Spectroscopy of molecular Rydberg states using OODR: LIF excitation and emission spectra of ZnAr and Zn_2 based on experimental and *ab-initio* calculated potentials

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Molecular Spectroscopy and Quantum Information

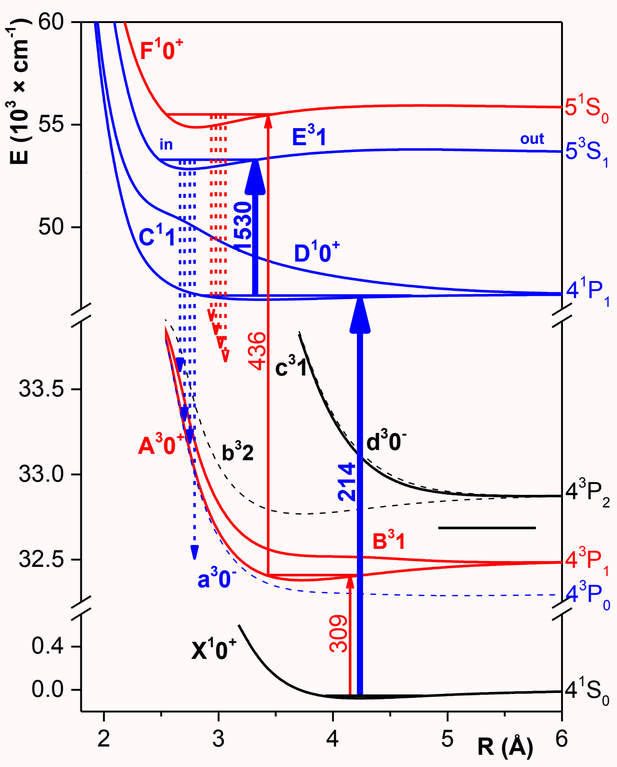
Introduction

Studies of Rydberg electronic energy states of **ZnAr** and **Zn_2** van der Waals (vdW) complexes are presented. *Ab-initio* calculated Rydberg-state interatomic potentials and transition dipole moments (TDM) for **ZnAr** [1,2] (Figs. 1a and 1b) and **Zn_2** [2,3] (Figs. 2a and 2b) have been used to simulate LIF excitation and emission spectra to and from selectively excited vibrational levels, respectively. The aim is to assess the optimal schemes for the excitation of the higher-lying (Rydberg) electronic energy states using optical-optical double resonance (OODR) method. Up to date, *ab initio* calculations of Czuchaj *et al.* [1] and Krośnicki [2] have been devoted to Rydberg electronic energy states of ZnRg correlating with the 5^3S_1 and 5^3S_0 atomic asymptotes, while only one, namely the $E^3\Sigma_1(5^3S_1)$, Rydberg state of **ZnAr** was experimentally investigated by Bennett and Breckenridge [4] using vaporization-optical excitation in a supersonic beam. For **Zn_2**, despite availability of lowest-lying Rydberg state potentials [2,3], no attempt has been made so far to investigate them using OODR and the supersonic beam technique.

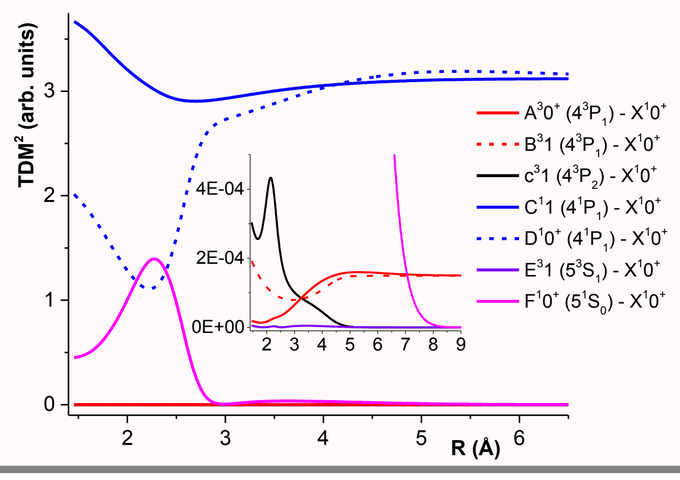
Our experimental procedure (Fig. 4) uses OODR scheme to excite, in general, all **ZnRg** (Rg=rare gas atom) and **Zn_2** complexes employing newly constructed supersonic molecular beam apparatus for highly invasive elements. It is well known that Zn is an aggressive element, especially in high temperatures, and a special effort has to be made to avoid unwanted deterioration of the beam source.

