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Direct observation of circular Rydberg electrons in a Rydberg matter surface layer by electronic circular dichroism

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Abstract

The circular dichroism of a surface layer containing K (potassium) Rydberg species and K_N Rydberg matter clusters is studied. The scattering that is apparently shifted in wavelength from the laser line is due to a phase-delay Rabi-flopping process, caused by the Rydberg species in the surface layer (Holmlid 2004 *J. Phys. Chem. A* **108** 11285). With circular polarized light, a strong right–left polarized intensity asymmetry is observed in the Rabi-flopping scattered light, which indicates a chiral scatterer in the Rydberg surface layer. We conclude that the chiral entities are the circular Rydberg electrons with their large magnetic momenta.

1. Introduction

The condensed-phase Rydberg matter (RM) is formed from interacting Rydberg species in atomic or molecular form, with the Rydberg electrons in circular orbits [1]. These circular orbits determine the planar shape of the clusters that form the RM phase; the cluster form has recently been observed directly from rotational spectroscopy [2]. This phase has also been studied by other groups with laser cooling and thermal plasma methods [3, 4]. The present study is concerned with the direct identification of the circular electron orbits by circular dichroism in the visible range, thus using the electronic degrees of freedom for the interaction with light. A circular Rydberg orbit with large principal quantum number n and with the angular momentum quantum number $l = n - 1$ has a large magnetic moment $m = (n - 1)\mu_B$ pointed perpendicular to the electron orbit according to the general rules for electromagnetism. Such an electron orbit is a chiral unit which should be detectable by circular dichroism. Even for ordinary molecules, circular dichroism is often due to magnetic dipole transitions [5].

The interaction of light with RM in the visible range is very weak. There is no absorption in the visible if the RM is not fragmented, as has been shown in many studies. For example, only

Raman processes could be observed in RM with an intense nanosecond pulsed laser [6]. The emission or absorption that can be observed in RM is generally due to processes in fragmented RM, as proposed for the absorption bands (diffuse interstellar bands, DIBs) observed in interstellar space [7]. However, very weak bands extending into the visible range from the infrared (IR) can be observed by stimulated emission of electronic transitions [8]. The main interaction observed from surfaces covered with Rydberg layers, partly in the form of RM clusters, is a reflection process based on Rabi-flopping scattering [9, 10]. We use this type of coherent scattering here since this scattering process is known to be due to the Rydberg species, not to the emitter material used to produce the Rydberg species.

The method used here employs a material that emits K atoms in Rydberg states and K_N RM clusters at low heating in a vacuum. A layer containing Rydberg species is formed on top of the emitter in this way. This method to form Rydberg species and RM clusters has been demonstrated and used in numerous publications, with a few recent examples in [2, 11–15]. The interaction of circular polarized light from a small laser with the surface layer is studied, looking for the coherent Rabi-flopping signal from the Rydberg (RM) layer. In this way, we only observe the interaction with the Rydberg layer. The results are displayed in the form of spectra by a standard grating spectrometer. Since the light is backscattered with no shift in frequency but with a delay due to the Rabi-flopping process [9, 10], the results are quasi-spectral. However, this means that the non-coherent scattering observed as part of the laser line in the spectra can be separated out, and only the coherent Rabi-flopping Rydberg-scattered part observed away from the intense laser line in the quasi-spectral plots is of interest here. This study follows the type of experiment where a hypothesis is formulated (that the circular Rydberg species will give circular dichroism) and a test of the outcome of an experiment is performed, which shows the hypothesis to be correct. It is thus not a full survey of the complex polarization properties of the Rydberg surface layer.

