

Time resolved absorption spectroscopy of helium dimers

Á. Kálosi¹, P. Dohnal¹, R. Plašil¹, J. Glosík¹

¹*Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University in Prague, Czech Republic*

The experimental study of He₂ excited dimer in a plasmatic environment is presented. We observed several previously not studied absorption features in the near infrared region by means of continuous wave cavity ring down spectroscopy. These absorption lines originate from the ground and first vibrational states of the $a^3\Sigma_u^+$ electronically excited state of He₂. Reactions of the molecule with argon and hydrogen gas have also been observed.

1. Introduction

While the ground state potential is very shallow, the excited potentials for the He₂ excimer (excited dimer) are of Rydberg character and this excimer represents the prototype for all Rydberg molecules.

The He₂ molecule with only four electrons has been a frequent target of experimental and theoretical works. The extensive study by the classical grating measurements of Ginter and co-workers [1,2] provided information for tens of electronic states. The properties of the excited states have also been calculated, most notably by Yarkony [3]. Transitions between these states have been measured by various other techniques, like infrared Fourier transform emission spectroscopy [4] or fast beam laser spectroscopy [5] for the systems in the infrared and visible region.

Highly precise radio frequency measurements of the He₂ fine structure transitions have been also carried out [5,6].

In our laboratory ion-electron recombination processes have been studied by means of stationary and flowing afterglow (see example Ref. [7]), with helium as the primary buffer gas. In these experiments a chain of reactions is present, with the desired ion at the end of it, but always starting from a discharge in helium gas (with or without admixtures of reactants) as the ion source. In order to trace the reactants in the afterglow, we employ a model of chemical kinetics [8] specifically constructed for each experiment, with initial reactants according to the experimental conditions.

Part of these reactants are excited metastable molecules, which have the ability to release energy later in the afterglow given their relatively long lifetime in the order of milliseconds (comparable with the lifetime of the afterglow). One could assume, that the He₂ dimer behave likewise (as a particle with the

potential to release its energy), and that it plays a similar role in the energetic balance and chemical kinetics of the afterglow plasma.

One needs to study the presence and influence of this molecule to rule out any eventuality, in which it could impact the plasma composition or other plasma parameters (like the electron temperature) during the afterglow.

The He₂ dimers are according to Fig. 11 in Ref. [9] produced via recombination of He₂⁺ and He₃⁺ ions with electrons in a reaction pathway leading to the $a^3\Sigma_u^+$ electronic state.

The present paper presents time resolved spectra of some previously unpublished vibronic transitions in the (1–0) band of the $b^3\Pi_g-a^3\Sigma_u^+$ system of He₂ (for details on spectroscopic notation see Ref. [10]). The influence of Ar and H₂ on depopulation of He₂ dimers is discussed.

2. Experiment

The experiments were performed using SA-CRDS apparatus, a stationary afterglow apparatus combined with continuous wave cavity ring down spectrometer. A detailed description of the applied techniques can be found elsewhere (see e.g. Refs. [11,12]), so only a short summary of the important details will be given here. In a typical experiment the plasma is formed in a pulsed microwave discharge in a mixture of He/Ar/H₂ (with typical composition $\sim 10^{17}/10^{14}/10^{14}$ cm⁻³) or in He only (with reactive impurities less than 0.1 ppm). The power to the microwave generator is cut off by an external high voltage switch within a fall time of < 30 μ s. The fused silica discharge tube (inner diameter ~ 1.5 cm) is cooled by liquid nitrogen or pre-cooled nitrogen gas in the range of 77–300 K. the length of the plasma column is 5 cm. To avoid the excessive heating of the gas during the discharge a

fairly low microwave power is used (2.45 GHz in the range of 5–15 W, with ~ 50% duty cycle).

The absorption measurement is based on cavity ring down measurements in the continuous wave modification (cw-CRDS), for details see Ref. [13]. The light source is a fiber-coupled distributed feedback (DFB) laser diode with a central wavelength of 1546.92 nm, linewidth < 10 MHz and maximal optical output power of 10 mW. The wavelength is measured absolutely by an EXFO WA-1650 Wavemeter (Michelson interferometer-based technology).

