state Rb at 420 K. Theoretical studies (Fabrikant, 1993) predict cross sections of $10^4\,\mathrm{nm}^2$ in collisions between Ca Rydberg atoms and ground-state Ca atoms, and experiments have taken advantage of the huge cross section for this type of process (McLaughlin and Duquette, 1994). A few studies exist of collisions of Rydberg-rich gases, which should be the most relevant type of laboratory system. Olsson et al. (1997) observe Rydberg charge transfer processes with cross sections of 40–80 nm^2, while Hagström et al. (1998) derive cross sections of 400 nm^2 for electron drift in a Rydberg gas. Li et al. (2004) discuss the cross sections in a cold ("frozen") Rydberg gas, and conclude that they are one order of magnitude larger than the geometrical cross sections.

However, collision processes of the charge transfer type are probably not the most important type of process for planetary atmospheres. Instead, the collisions between Rydberg atoms and RM clusters, and collisions between RM clusters should be the important ones for the redistribution of kinetic energy and for the decreased rate of loss from the planetary surface. Thus, the geometrical dimensions should be decisive as some kind of lower limit. An average RM cluster with 37 atoms in excitation level n has a geometrical area $3.75\pi \times 2.8^2 n^4 a_0^2$. At $n = 40$, the cross section is then approximately $7 \times 10^{11}\,\mathrm{nm}^2$ or $7 \times 10^{-7}\,\mathrm{m}^2$, while at $n = 6$, the cross section is $3.5 \times 10^8\,\mathrm{nm}^2$. Note that a distribution of cluster excitation levels and sizes will exist in the planetary atmospheres.

The long-range interaction between two polarizable collision partners depends usually directly on the product of the polarizabilities, e.g., in the universal dispersion interaction. This type of interaction determines the deflection of a particle passing a scattering partner at large distance, and is thus the most relevant interaction for determining if an atmosphere is collision free, allowing direct escape from the planetary surface, or not. For circular Rydberg species, the polarizability varies as $\alpha \propto n^7$, which means that at $n = 50$, the collision cross sections for Rydberg atoms may be of the order of $10^9\,\mathrm{nm}^2$. If such a Rydberg species approaches an RM cluster with a large number of easily polarizable species, the cross section could be larger by several orders of magnitude. The values for interaction of Rydberg species and RM clusters are not well known, but a reasonable first estimate may be $\sigma = 10^9\,\mathrm{nm}^2$, or $10^{-9}\,\mathrm{m}^2$ for low values of n in the RM cluster, as calculated above. The expression $f/f_0 = \exp(-n\sigma l)$ describes how large the attenuation of a flux density f_0 is in a medium with density n, e.g., for a Na flux from the surface of the Moon or from RM clusters close to the surface. Using the Na column density $1.4 \times 10^9\,\mathrm{cm}^{-2}$ (Mendillo et al., 1999) for the column density of the RM clusters as the product nl means that even a relatively small cross section of $10^5\,\mathrm{nm}^2$ gives a large collision probability at the Moon, while a cross section as small as $10^3\,\mathrm{nm}^2$ is sufficient to give strong collisions at Mercury, using the column density $2 \times 10^{11}\,\mathrm{cm}^{-2}$ from Potter et al. (1999). This means that the atmospheres are not transparent from the point of view of Rydberg species and RM clusters. The larger density at Mercury means that the atmosphere there is dense for Rydberg species. One can conclude that collisions between the Rydberg fragment released from a cluster and other RM clusters will also take place. Release of Rydberg atoms with later re-adsorption in the RM clusters should, thus, be an important mechanism in the atmosphere.

3.2. Escape velocities of RM clusters

The escape velocity from a body with mass M is given by

$$v_\mathrm{f} = (2CM/R)^{1/2}, \tag{3}$$

where C is the gravitational constant and R the distance from the center of the body with mass M. This means that the escape velocity at the Lunar surface is $2400\,\mathrm{m\,s^{-1}}$, while it is $690\,\mathrm{m\,s^{-1}}$ at a distance $R = 12R_\mathrm{Lu}$, where R_Lu is the Lunar radius. The thermal peak velocity for a Na atom at 500 K is $600\,\mathrm{m\,s^{-1}}$. Since a substantial fraction (order of 10^{-7}) of the thermal distribution is above the value of v_f at the surface, and 45% of the Na atoms will have a velocity larger than v_f at $12R_{Lu}$, Na atoms will escape slowly from the Moon. Despite this, an extended atmosphere of Na is observed out to this large distance (Mendillo et al., 1999). The radial variation $\propto r^{-\alpha}$ of this atmosphere (with exponent $\alpha = 1.39$) does not correspond to neither a purely escaping ($\alpha = 1$) nor a stationary ($\alpha = 4$) atmosphere (Mendillo et al., 1999).