2. Theory

The time-dependent processes which take place in an atom with two states a and b due to a radiation field has been analysed in many monographs [16–18]. The analysis usually starts with the time-dependent Schrödinger equation and is called the Rabi two-level problem. Our problem is somewhat more complex. We use the Bloch vector model [16] to describe the time dependence of the Rydberg species plus photon system. The optical Bloch equation [17] gives the motion of a dipole (pseudo-polarization) vector \mathbf{R} [16, 19]

$$d\mathbf{R}/dt = \mathbf{R} \times \boldsymbol{\Omega} \quad (1)$$

as a nutation of the vector \mathbf{R} on the Bloch sphere around the vector $\boldsymbol{\Omega}$. See figure 1. The pseudo-polarization vector represents the state of the system, being in state a at the south pole and in state b at the north pole of the sphere, and in a superposition of the two states otherwise. The optical nutation vector $\boldsymbol{\Omega}$ has the components $(R_{ab}, 0, -(\omega - \omega_{ab}))$ [16, 20] (under reasonable conditions) with R_{ab} the transition moment between the states a and b . A calculation of these components shows that R_{ab} is of the order of $5 \times 10^{10} \text{ s}^{-1}$ for an allowed transition in a small atom, while $\omega - \omega_{ab}$ is of the order of $5 \times 10^{14} \text{ s}^{-1}$. Thus, the vector $\boldsymbol{\Omega}$ points close to the direction of the negative z axis as shown in figure 1, and the pseudo-polarization \mathbf{R} vector precesses (nutates) around this vector with the angular frequency

$$\Omega = ((\omega - \omega_{ab})^2 + R_{ab}^2)^{1/2} \quad (2)$$

which at large values of $\omega - \omega_{ab}$ (off-resonance) is approximately equal to $|\omega - \omega_{ab}|$. Thus, it is much larger than R_{ab} . This equation shows that the nutation process far off-resonance is

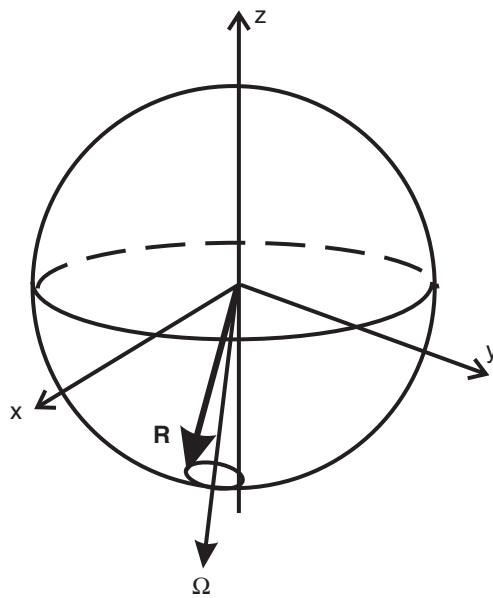


Figure 1. The polarization vector \mathbf{R} which moves around the optical nutation vector $\mathbf{\Omega}$ on the Bloch sphere. State a is at the south pole and state b at the north pole of the unit sphere.

much faster than the transfer from state a to state b at resonance, even for an allowed transition. In the present case, the nutation is approximately 10^4 times faster than an allowed transition at resonance. The amplitude R_{ab} of the nutation is smaller for forbidden transitions; however, the value of R_{ab} is finite and a nutation takes place. The very large scattering cross sections as described below mean that a signal is easily obtained. The system will in general make several nutations before giving off the photon from the dressed (atom–photon) system. As shown in [9, 10], this implies a multiple delay of part of the radiation for each cycle of nutation, giving rise to the Rabi-flopping spectra used here.