The goal of the study is to perform theory-to-experiment-comparison investigation for the lower-lying Rydberg states of **ZnAr** and **Zn_2** followed by as complete as possible studies of the whole **ZnRg** and (**Zn_2-Cd_2** [5]-**Hg_2** [6]) groups of complexes. New *ab initio* calculations of **ZnAr** and **Zn_2** Rydberg-state interatomic potentials are underway in our laboratory [7].

ZnAr: Interatomic potentials



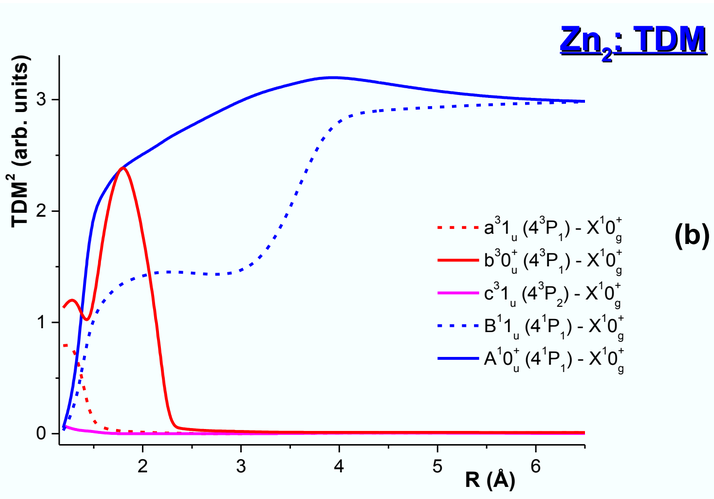
(a)



(b)

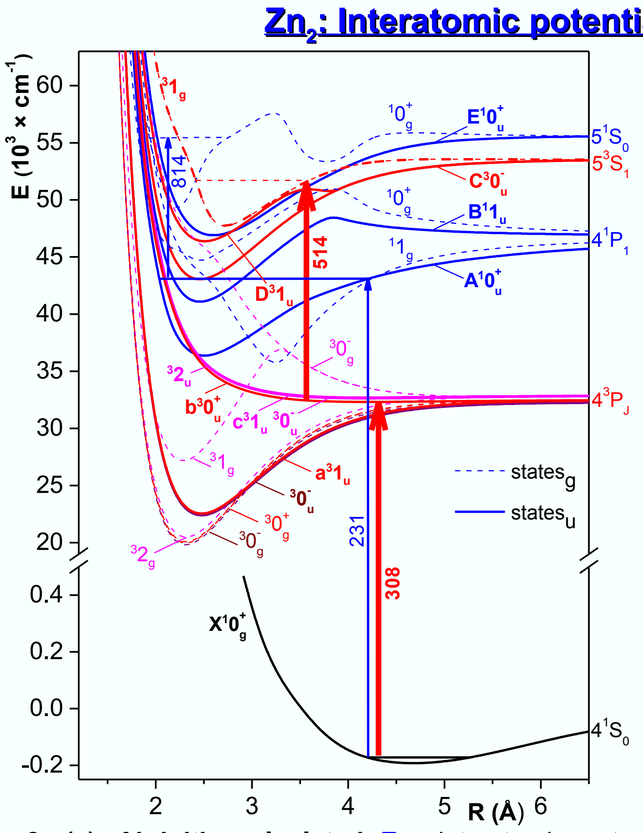
Fig. 1. (a) ***Ab-initio* calculated ZnAr** interatomic potentials showing two $E^3$1 and $F^1$0$^+$ lower-lying Rydberg electronic energy states correlating with the 5^3S_1 and 5^1S_0 atomic asymptotes, respectively, and their possible OODR excitation from the $X^1$0$^+$ *via* intermediate $C^1$1(4^1P_1) or $A^3$0$^+$(4^3P_1) states. Excitation wavelengths in (nm). **(b) TDM²(R)** for several 1st-step transitions.