Since the RM clusters contain a large number of atoms, their velocity will be much smaller than for the separate atoms. A 19-atom cluster Na_{19}* will have a thermal peak velocity at 140 m s^{-1}, and Na_{61}* will have 80 m s^{-1}. This means that such clusters have a fair chance of staying in the atmosphere at large distance from the surface for a considerable time. (Note that the evidence points to a collision-rich atmosphere for alkali, as described above.) Even at $12R_{Lu}$, only a fraction 5×10^{-13} of the clusters Na_{19}* will have velocities above the escape velocity. For the cluster Na_7*, the corresponding fraction is 3.5×10^{-4}. Thus, such small clusters are slowly lost from the outer part of the atmosphere.

3.3. Large kinetic energy of cluster fragments

Most experimental results on release of fast fragments from RM clusters have utilized laser pulses with duration

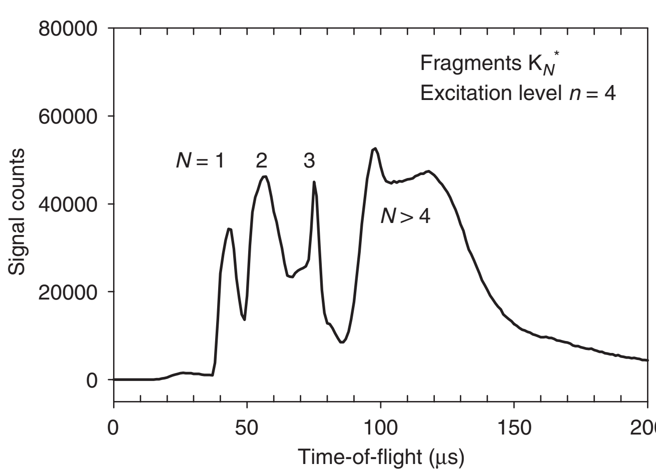

Fig. 2. Time-of-flight spectrum of neutral K_N* RM clusters observed under field-free conditions. The magic numbers of the clusters are indicated. $N = 1$ indicates an atomic fragment in a Rydberg state, detected by weak field ionization. See further Badiei and Holmlid (2002d).

of 5 ns of visible light. RM forms a cloud in ultrahigh vacuum, and the TOF of the fragments released by the laser pulse is measured. Both neutral TOF as well as ion TOF can be used, in the latter case also taking into account the excess kinetic energy received by the light fragments in the laser fragmentation of the RM. An example of such an experiment is shown in Fig. 2. If ions are observed, they are usually due to field ionization of the Rydberg or RM species in the experiment, while the fragments formed by the laser pulse are neutral. The kinetic energy release observed in the experimental studies should be quantized, as shown in the theoretical section. Thus, the values found correspond to the quantized values of n that describe the excitation state and the bond distance in the RM before the electron displacement process starts, as observed in the experiments.

Large values of n will give such a small energy release according to Eq. (1) that it is of the same size as or smaller than the initial thermal kinetic energy, but levels $n = 3-8$ have been identified positively. How small values n are found depends on the special atoms or molecule studied. It is, e.g., not possible that RM formed by K atoms can have $n = 3$, since the inner electrons in the core ions are so far out that they prevent the binding electron to move in the required orbit at a distance of 480 pm from the core. The core K^+ already has filled 3 s and 3p orbitals. For H_2 and N_2 in RM form, $n = 3$ is routinely observed, since the inner electrons are more contracted in space in the cores N_2^+ and H_2^+. Only in the case of H in RM form has $n = 1$ been observed so far. The kinetic energy release for different n values is shown in Table 1. $n \geqslant 3$ is possible for Na, while $n \geqslant 4$ is possible for K. The temperature values given correspond to the energy release in the table and will thus determine the velocity distributions after randomization by collisions.