The intensity of scattered light is primarily determined by the polarizability of the system in its interaction with the radiation field. The Rabi-flopping process is a type of scattering often included in the Rayleigh scattering. The induced dipole moment is $\mathbf{p} = \alpha \mathbf{E}$, where α is the polarizability tensor of the Rydberg species and \mathbf{E} is the electric field strength from the radiation field. The scattering cross sections vary with the square of the polarizability as α^2 [21, 22]. Since the polarizability to a first approximation is proportional to the volume of the scattering species and also increases for weakly bound electrons, Rydberg species will give very strong scattering and large intensity of the Rabi-flopping process. In fact, the polarizability of a circular Rydberg species increases very rapidly with principal quantum number n , as the seventh power of n , i.e., as n^7 . Thus the scattering cross section increases $\propto n^{14}$. At $n = 30$ the scattering cross section of a hydrogen circular Rydberg atom is approximately 10^{20} times larger than for the ground state $n = 1$. Thus, as also found experimentally, the Rabi-flopping spectra are only observed for Rydberg species.

3. Experimental details

The emitter material used to form the Rydberg layer is a commercial catalyst normally used for dehydrogenation of ethyl benzene. It is an iron oxide material with certain additives, especially K at about 8 wt% [23]. The processes of transformation of the initial K-doped hematite to the

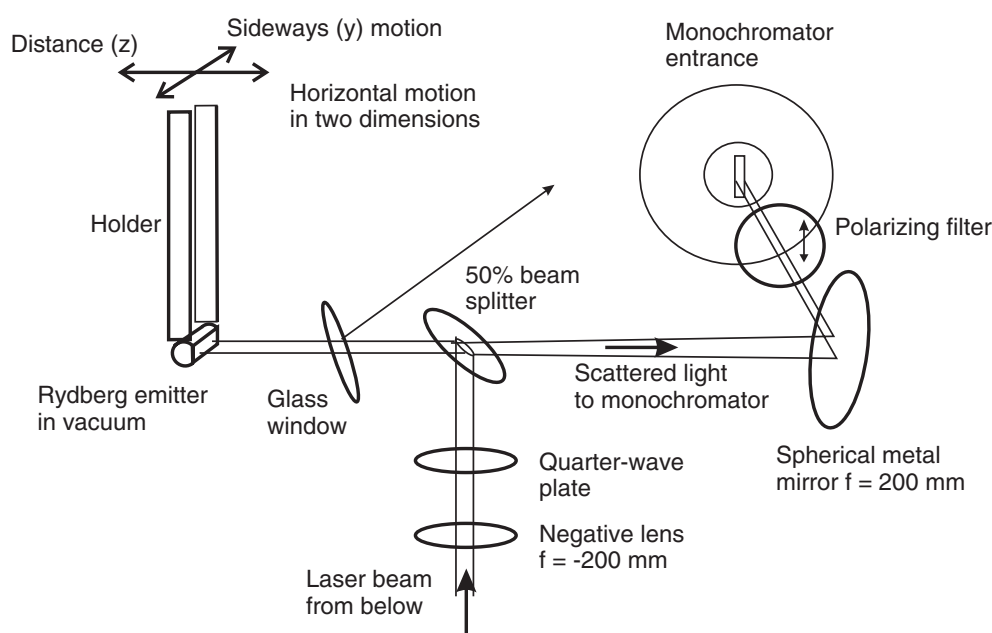


Figure 2. Perspective schematic view of the set-up without a microscope. The laser beam can be further adjusted in two directions by a roof prism below the drawn parts while keeping the direction of the beam unchanged. The sample studied can be moved in two directions. For a view with the microscope in place, see [10].

