Spectroscopy of CdRg complexes using OODR method: New analysis of the $E^3\Sigma_1^+{}_{out}$ (6^3S_1) Rydberg state potential in CdKr

T. Urbańczyk and J. Koperski

Smoluchowski Institute of Physics, Jagiellonian University, Łojasiewicza 11, 30-348 Kraków, Poland

UNIWERSYTET JAGIELLOŃSKI W KRAKOWIE

Molecular Spectroscopy and Quantum Information Group

Department of Photonics

Idea of OODR method

In the experiment conducted in our laboratory, the optical-optical double resonance (OODR) method was applied to excite CdKr molecules from the ground state $X^1\Sigma_{0+}$ to the outer well of higher-excited Rydberg electronic state $E^3\Sigma_1^+{}_{out}$ *via* intermediate state $B^3\Sigma_1^+$ (see Fig.1). Generally, using OODR method there is a possibility to reach electronic states, which will be difficult to excite using one photon excitation due to difficulty with finding appropriate tunable source of light. For example energy of excitation to $E^3\Sigma_1^+{}_{out}$ state in CdKr is about 51500 cm^{-1} which correspond to 194 nm. Applying OODR technique we can reach $E^3\Sigma_1^+{}_{out}$ state with using of two tunable dye lasers (325 nm for the $B^3\Sigma_1^+ \leftarrow X^1\Sigma_{0+}$ excitation and 480 nm for the $E^3\Sigma_1^+{}_{out} \leftarrow B^3\Sigma_1^+$ excitation). For details see experimental set-up in Fig. 2.

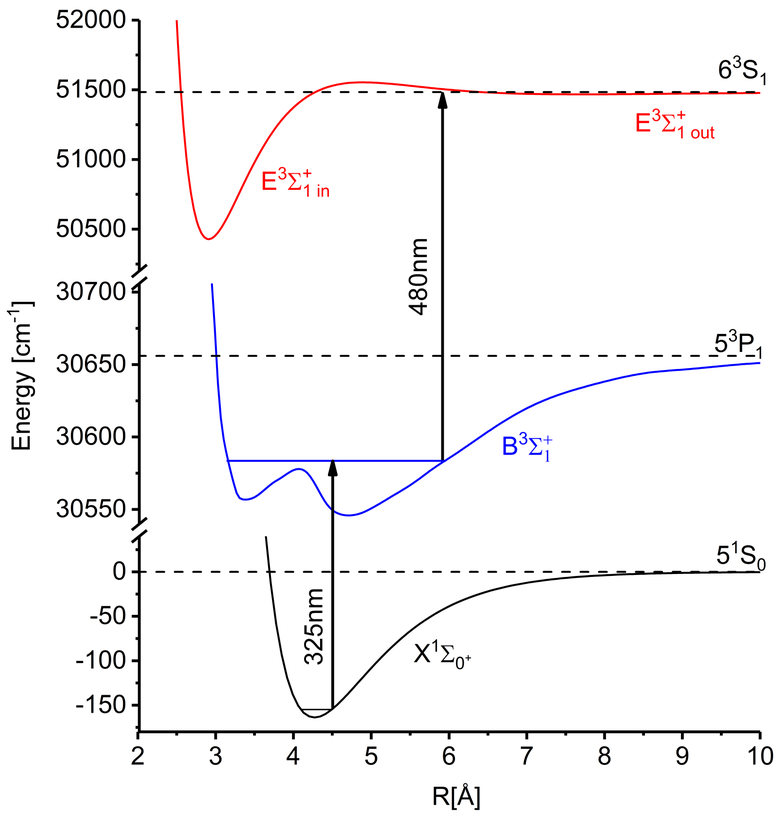

Fig. 1. The general scheme of OODR method in CdKr molecule using the $X^1\Sigma_0^+$, $B^3\Sigma_1^+$ and $E^3\Sigma_1^+{}_{out}$ states.