The kinetic energy release can be measured both for neutral and ionic RM cluster fragments. Not all alkali metals have been studied in RM form thus far, but mainly K and Cs. In the case of K, small fragments like K_2^+ and K^+ have been studied and shown to carry an excess kinetic energy of the order of 0.4 eV corresponding to $n = 5$ (Wang and Holmlid, 2000). More precise measurements of the energy release are easier to do for neutral fragments as K_2, as seen in Badiei and Holmlid (2002d). Good results for K monomers have been reached, as shown in Fig. 2. For H_2 RM clusters, the self-cooling also observed for K clusters is

Table 1
Energy release from different excitation levels (bond distances) in RM, according to Eq. (1)

Excitation level n	3	4	5	6	7	8
Energy release W (eV)	1.04	0.59	0.38	0.26	0.191	0.147
Temperature (K)	12,000	6850	4410	3020	2200	1700
Bond distance d (nm)	1.38	2.46	3.84	5.53	7.52	9.82

$n \geqslant 3$ is possible for Na, while $n \geqslant 4$ is possible for K.

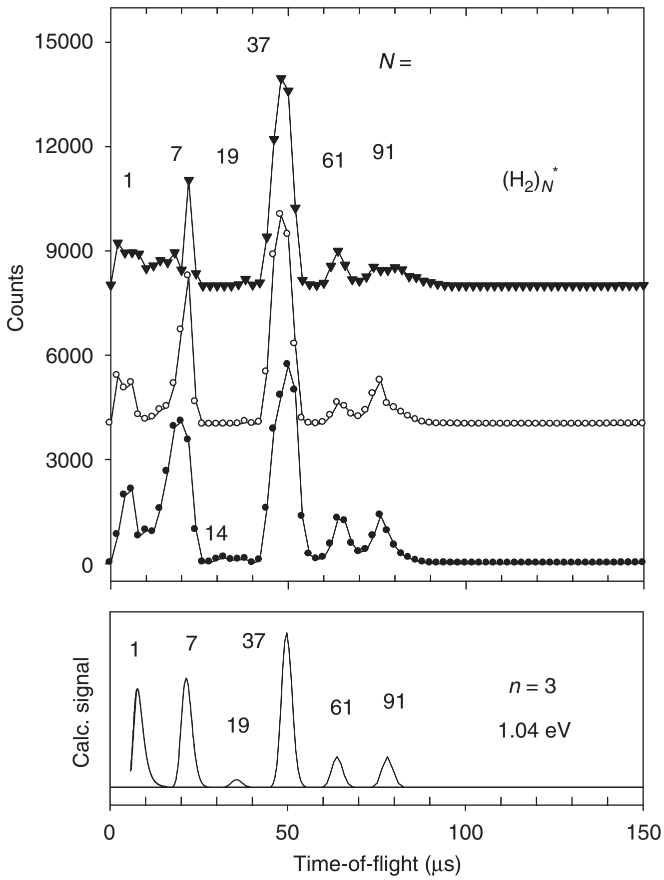

Fig. 3. Time-of-flight spectra of neutral $(H_2)_N$* RM clusters observed under field-free conditions. The magic numbers of the clusters are indicated. $N = 1$ indicates an atomic fragment in a Rydberg state, detected by weak field ionization. See further Wang and Holmlid (2002).

very efficient, and well-resolved results can be found for monomers and larger clusters simultaneously, as shown in Fig. 3. Such results confirm the energy release values in Table 1.

3.4. Desorption of RM clusters

The desorption of ground-state alkali atoms from non-metal surfaces is usually slower than desorption of Rydberg species, especially of RM clusters. This effect is kinetic in nature, and the desorption of ground-state atoms is inhibited since the number of ionically bonded alkali atoms (sites) on the surface is very small. This lowest ionic bonded state correlates with the atomic ground state outside the surface, and a low density of such states on the surface means that almost no ground-state atoms are formed in desorption (Holmlid, 1998b). Instead, the desorption goes via covalently bonded states that correlate with higher p and d states outside the surface. During desorption, such states easily cross over to Rydberg states at the surface. The Rydberg states have a very long-range adsorption well, enabling them to make large jumps over the surface (Engvall et al., 1999). Such states are short lived at impact on the surface but condense rapidly to RM clusters in the surface boundary layer during the desorption process. The condensation process to RM clusters was studied directly by molecular beam methods at a metal oxide surface (zirconia) (Wang et al., 1999), and also less well resolved in Holmlid (1995) for an iron oxide surface. The number of atoms in the RM clusters is 2–6 in most cases studied. In Kotarba et al. (1995), the angular distributions in the desorption show that 10–30 atoms form the clusters. The Rydberg condensation process has been confirmed also in the gas phase (Peng et al., 2000).