active ferrites and of release of K from the material have recently been described in detail [24]. The process of formation of Rydberg species like K^* at surfaces has been studied by different methods (with typical results in the references given), (1) desorption kinetics [25], (2) surface scattering [26], and (3) field ionization [27]. The highly resolved desorption kinetics study in [25] used field-reversal kinetics to identify several kinetic steps in the system K on graphite (graphite layer on iridium formed by hydrocarbon decomposition). It was shown that the preferential desorption of K Rydberg states is due to the lack of an ionic state on the surface that correlates with the K ground state outside the surface: for this reason, electronically excited states are desorbed instead from covalent states on the surface, and they easily cross over to the long-lived Rydberg species while leaving the surface by thermal excitation. This type of process is preferred also at metal oxide surfaces. At a metal surface with bound ionic states, ground-state atoms desorb instead. Recent results from various metal oxide catalyst surfaces indicate that the electronic properties of the surface determine if K Rydberg atoms are formed or not: one of the most relevant cases studied [28] is a comparison between the surfaces of $KAlO_2$ and $KFeO_2$, where only the catalytically active ferrite $KFeO_2$ gives desorption of K Rydberg species. Recent results from EPR studies of K atoms on metal oxide surfaces [29] give direct evidence for a special type of bonding of K atoms to the oxides, being neither a charge transfer nor a covalent bonding. The K 4s orbital is clearly destabilized and the resulting species is an ‘expanded’ atom that is similar to a Rydberg state. These results are very relevant for the nature of the K^* Rydberg atoms observed here in the Rydberg surface layer.

For the experiments, a small diffusion pumped vacuum chamber is used, where the catalyst sample is mounted in a Ta foil holder [9]. The foil can be heated by an AC current through the foil. The base pressure in the chamber is 1×10^{-6} mbar. The cylindrical catalyst sample is cut with a flat surface exposed. See figure 2, where the set-up without the microscope objective is

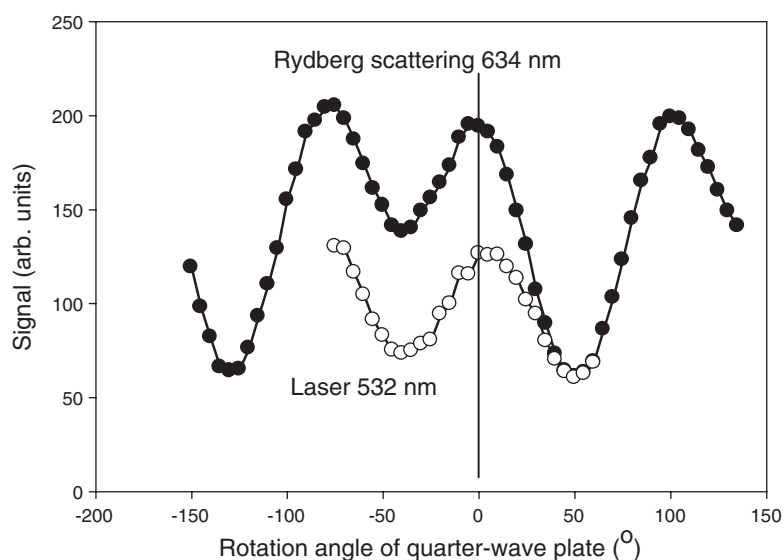


Figure 3. Signals as a function of the angle of the quarter-wave plate. Note the large asymmetry of the Rydberg scattered signal observed with the monochromator nominally at 634 nm for the angles $+45^\circ$ (right circular light) and -45° (left circular light). A microscope was used for this experiment to exclude all scattered light from surrounding parts.

shown. In that case, a glass window in the vacuum wall is used to transmit the light into the vacuum chamber with the catalyst sample. The window is tilted at an angle of 20° to remove reflections from the beamline. A microscope objective with a magnification of $60\times$ is often used in this set-up replacing the tilted glass window, focusing the laser light on the surface in a confocal arrangement. See the figure in [10]. A CW Nd:YAG laser at 10 mW power has been used for the experiments reported here. With a typical beam waist of $10\ \mu\text{m}$ and the laser focus on the surface, the power density is of the order of $10^4\ \text{W cm}^{-2}$. Without the microscope, the power density is less than $0.1\ \text{W cm}^{-2}$. A non-polarizing beam splitter and metal mirrors are used to reflect the laser and signal beams. Reflections due to various optical surfaces are adjusted out from the beam reaching the spectrometer slit, so that only the light scattered from the sample is observed by the spectrometer. The monochromator is a Czerny–Turner type with 500 mm focal length and a holographic grating with $1800\ \text{grooves mm}^{-1}$. The grating has its axis of turning in the vertical direction, parallel to the entrance slit and the polarizing direction of the Polaroid filter. The signal intensity is low, and pulse counting is used. The total light power at the entrance slit to the monochromator is $<10\ \mu\text{W}$. The entrance slit width is 0.1–2 mm and the exit slit width is $200\ \mu\text{m}$.