ZnAr: TDM



(b)

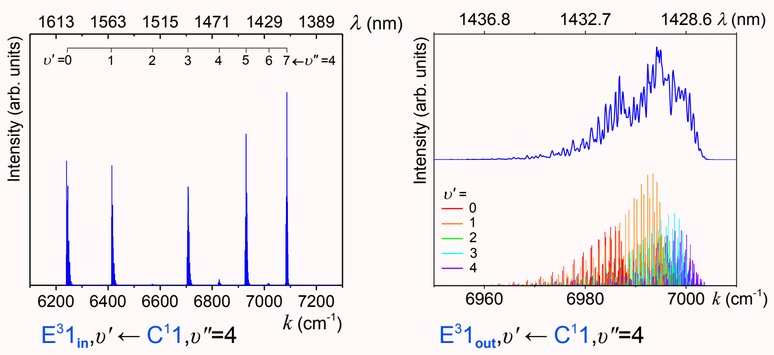
Zn_2: Interatomic potentials



(a)

Fig. 2. (a) ***Ab-initio* calculated Zn_2** interatomic potentials showing two ^{3}1$_g$ and ^{1}0$_g^+$ lower-lying gerade Rydberg electronic energy states correlating with the 5^3S_1 and 5^1S_0 atomic asymptotes, respectively, and their possible OODR excitation from the $X^1$0$_g^+$ *via* intermediate $A^1$0$_u^+$ or $b^3$0$_u^+$ states. Excitation wavelengths in (nm). **(b) TDM²(R)** for several 1st-step transitions.

ZnAr LIF excitation spectrum of the 2nd-step transition



ZnAr LIF emission spectrum from the 2nd-step transition

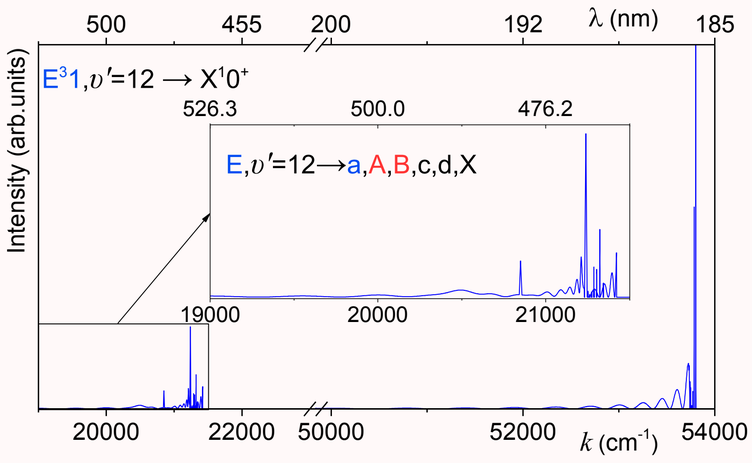


Fig. 3. Examples of simulated LIF excitation (upper part, LEVEL [8] and Pgopher [10]) and emission (lower part, BCONT [9]) spectra in **ZnAr** using *ab-initio* calculated potentials [2]: the $E^3$1,$\upsilon' \leftarrow C^1$1,υ''=4 (upper part) and $E^3$1,υ'=12 ⟶ $a^3$0$^-$, $A^3$0$^+$, $B^3$1, $c^3$1, $d^3$0$^-$, $X^1$0$^+$ (lower part).