The effective desorption barrier found in experiments where desorption of Rydberg species and RM clusters is studied is usually close to 0.9 eV (Holmlid and Menon, 2001). The pre-exponential for this type of process is, however, usually quite small, since the barrier found corresponds to a rate determining diffusion step, not to the final desorption step (Holmlid, 1998b). The desorption rate f will depend strongly on the density of alkali atoms on the surface since $f \propto n_s^N$, where n_s is the surface density of alkali and N the number of atoms in the final desorbing cluster. Thus, the total alkali desorption by this process is difficult to predict exactly. However, in the cases studied with alkali doped metal oxide materials, the desorption of RM clusters is the most rapid desorption process. In the RM laser studies, stimulated emission from the RM clusters is observed at low temperature, 425 K being the lowest data reported in Holmlid (2004a). Direct measurements are anyway needed on materials typical for Mercury and the Moon. Due to the low effective desorption barrier for RM clusters, a thermal process for bringing Na into the atmosphere in the form of RM clusters may be important both on Mercury and the Moon, and this process is usually found experimentally to be faster than atom desorption.

4. Discussion

4.1. Extension of the atmosphere

RM clusters desorbing from the surface will have their velocity directed normal to the local surface due to the special form of cluster desorption process involved. The cluster velocity is a combination of the individual velocities of the atoms forming the cluster, which means that the cluster velocity is of the same size as the velocities of the atoms. Since the atoms combining to form the cluster all move out from the surface, the angular distribution of the clusters will be narrow. This has been demonstrated in desorption experiments (Wang et al., 1999; Kotarba et al., 1995). The clusters desorbing directly from the surface will have a typical velocity of 540 m s^{-1} at 400 K, with a narrow non-thermal distribution. This means that these clusters cannot move far out from the surface since they will fall down due to gravity if they do not receive a larger velocity by collisions with particles in the hot atmosphere. Coulomb explosions will give high kinetic energy to the light fragments but less energy to the heavier fragment; thus, such explosions will not influence the transit time of the clusters strongly. However, due to collisions in the high temperature atmosphere, the clusters are likely to stay in the atmosphere for a longer time than would be the case without collisions.

Coulomb explosions due to photon or particle impact on the RM clusters give excess kinetic energy release of the small fragments formed in this process. As shown in Table 1, an excitation state $n = 4$ gives 0.59 eV kinetic energy. This kinetic energy given to Na atoms is enough to bring them to a distance of $7.8R_{\mathrm{Lu}}$ from the Moon. In the case of K atoms, they can reach $2R_{\mathrm{Lu}}$, i.e., $1R_{\mathrm{Lu}}$ above the surface. Adding the initial cluster velocity of $540\,\mathrm{m\,s^{-1}}$ gives the possibility of easy escape for Na and just escape for K without collisions in the atmosphere. If a cluster is higher in the atmosphere and moving at thermal energy, the spread in possible heights that can be reached by the atoms released is of course much larger. The kinetic energy derived from the Coulomb explosions is thus in good agreement with the observed extension of the atmosphere on the Moon.

The radiative pressure acceleration, observed by Killen et al. (1999) in their line profile measurements at Mercury, will give an acceleration in the anti-sunward direction. Thus, with no collisions in an exosphere the alkali atoms cannot move far from the surface in a direction perpendicular to the direction of the Sun due to this acceleration. The observations of Na atoms at $12R_{\mathrm{Lu}}$ in this direction at the Moon by Mendillo et al. (1999) can thus not be explained by such a process, but requires other energetic processes and/or a real atmosphere with collisions due to RM clusters.