Experimental set up

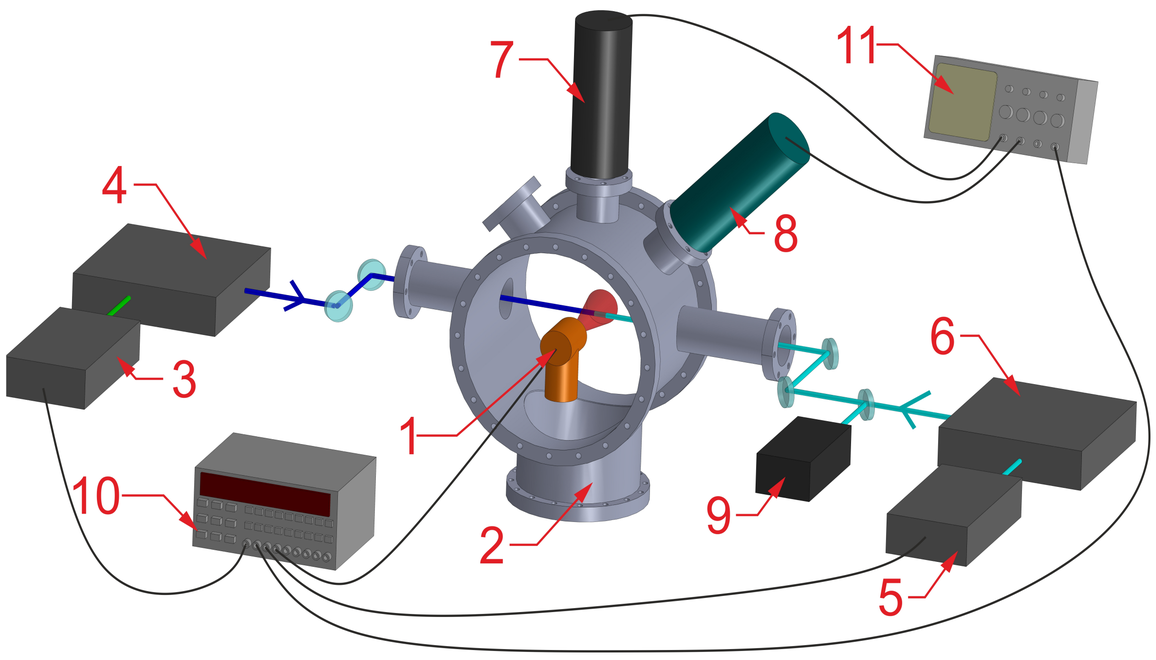

Fig. 2. Experimental scheme used in OODR experiment. (1) High-temperature, high-pressure, pulsed source of supersonic molecular beam. (2) Vacuum chamber. (3) and (5) Pulsed Nd⁺:YAG lasers. (4) Frequency-doubled tuneable dye laser (first-step excitation in OODR scheme). (6) Tuneable dye laser (second-step excitation in OODR scheme). (7) Photomultiplier (PM) tube screened from the UV radiation for recording fluorescence from the final Rydberg state. (8) Auxiliary PM tube recording fluorescence from the intermediate state. (9) Wavemeter. (10) Digital delay generator used for time synchronization of the pulsed beam source, Nd⁺:YAG lasers and triggering of the oscilloscope. (11) Oscilloscope averaging signals from the PM tubes. For details see [1].

References

[1] T.Urbańczyk, J.Dudek, J.Koperski, *Quant. Spectrosc. Radiat. Transf.* **212** (2018) 32.

[2] J. Koperski, M. Czajkowski, *Phys. Rev. A* **69** (2004) 042509.

[3] M. Krośnicki, http://iftia9.univ.gda.pl/~kroch/potentials.htm.

