Superheating effects in line broadening of dense alkali vapors

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Abstract. We used the superheating of the dense alkali vapor in order to separate atomic from the molecular photoionization spectrum. Homonuclear and heteronuclear alkali molecules are essentially two electron systems and therefore simultaneous excitation of two atoms above the ionization limit will form autoionizing potential curves which will bring about new bands in the photoionization spectrum. We present a satisfactory comparison between experimental and theoretical emission coefficient function of diffuse bands (cesium dimer excimer) at temperatures up to 1000 °C, where the metal vapor was heavily superheated. New results for Rb₂ photoionization process reveal similar structured photoionization continuum but with reduced number of photoionization bands.

1. Introduction

Diatomic alkali molecules became of high interest because of the laser cooling effects which bring them into the most interesting quantum mechanical regime with numerous important applications. However, the process of the ionization of alkali molecules did not captured enough attention although it might also have various applications, especially toward efficient energy conversion processes.

The superheating of the dense alkali vapor enables clear separation of atomic from the molecular photoionization spectrum [1]. The molecular photoionization continuum structure is about two orders of magnitude stronger than the atomic photoionization continuum [2].

We performed numerous experiments with different pure and mixed alkali vapors with the main goal to investigate above threshold ionization process of the diatomic alkali molecules. Beside the method of superheating [3] the time-of-flight method [4] was also used in order to distinct the molecular from atomic photoionization process. As the source of electrons in possible novel plasma devices this molecular contribution becomes highly important [5, 6]. This is because of much greater cross-sections than their atomic cross-sections. Thus the strong influence of molecular component in the photoionization process opens up a new vista in the energy conversion research.

2. Experiment

Experiments with sapphire cells are extremely simple. The continuum background source is a xenon high pressure light bulb or a Laser Driven Light Source (LDLS). The absorption or emission cells are either longitudinal all-sapphire cells or T-type sapphire cells with special glass extension as an alkali container. After the light transmission through the cell it was collected on the entrance slit of the OceanOptics digital spectrometer. In order to obtain the absorption coefficient curve we used a Beer-Lambert law using Origin 8.5 software.
3. Results

The result of the pure cesium vapor absorption experiment is shown in Fig. 1 for the temperatures of 350, 420, 502 and 900 °C. For temperatures of 350 and 420 °C there was no superheating yet, but above 420 °C, for temperatures of 502 and 900 °C superheating is observable bringing the spectrum at 900 °C close to pure atomic photoionization spectrum. Rydberg spectral lines from the principal series are much better visible approaching the atomic ionization limit at 318.3 nm. Molecular destruction effect is also nicely visible for bands peaks at 352 and 395 nm.

Figure 1. Absorption spectrum for cesium vapor in equilibrium with the liquid droplet (350 °C and 420 °C). Spectrum of superheated cesium vapor (no cesium droplet at 502 °C and 900 °C). A much more detailed description of the absorption photoionization measurements with superheated cesium vapor is given in ref. [1].

Thermal emission from the superheated cesium vapor was additionally studied to very high temperatures from 700 °C to 1000 °C. We observed a number of atomic and molecular spectral features simultaneously in emission and absorption, especially peculiar thermal emission of cesium dimer diffuse bands (2 \( \Pi_g \rightarrow a \ \Sigma_v^+ \) transitions) around 710 nm coexisting with absorption bands around first resonance lines at 852 nm.
and 894 nm. The main result is the comparison between the absorption and emission profiles of the above mentioned diffuse bands. For the emission experiment at high temperatures we obtained the following expression:

\[
I(\nu, T) = A \frac{2h\nu^3}{c^2} \left(1 + B\right) - e^{-LK(\nu, T)} \left[1 - \exp\left(-\frac{h\nu}{k_BT}\right)\right] e^{\frac{h\nu}{k_BT}} - 1
\]

There are two distinct contributions in the equation above. The first one is the hot superheated cesium vapor, and the second is the blackbody of the oven. Parameters A and B are optimized in order to obtain best fit to the observed emission profile. K is the absorption coefficient measured in the spectral interval of 680-740 nm. Much more detailed description of the self emission measurements with superheated cesium vapor is given in ref. [3].

![Figure 2. a) Observed emission spectrum of the diffuse bands, b) theoretical calculations of the emission spectrum with absorption coefficient taken into account.](image)

Preliminary rubidium case was studied without efficient superheating of the T-type sapphire cell (L=0.5 cm). In Fig. 3 we present absorption coefficient function plotted from 233 up to 325 nm for temperatures from 550 to 640 °C. The above threshold molecular bands at 245 nm and 268 nm are clearly visible, as well as the Rydberg spectral lines up to the main quantum number n = 17. Previous TOF work [4] already firmly established molecular origin of 245 and 270 nm photoionization bands. This experiment did not enable superheating separation process within present rubidium vapor conditions as previously performed in the case of cesium vapor [1]. However, since the ratio of [Rb₂]/[Rb] densities increases with increasing temperature it is clear that at elevated temperatures photoionization bands of Rb₂ become better visible in the spectrum. Details of the corresponding analysis can be found in ref. [2]. Previous measurements were also done in absorption for Cs, Rb and some heavy alkali mixtures [7].
Numerous improvements are necessary in order to illuminate the detailed structure and the origin of the photoionization bands of alkali molecules. Accurate molecular calculations are needed in order to explain the differences in the appearance of the heavy alkali cases. This will include the autoionization process connected with the doubly excited molecular states.

4. Discussion

There are many spectral phenomena connected with the ionization of the cesium dimers. Since the coexistence of cesium atoms and molecules is precluding easy separation of the two we decided to study absorption spectrum of dense cesium vapor in an all-sapphire cell employing superheating of the vapor, with a special emphasis on the highly structured photoionization continuum. This continuum appears to be composed of atomic and molecular contributions which can be separated by means of additional superheating of cesium vapor in the sapphire cell. This was possible due to the small amount of cesium filling which completely evaporated at temperature of about 420 °C. This enabled the overheating of cesium dimers which greatly reduced its concentration at a temperature of 900 °C leaving almost pure atomic Cs vapor. The analysis of the thermal destruction indicated that the highly structured molecular component of the photoionization continuum can be attributed to cesium dimers. We discuss the possible origin of the structured photoionization continuum as stemming from the absorption process from the
ground state of the Cs₂ molecule to the doubly excited Cs₂** molecule above Cs₂⁺ limit. The corresponding potential curves are presently unknown, and their calculations will illuminate this interesting phenomenon. At the moment we assume that the relevant potential curves are subjected simultaneously to mutual interactions and autoionization.

5. Conclusion

Much more relevant data on photoionization structures for heavier alkali molecules are needed. These involve homonuclear and heteronuclear alkali systems. The low resolution measurements could be extended to high resolution experiments at ultracold conditions, which may reveal yet unexpected structures. A possible application of the observed phenomena will be discussed, in the near future, in terms of the solar energy conversion using dense cesium vapor. Another possibility is to make laser action at the excimer transition of diffuse bands if the superheated vapor is located within an appropriate laser cavity. At elevated temperatures in addition to monomers and dimers the coexistence of trimers and tetramers cannot be excluded. Their ionization behavior is not well investigated, but can definitely contribute to better source of free electrons [8].

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