4.2. Temperature of the atmosphere

There exist a number of studies of the average kinetic energy of the sodium atoms in the atmospheres, based mainly on the radial density variation of the atmospheres. Cremonese and Verani (1997) found several temperatures on the Moon in different observations. They generally found temperatures of the order of 1000 K, but they also report values of 2700–2800 K. Verani et al. (1998) derived approximately 2800 and 1900 K in two different cases at the Moon. The Na temperature on Mercury was reported in early measurements to be between 1000 and 2200 K. More detailed measurements (Killen et al., 1999) using Na D2 line profiles indicate Maxwellian velocity distributions with typical temperatures of 750–1500 K, with the lowest temperatures found at the poles. The gas temperature was of the order of 600–700 K higher than the surface temperature below.

The report of thermal velocity distributions by Killen et al. (1999) at temperatures higher than the surface temperature demonstrates clearly that the atmosphere is not collision free (not an exosphere) and that it absorbs radiative energy by mechanisms not located at the surface. This agrees with the RM cluster model described here. Other absorption mechanisms may also be important in the Na atmosphere. Radiation pressure acceleration also exists, as shown by the skewed (red excess) distributions reported. That this effect is observed indicates that the Na ground-state atoms stay for a rather long time in the atmosphere without accommodating at the surface: surface collisions would remove any such velocity component. Thus, an atmosphere exists. Detailed modeling calculations would be interesting.

4.3. Fast component of the atmosphere

In many studies, a high-velocity component is reported for the exospheres at Mercury and the Moon, mainly based on the radial dependence of the D-line emission from Na or on the distance from the surface. Since such derivations are based on the exosphere model with no collisions, they are not directly useful to determine a fast component in an atmosphere. Cremonese and Verani (1997) found some quite high temperatures at the Moon. They report values of 1000–1500 K as well as 2700–2800 K (corresponding to $n = 6$ from Table 1) and 4000 K (possibly corresponding to $n = 5$). Verani et al. (1998) derived approximately 2800 and 1900 K in two different cases at the Moon, slightly less than the temperatures 3020 for $n = 6$ and 2200 K for $n = 7$ calculated from the energy release in these two cases, as seen in Table 1. Potter et al. (2000) found temperatures between 1200 and 2900 K ($n = 6$ and above) varying with the Lunar phase. They found the highest temperature (largest height) at full Moon when the light intensity at the surface was lowest. This is very interesting, since one would expect the reverse to be true if the origin of the kinetic energy of the Na atoms was the direct sunlight. They attribute this to a partial observation of the Earth's magnetotail at the Moon, but there is no indication of this from the height variation of the signal which follows the ordinary exponential form.

Potter and Morgan (1997) found the temperature of 6500 K at Mercury, based on the density profile found from the sodium emission. In this case, the agreement with $n = 4$ (6850 K) is good. The study by Killen et al. (1999) could not exclude a high energy component but estimated that the fraction of the atmosphere at Mercury at 4500–6500 K was only 1% from line profile measurements.

Since alkali forms a real atmosphere of RM clusters and Rydberg species in the gas phase, neither the extension of the atmosphere nor the radial distribution can be taken as a true indication of a high velocity of the observed Na atoms. It is concluded here that line profile measurements as done by Killen et al. (1999) is the only reliable way to find the kinetic energy of the Na atoms. In that case, the authors observed Maxwellian distributions thus indicating an ordinary atmosphere for the alkali species.

Other processes giving fast alkali atoms may exist at the surface, like photon stimulated desorption (PSD). This process has been studied especially by Yakshinskiy and Madey (2000, 2003) and Madey et al. (2002). The variable temperature observed by Potter et al. (2000) at the Moon is at variance with such a process; it is unlikely that the excess energy in the PSD process should change for different phases of the Moon. PSD and similar processes may contribute to the energetic heating of the atmospheres, giving a temperature increase of 600–700 K as reported by Killen et al. (1999) at Mercury. However, these processes need to be very efficient if the observed high gas temperature should be maintained. Since the alkali atoms are part of an atmosphere, the lower layers close to the surface should have a higher temperature if surface based processes like PSD are important. Such results have not been reported. In the RM cluster model, energy from the photons absorbed by the clusters is directly channeled into kinetic energy of the atoms observed. Alternatively, thermal desorption of Rydberg species transfers thermal energy from the surface to the clusters, and from there to the atoms. Thus, the high kinetic energy is easily obtained in the RM cluster model.