Acknowledgements

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Nonlinearity of Birge-Sponer plot

Fig. 3 presents Birge-Sponer (B-S) plot for the $E^3\Sigma_1^+{}_{out}$ state in CdKr drawn basing on experimental spectrum of the $E^3\Sigma_1^+{}_{out}(v') \leftarrow B^3\Sigma_1^+(v''=6)$ transition (see Fig. 4). There is a strong nonlinearity of the plot for the small values of v'. This indicates on the existing non-Morse behaviour of the $E^3\Sigma_1^+{}_{out}$ state potential near the bottom of the potential well (see **Result of IPA method**).

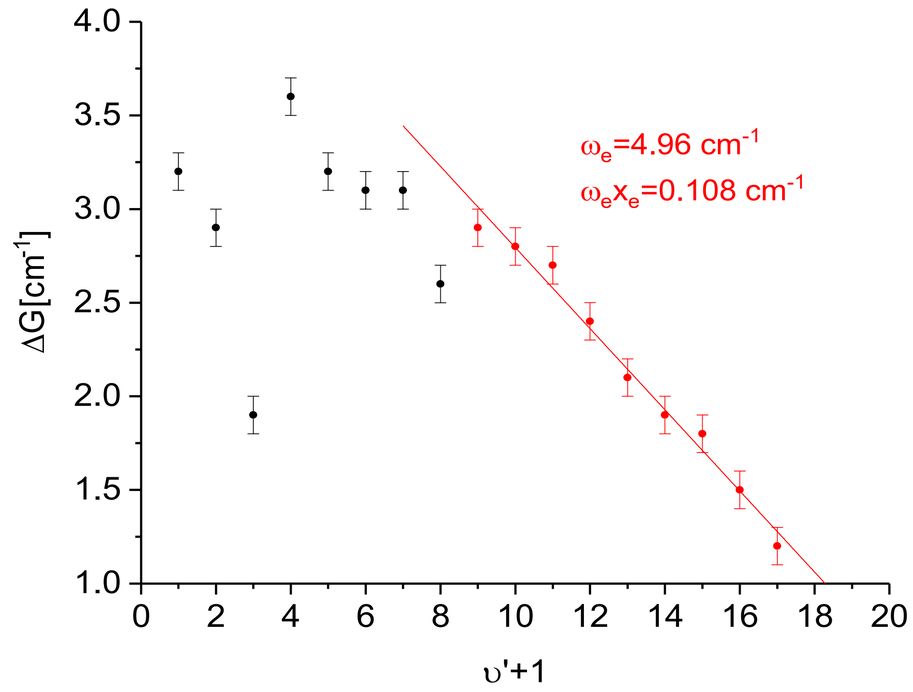

Fig. 3. Birge-Sponer plot for the $E^3\Sigma_1^+{}_{out}$ state in CdKr. Linear part of the plot (**red points**) and nonlinear part of the plot near bottom of the potential well (**black points**). Linear fit to the red points is also shown (**red line**).