4. Results and discussion

A modest right–left asymmetry is observed for the scattering of the laser beam from the catalyst (Rydberg emitter) sample, i.e. for the laser peak in the quasi-spectrum. See figure 3. Of course, this reflected beam is to just a small extent due to specific atomic or molecular processes in the surface layer and mainly due to reflection from the bulk material of the sample. This experiment used a microscope to focus the light at the surface, thus entirely excluding reflections from other parts like the metal foil holder. The light scattered from the surface layer in the Rabi-flopping

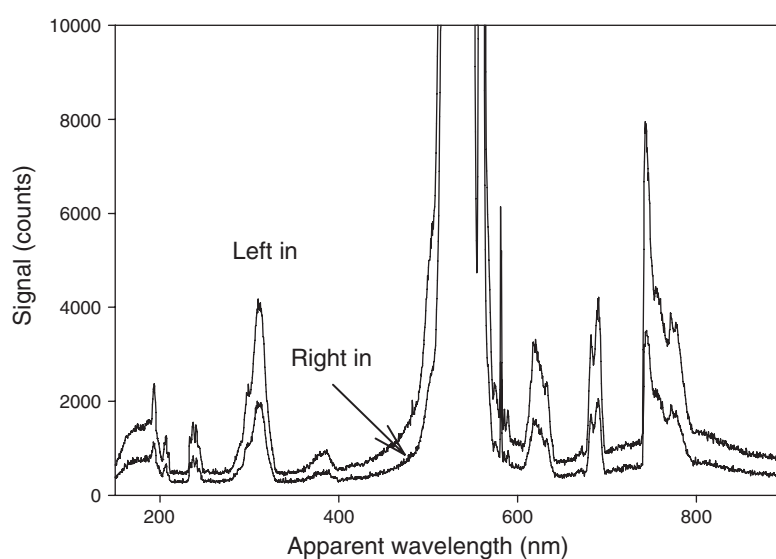


Figure 4. Typical results from the quasi-spectral analysis without a microscope, showing the apparent wavelength on the horizontal axis at a degassed surface at 900 K. The wavelength of the light is unchanged and the apparent shifts from the laser are due to the delays inherent in the Rabi-flopping process. The lower curve is found with right circular light and the upper one with left circular light to the Rydberg sample. The average right–left ratio is 0.55.

process [9, 10], in contrast, shows a considerable asymmetry. In figure 3, the signal at the laser peak (532 nm) and at one Rabi-flopping peak (634 nm) are compared (shifted in intensity to be on comparable scale) as a function of the turning angle of the quarter-wave plate. The strong right–left asymmetry in the case of the Rabi-flopping is easily observed.

The right–left asymmetry is also easily seen in the case of quasi-spectral scans. Such a scan means that the spectrometer is scanned giving the scattered signal (of the unchanged laser wavelength) as a function of the apparent wavelength corresponding to the grating angle. The apparent spectrum observed is due to the delays inherent in the Rabi-flopping process, as described in detail in previous publications [9, 10]. An example is shown in figure 4 without a microscope and thus with the unfocused laser beam reflected from the surface. (The band structure shown contains chemical information as described in [9, 10, 30], but this is of no concern here where we are only interested in the intensity of scattered light from the sample.) In the case shown in the figure, the sample was heated to 900 K to remove adsorbed permanent gases from the surface to ensure that only the Rydberg (RM) surface layer exists on the solid surface. This circular dichroism is also found at room temperature and with a microscope (see further below), but the ratio between the left- and right-excited signals varies slightly with the conditions; however, the left-excited signal is always approximately a factor of two larger than the right-excited one.