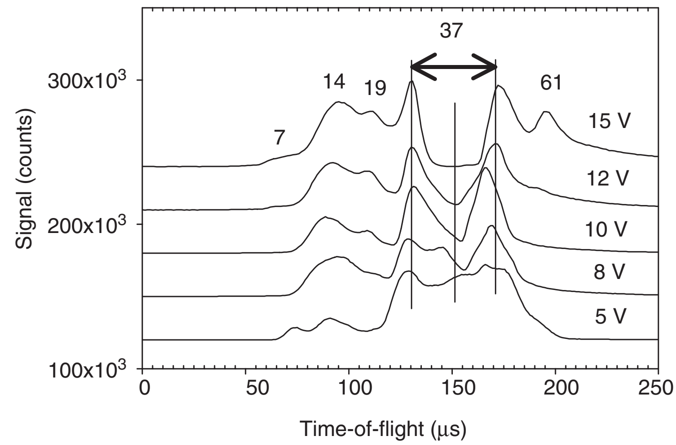

Fig. 4. Time-of-flight spectra of field ionized K_N* RM clusters. The accelerating voltage on the RM emitter is indicated. The spectra are rescaled on their time axes to agree with the 10 V scale, compensating for the changes in time-of-flight caused by the different voltages. Note the forward-backward symmetry for the $N = 37$ cluster caused by the kinetic energy release from state $n = 5$ in all directions. Data thank to S. Badiei.

4.4. Cluster height distributions

The RM cluster model described here provides a mechanism of temporary storage of alkali atoms far out in the atmosphere. This means that a temporary storage at the surface as assumed by several authors (Kozlowski et al., 1990; Stern, 1999; Leblanc and Johnson, 2003) is not necessary. Of course, with an atmosphere with collisions, a storage at the surface may not be able to deliver the observed amount of alkali atoms to the atmosphere fast enough. Thus, a storage in the atmosphere which will react rapidly to the impinging light from the Sun may be a better alternative for modeling the observations.

The density of the atmosphere is not known accurately, and it may be useful to also discuss the case with relatively large mean free paths between collisional events. Even if the RM clusters formed at the surface cannot move directly to large distances from the surface, Coulomb explosions will give intermediate mass fragments with the same high energy given to lighter fragments, if the release is from a larger cluster or cloud. This type of mechanism is easily observed in the laboratory, see Fig. 4. Such clusters will be able to climb to larger distances from the surface. By incorporating also faster fragments in their structure, the RM clusters may obtain an even higher kinetic energy. Note that the cross sections for collisions between Rydberg species are very large, as discussed above. This means that the spread in kinetic energy for the RM clusters may be quite large, and that substantial numbers of clusters may exist at large distances from the surface. These clusters will then function as sources and sinks for the ground-state alkali atoms which are the only parts of the alkali cluster population that can be observed from the D resonance line emission. RM is almost invisible (Svensson et al., 1991; Svensson and Holmlid, 1992, 1999) since there is no emission or absorption in the visible, only in the IR (Holmlid, 2004a). This means that a temporary storage of alkali atoms exists at a large distance from the surface, giving a better recycling and trapping mechanism than the surface storage proposed by other authors.

The main loss of alkali atoms from the atmospheres is assumed to be photoionization of the atoms and loss of the ions in the electric fields around the bodies (Stern, 1999; Killen and Ip, 1999). The collision cross sections for interaction between Rydberg species, especially RM clusters, and ions are not known but they are probably very large since the electric field from the ion will strongly polarize, e.g., an RM cluster. See the discussion above about the collisions in the atmospheres. This means that ions will tend to attach to the RM clusters that are heavy and move slowly. This increases the possibility for attracting relatively low energy electrons, giving recombination and thus re-neutralization of the ion. In the RM cluster form, the alkali atoms are not easily photoionized, as observed in the laboratory experiments with intense pulsed lasers, where alkali ions are not observed despite the intense focused light. Thus, it is proposed that the loss rates of alkali from Mercury and the Moon are much smaller than previously assumed.