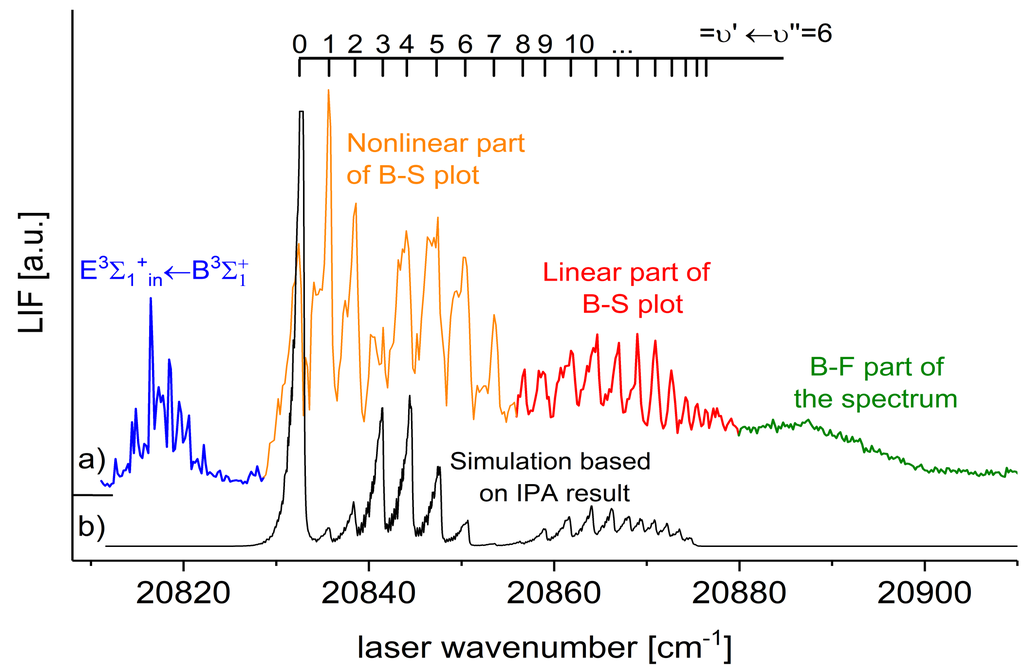

Fig. 4. a) Experimental LIF excitation spectrum of the $E^3\Sigma_1^+{}_{out}(v') \leftarrow B^3\Sigma_1^+(v''=6)$ transition in CdKr. b) Simulation of the spetrum based on result of IPA method (T_{rot}=3K, $\Delta_{gauss}=\Delta_{lorentz}$= 0.1$cm^{-1}$).

Result of IPA method

Due to observed nonlinearity in B-S plot presented in Fig. 3, an Inverted Perturbation Approach (IPA) method was applied to obtain a representaiton of the $E^3\Sigma_1^+{}_{out}$ state potential. The result of this approach is presented in Fig. 5.

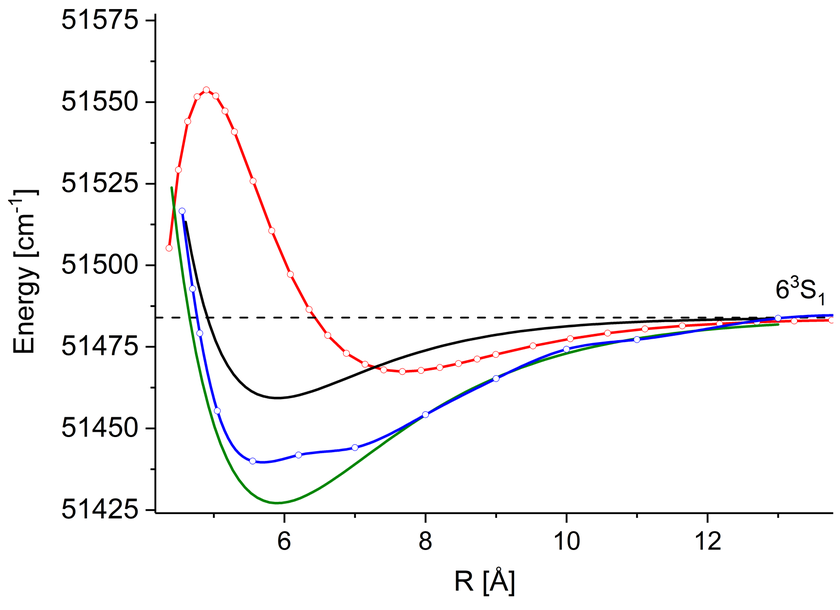

Fig. 5. Different representations of the $E^3\Sigma_1^+{}_{out}$ state potential in CdKr. Morse representation [2] (**black solid line**), ab initio potential [3] (**red empty points and solid line**), result of IPA method using data from experimental spectrum shown in Fig. 4a (**blue empty points and solid line**). The initial Morse potential used for IPA method based on the result of BS fit (see **Nonlinearity of Birge-Sponer plot**) is depicted with **green solid line**.