Since the total reflected beam at 532 nm shows much less circular dichroism than the Rabi-flopping signal in figure 3, it can be concluded that the material in the sample is not chiral. Test experiments where the Rydberg emitter sample is replaced by a piece of cardboard show no dichroism, as demonstrated in the two lower curves in figure 5 (note the logarithmic scale). Immediately after this measurement, the two upper curves in the figure were measured from the emitter at room temperature, with the same settings of the quarter-wave plate. They show

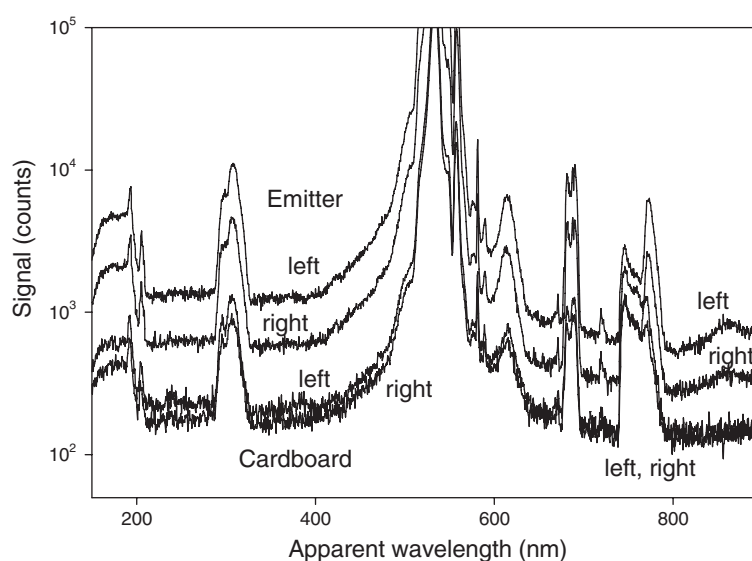


Figure 5. Effect of the nature of the studied sample at room temperature, showing the logarithm of the signal on the vertical axis. The set-up in figure 2 with no microscope was employed. The two lower curves are found with a piece of cardboard instead of the Rydberg sample, with almost no difference between right circular light and left circular light to the sample, thus showing no circular dichroism. The two upper curves are from a Rydberg sample shortly afterwards with identical angles for the quarter-wave plate, showing a strong circular dichroism. Note that the left circular signal is much higher relative to the cardboard signal. The average right–left ratio for the emitter sample is close to 0.5.

a strong circular dichroism and a much higher scattered intensity. New spectral features are also observed in the spectra from the Rydberg emitter. The same type of measurement on the stainless steel support holding the sample also shows a much lower signal than from the Rydberg emitter, since the metal surface does not form a Rydberg or RM surface layer (some spill-over from the Rydberg emitter is of course possible); further, this surface is non-porous and the amount of K on the surface will be small. Thus it is concluded that intense Rabi-flopping scattering with circular dichroism is only observed from the Rydberg emitter. We will go on to prove that the dichroism is only observed from the Rydberg (RM) layer on the emitter surface.

After heating the surface to 1000 K for a few hours, the Rabi-flopping bands become much weaker since the K atoms in the topmost layers are depleted and give a less dense Rydberg layer on the surface. After a few days at room temperature, the Rabi-flopping signal is restored, since the slow diffusion of K atoms in the bulk replenishes the surface layer of K and thus also the Rydberg species formed by thermal excitation of the K atoms, as described above. More prominent graphite and hydrocarbon fragment bands are observed [10] after such heat treatment, since the high-temperature treatment decomposes hydrocarbons that always exist in the vacuum system. Impurities in the Rydberg (RM) layer may give trapping of the Rydberg electrons [31]. However, the surface layer observed here is normally in a steady state relative to loss of material by desorption and gas collisions, and is replenished by desorption from the bulk material below. Impurities will thus probably have relatively small influence on the properties of the Rydberg layer. The bulk Fe–O catalyst does not change strongly under the heat treatment described. It is designed to function under much harsher conditions at 900 K when