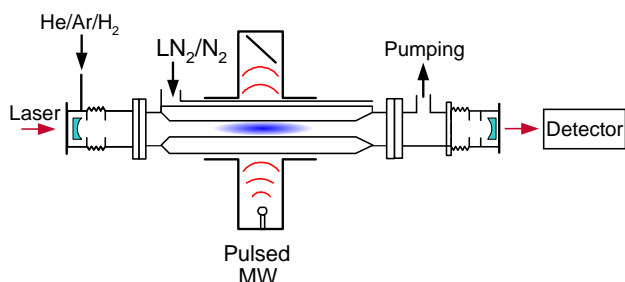


Figure 1. Schematic diagram of the Stationary Afterglow apparatus with cw-CRDS absorption spectrometer. Two highly reflective mirrors (reflectivity ~ 0.995) form an optical cavity. The laser radiation enters the optical cavity from one side and the ring down signals are collected by an InGaAs avalanche photodiode detector positioned on the other side of the optical cavity. The discharge tube at the center (containing a He/Ar/H₂ gas mixture in this case) is immersed in liquid or pre-cooled gaseous nitrogen. The plasma is ignited periodically by pulsed microwave discharge (MW) inside the optical cavity.

By synchronizing the ring down acquisition with the microwave pulse, time resolved spectroscopy can be achieved with time resolution proportional to the ring down time (typically ~ 32 μs). The repetition rate of the microwave pulse is ~ 200 Hz with data acquisition rate of 500 ring downs per second [11].

3. Experimental data and results

An example of measured absorption lines in the (1-0) band of the $b^3\Pi_g-a^3\Sigma_u^+$ system is shown in Figure 2. The lines are labelled according to the notation used in Ref. [10]. The lines were fitted by a Voigt profile and the inferred line positions are listed in Table 1 (experimental uncertainty ± 0.002 cm⁻¹). The values of ν_{calc} were calculated using an effective Hamiltonian for $^3\Sigma$ and $^3\Pi$ states [14] with matrix elements from Ref. [15] and spectroscopic constants from Ref. [10]. Note that the matrix elements listed in Ref. [15] are for $^3\Sigma^-$ state.

The matrix elements for the $^3\Sigma^+$ state are the same, except that “f” is replaced by “e” and “e” is replaced by “f”.

Overall, more than twenty transitions, belonging to the (3–2), (2–1), and (1–0) bands of the $b^3\Pi_g-a^3\Sigma_u^+$ system of He₂, were found in the probed wavenumber range of 6460 – 6470 cm⁻¹.

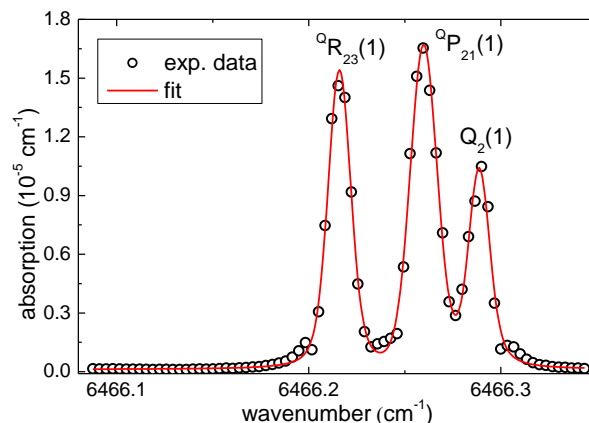


Figure 2. Example of vibronical absorption lines of the He₂ molecule measured in 900 Pa liquid nitrogen cooled He/H₂ gas mixture ($T_{\text{gas}} \sim 80$ K). Full lines indicate the best fits by Voigt profile.

The absorption lines shown in Figure 2 were obtained at $T_{\text{gas}} = 80$ K. As at this temperature the measured absorbance was too high for our cavity ring down spectroscopy setup (the measured absorption coefficient at the center of the absorption line was in the order of 10^{-4} cm⁻¹ or higher) the actual spectra for 80 K were obtained with a small admission of H₂ and Ar in the helium gas (typically [He] = 8×10^{17} cm⁻³, [Ar] = 2×10^{14} cm⁻³, and [H₂] = 2×10^{14} cm⁻³). After admixture of argon and/or H₂ the measured absorption coefficient at the center of the absorption line lowered by more than an order of magnitude (see discussion below).

Table 1. Observed and calculated line positions of the example set of lines

band	line	ν_{obs} (cm ⁻¹)	ν_{calc} (cm ⁻¹)
(1-0)	$^{\text{Q}}\text{R}_{23}(1)$	6466.216	6466.217
(1-0)	$^{\text{Q}}\text{P}_{21}(1)$	6466.260	6466.261
(1-0)	$\text{Q}_2(1)$	6466.289	6466.290

The measured time evolution of the absorption coefficient at the center of the $\text{Q}_2(1)$ line of the (1–0) band is shown in Figure 3. Note the fast increase of the measured absorption coefficient after switching off the discharge and then slow exponential decay.