New source of molecular beam

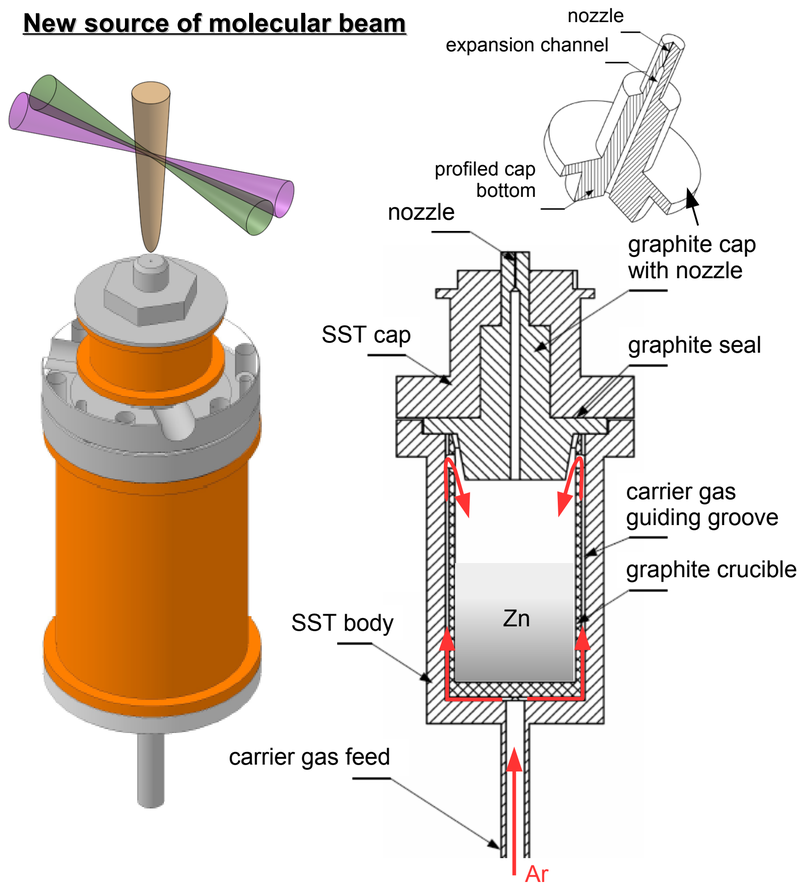
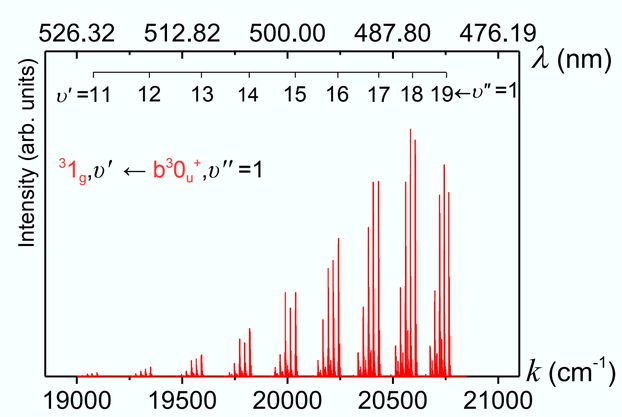


Fig. 4. New source module of a molecular beam devoted to production of internally cooled molecules that consist of highly aggressive elements (here, Zn). Patent application in Republic of Poland (P.428617).

Zn_2 LIF excitation spectrum of the 2nd-step transition



Zn_2 LIF excitation spectrum of the 1st-step transition

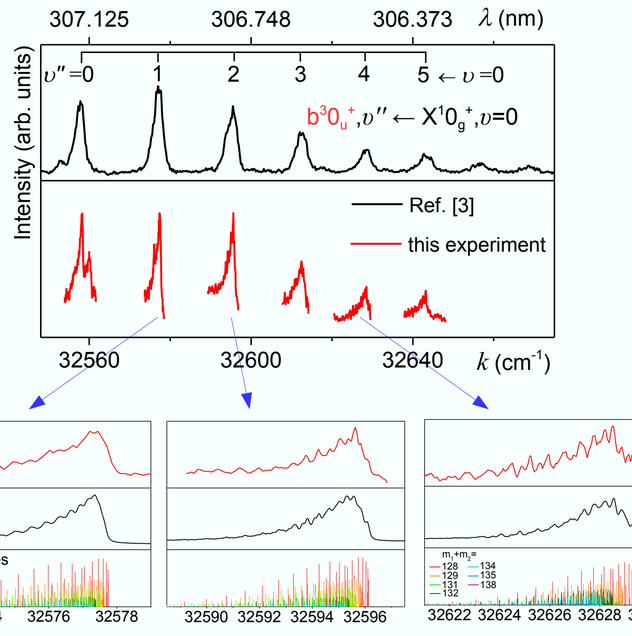


Fig. 5. Examples of simulated LIF **Zn_2** excitation spectrum of the ^{3}1$_g$,$\upsilon' \leftarrow b^3$0$_u^+$,υ''=1 2nd-step transition (upper part), and experimental and simulated excitation spectrum of the $b^3$0$_u^+$,$\upsilon'' \leftarrow X^1$0$_g^+$,$\upsilon$=0 1st-step transition with several vibrational bands simulated taking account the isotope and rotational energy structures (lower part). LEVEL [8] and Pgopher [10] were used.

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