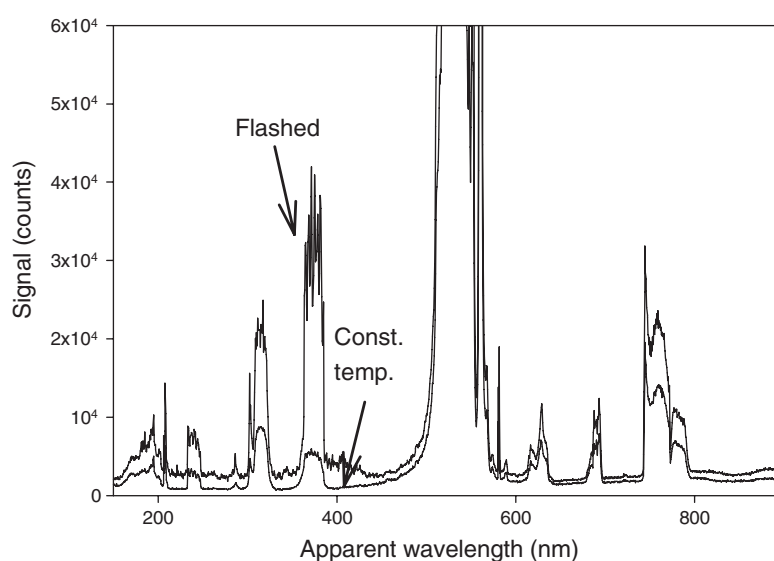


Figure 6. Demonstration that the Rabi-flopping signal is from scattering in the Rydberg (RM) surface layer. Both spectra are taken with the microscope set-up with the emitter at 500 K. The upper spectrum is measured when the heating current has just been started (flashing) and shows the formation of a dense desorbing layer of scattering Rydberg species on the surface, while the lower spectrum is measured shortly afterwards with a lower constant Rydberg density corresponding to the new steady-state conditions.

used as a catalyst in styrene production, described in [23] and references given therein. Thus, it is observed experimentally that the catalyst bulk material is not the source of the Rabi-flopping bands and thus is not the source of the circular dichroism observed. Milder degassing of the surface does not remove the circular dichroism of the Rabi-flopping signal, as described above. Thus, it is also concluded that this asymmetry is not due to adsorbed gas on the surface. Instead, the surface layer contains circular Rydberg electrons in various chemical forms, as studied in detail by spectroscopy of this surface layer [9, 10, 30, 32], and they are the source of the circular dichroism. A further demonstration of this is given in figure 6, where a relatively fresh but previously degassed sample is studied with the microscope setup at high temperature. Note that several new and shifted peaks are observed in this case relative to the spectra in figures 4 and 5. The upper spectrum shows the large signal observed during rapid heating (flashing), during which a relatively dense and desorbing RM layer is formed on the surface, while the lower spectrum is taken a few minutes later under the new steady-state conditions. The origin of the dichroism, as described in the introduction of this paper, is probably the magnetic dipole moment from the orbiting electrons in the RM layer. The RM phase consists of RM clusters, each with a very large magnetic momentum due to the coupling of the atomic momenta. Such clusters of the form K_{19} in three different excitation levels have recently been observed directly by rotational spectroscopy due to magnetic dipole transitions [2].

5. Conclusions

The circular dichroism observed in the Rabi-flopping signal is not due to the bulk material or other non-specific processes in an adsorbed gas layer, but to reflection in the Rydberg (RM) surface layer which gives the Rabi-flopping signal. It is concluded that the circular dichroism

has its origin in the Rydberg species in the surface layer, and is caused by the chirality of the Rydberg orbits. The left–right asymmetry is a factor of two.

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