4.5. Conductance of the atmosphere

A problem with the conductance of the Mercury surface environment exists due to the fields created around the planet (Grard et al., 1999; Killen and Ip, 1999), where the conductivity around the planet is much too small to support the currents suggested by other authors. The ordinary exosphere is estimated to have a conductance of 5×10^{-6} S, while 100 S would be necessary for the estimated currents. The RM cluster description can change the situation, giving much higher conductivities in the atmosphere. In the RM clusters, the energy necessary to release electrons by field ionization is very small, of the order of 10 meV or less at the high excitation levels normally found at low densities. This means that a very weak electric field can release electrons, or accelerate thermally or kinetically emitted electrons from the RM clusters to drift from cluster to cluster in the atmosphere. (Note that this static field ionization is strongly different from the case with ionization by light discussed above, which implies a rapidly varying field.) A simple description of the drift of charged particles in a medium with collisions gives the drift velocity of the light particles, i.e., the electrons in this case (Skullerud, 1973; Andersson et al., 1986; see references to older literature in them) as

$$u = \frac{qE}{3Nm_e\sigma}\left(\frac{2\pi m_e}{kT}\right)^{1/2}, \tag{4}$$

where q is the charge of the drifting particle (electron), E the electric field strength, N the density of the collision partners, in this case the RM clusters, m_e the mass of the electrons, σ the collision cross section, k the Boltzmann constant and T the temperature of the electrons. The conductance in a tube with base area A and length L is then

$$G = \frac{n_e A q^2}{3N\sigma L}\left(\frac{2\pi}{m_e kT}\right)^{1/2}. \tag{5}$$

If we assume that the electron density n_e is equal to the density of the clusters N, and that A/L is of the order of one-tenth of the radius of Mercury ($R = 2\times10^6$ m), G becomes the order of 100 S for RM clusters with a cross section of $5\times10^{-10}\,\mathrm{m}^2$ ($5\times10^8\,\mathrm{nm}^2$) which implies an excitation level of only $n = 6$ in an $N = 37$ Na cluster. A low value of $T = 600$ K has been used. It should be emphasized that the model used is very simple, but that the required range of conductivities is easily found. Note that a distribution of excitation levels of the RM clusters will exist. (The value of u in Eq. (4) is more difficult to calculate since the field strength and the cluster densities are not known very well, but reasonable assumptions give velocities of the order of $10^3\,\mathrm{m\,s^{-1}}$.) It is, thus, clear that the easily ionized RM cluster gives a much higher conductivity to the atmosphere than assumed previously. This should give a better understanding of the charging and currents at the surface of Mercury.

4.6. Inhomogeneous and time variable light emission

Time variable light enhancements are observed in the alkali light emission from Mercury (Killen and Ip, 1999; Stern, 1999). Such features are observed, e.g., at high latitudes. Rapid, planet-wide changes of sodium emission are reported by Potter et al. (1999). This means that the bright parts of the emission are moving over the surface, one day in the northern part and the next day in the southern part of Mercury. The explanation provided by the RM model is that the RM clouds are fragmented and emit much of their energy as Na D lines periodically, until they are re-excited by the sunlight and recombine to larger clusters and clouds. Further, the clouds may move long distances over the surface. RM forms clouds that can be observed from the laser fragmentation in the laboratory experiments (Badiei and Holmlid, 2002c, d). Relatively dense RM clouds may explosively break down in processes that still are not well understood, even if they have been reported in different types of experiments (Åman et al., 1992; Olsson et al., 1995).

The time variable total emission from Mercury observed during 6 days by Potter et al. (1999) was proposed by them to be caused by coronal mass ejection events from the Sun. The observed increase in the Na density and thus of the Na fluorescence by a factor of 3 was thought not be explainable by a simultaneous increase in solar activity, followed as an increase of the F10.7 cm flux by 16% during this period. Fragmentation of RM clusters is likely to start the cloud de-excitations and release of Na atoms from the clusters. Such processes have been observed by laser fragmentation to vary with visible light intensity I as I^n, where $6<n<8$ since the process is due to the absorption of 6–8 photons (Wang and Holmlid, 2000). Several photons are probably also needed for the release of electrons or atoms from the RM clusters by less energetic radiation. Since the RM clusters are very long lived and have many degrees of freedom, they act as efficient storages for energy and low energy photons may accumulate for hours. A recent example of the long-time storage of IR photons in RM clusters is provided by Badiei and Holmlid (2005). A calculation of 1.16^n gives 2.4–3.3, close to the observed increase in Na density. This means that a short-time variation of the solar activity of the observed size may give the observed increase in Na density through storage of the energy of several photons in the RM cluster. A long-time variation in solar activity will not give such a strong Na increase but probably only a linear response, since the energy in the clusters will have time to dissipate. Thus, the observed increase in the emission may be due to the increase in activity of the Sun observed in the F10.7 cm flux.