The measured time evolution of the absorption coefficient changes significantly after addition of hydrogen and/or argon. This is shown in Figure 4 for ${}^{\circ}R_{23}(1)$ line of the (1–0) band but similar behavior was observed also for other lines. After switching off the discharge the measured absorption coefficient (and hence also the number density of appropriate states of He_2 dimer) falls down abruptly with a time constant of less than 100 μs .

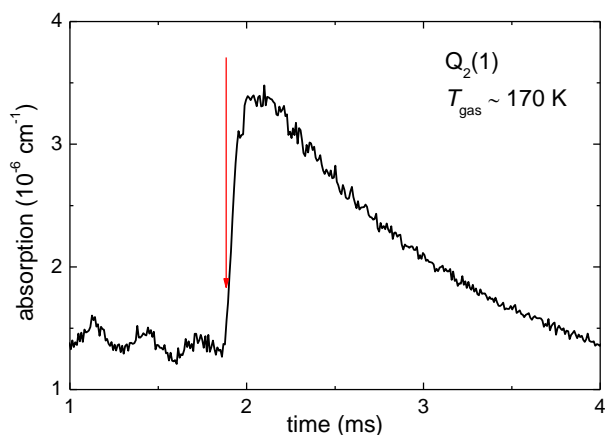


Figure 3. Time resolved decay curve of an absorption features of the He_2 molecule measured in 900 Pa of He gas ($T_{\text{gas}} \sim 170$ K). The absorption signal corresponds to the $Q_2(1)$ transition of the (1–0) band of the $b^3\Pi_g-a^3\Sigma_u^+$ system. The arrow indicates the time, when the magnetron power is switched off.

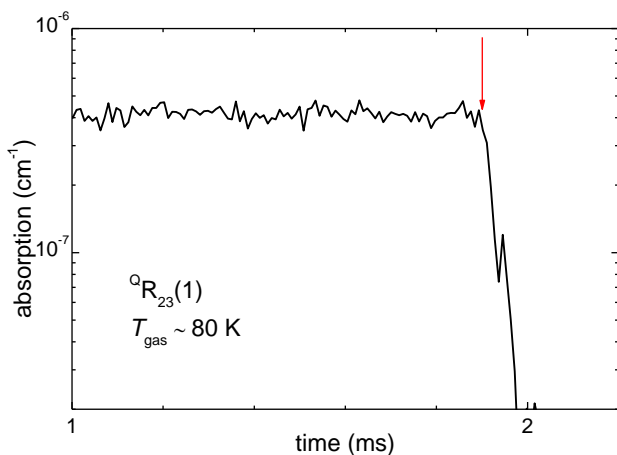
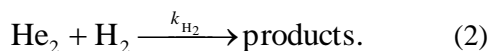
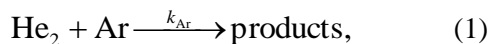


Figure 4. Time resolved decay curve of an absorption features of the He_2 molecule measured in 850 Pa of He/Ar/ H_2 gas mixture ($T_{\text{gas}} \sim 80$ K, $[\text{Ar}] = 3 \times 10^{14} \text{ cm}^{-3}$, and $[\text{H}_2] = 2.5 \times 10^{14} \text{ cm}^{-3}$). The absorption signal corresponds to the ${}^{\circ}R_{23}(1)$ transition of the (1–0) band of the $b^3\Pi_g-a^3\Sigma_u^+$ system. The arrow indicates the time, when the magnetron power is switched off.

Possible explanation for this effect could be that the He_2 dimers are destroyed in collisions with argon and H_2 :



The inferred rate coefficient would be then $k_{\text{Ar}} \sim k_{\text{H}_2} > 2 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$. For comparison, the rate coefficient for Penning ionization of argon by metastable helium atoms is $7 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$.

4. Summary and conclusions

We have studied time resolved spectra of three vibrational bands of the $b^3\Pi_g-a^3\Sigma_u^+$ system of He_2 . Our experimental studies have revealed, that these molecules are also produced in discharges in gas mixtures of He/Ar/ H_2 , and are quenched by reactions with Ar or H_2 , leading to immediate disappearance in the afterglow (less than 100 μs , at used experimental conditions).

Preliminary results show fast removal of He_2 molecules in the afterglow in gas mixtures of He/Ar/ H_2 . Further studies are needed in order to evaluate the role of the He_2 molecule in the discharge and the afterglow in various gas mixtures.

Acknowledgements

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