4.7. Depletion of K in the visible atmosphere

In a recent study (Potter et al., 2002), the ratio of Na and K densities in the atmosphere of Mercury was observed to be close to 100. Thus, the density of K is much lower relative to Na in the Mercury atmosphere than in the atmosphere of the Moon. A depletion of K also seems to exist relative to typical surface minerals. Potter et al. (2002) discuss the possible effects that may remove K from Mercury preferentially relative to Na, without reaching a convincing result.

With a large part of the alkali residing in RM clusters, the problem of K depletion is quite easily solved. There exist several factors that will increase the amount of K in the RM clusters relative to Na. The first factor is the cross section for collision between an alkali atom and an RM cluster, which determines the rate of incorporation of alkali atoms into the existing clusters. This process removes free alkali atoms from the gas phase (a near equilibrium or steady-state concentration will always exist), and thus determines how much of K and Na is left in the atmosphere. The collision cross sections depend directly on the polarizability of the atoms, with values $24 \times 10^{-24}\,\mathrm{cm}^3$ for Na and $43 \times 10^{-24}\,\mathrm{cm}^3$ for K. Thus, K will add to the RM clusters almost twice as fast as Na. This will give a depletion of free K atoms by a factor of 2, if the probability of loss of either Na or K from the clusters is the same, only depending on the amount of K and Na in the clusters.

If K and Na compete for the same positions in the clusters, some factors may be important for the incorporation in the clusters. Since the form of the clusters is six-fold symmetric with certain magic numbers, selective factors may exist. For example, the excitation of Na to a high Rydberg state with a certain value of the principal quantum number n (necessary for matching the excitation state of the RM cluster) requires a substantially higher energy than excitation of K: for a state $n = 30$, Na requires 18% more energy. Thus, K atoms are more easily attached to the RM clusters.

Another factor is also observed experimentally, namely a tendency for a selective emission of species with low values of n from the RM clusters. In principle, a stable cluster is only formed if all atoms in it are in the same excitation state with a common n value. Otherwise, the bonding will disappear since the electrons are no longer in phase. For K, values of n down to 4 have been observed (Badiei and Holmlid, 2002c, d), but Na will also form RM in the state $n = 3$. This means that in a mixed cluster with both Na and K, there exists a greater probability for emission of Na from the cluster than for K since Na may drop down to $n = 3$ by any external disturbance and be expelled from the cluster. It is less likely that a single atom in the cluster will transfer to a higher state, since this cannot be accommodated in the structure and thus the excess electron energy has to be redistributed without any particles being ejected.

Thus, the depletion of free K atoms in the Mercury atmosphere is proposed to be caused by the accumulation of K in the RM clusters. In the atmosphere of the Moon, the lower particle flux densities from the Sun means probably that the discussed selective expel mechanism of Na from the RM clusters will not be equally important. Any depletion of free K atoms on the Moon will, thus, probably primarily be due to the different polarizabilities of K and Na, as discussed above.

5. Conclusions

It is shown that several features of the alkali metal atmospheres of the Moon and Mercury can be understood, using the known properties of RM clusters. First of all, the model used implies that an alkali atmosphere is formed, even if the mean free path for alkali ground-state atoms may still be quite large. This is in agreement with the important results by Killen et al. (1999) showing Maxwellian velocity distributions of Na at Mercury. The high kinetic energy often reported for Na at Mercury and the Moon is also explained. Alkali atoms, initially in Rydberg states, are released with high kinetic energy from the RM clusters by solar photons and particles in Coulomb explosions. This effect can explain the very large dimensions of the visible ground-state atom atmospheres, the often reported high-velocity Na atomic component, the influence of the sunlight and the intermediate radial variation of the atomic density. The high conductance of the RM cluster atmosphere is important for understanding the currents and voltages generated at the surface of Mercury. The apparent depletion of K in the atmosphere of Mercury is explained by K accumulation in the RM clusters.

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