Rotational structures in excitation spectra of the $B^31(5^3P_1)\leftarrow X^10^+(5^1S_0)$ transition in CdAr

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Molecular Spectroscopy and Quantum Information

Atomic Scale Science for Innovative Economy

Experimental setup:

Pulsed supersonic source

In molecular beam experiments supersonic pulsed sources are preferred over those operating in continuous mode because they reduce consumption of analyzing substance and carrier gas. Moreover, pulsed sources enable using of larger nozzle diameters, higher carrier gas pressure and provide excellent conditions to work with pulsed lasers (supersonic pulse can be correlated with pulse of laser light). The main disadvantage of pulsed sources is fact that commercially available pulsed valves can operate only up to 590K, which is insufficient for many purposes (particularly for production of supersonic beam of cadmium dimers). To overcome this limitation we use long plunger attached to water-cooled commercial solenoid valve (Parker-General Valve Series 9).The details of our construction are presented in Fig.1 (on the right) and also in [1].

Principle of operation

In the experiment, cadmium metal is heated in the lower reservoir (13) up to 1000K and mixed with carrier gas (Rg= Ar, Kr, Ne) delivered by lower pipe (12). Next, the cadmium vapour (partial pressure 0.2 bar) enter the upper source chamber (17) which ends with a nozzle (usually D=0.15mm orifice diameter) through which the mixture expands to the vacuum chamber forming supersonic beam containing Cd_2 and CdRg van der Waals molecules.

Experimental details

In our experiment, molecules in supersonic beam were irradiated at distance of 11mm from the nozzle with a frequency-doubled dye laser beam (TDL90 system of Quantel with LDS(33%)-DCM(66%) mixture in ethanol, pumped with pulsed YG981C Nd-YAG laser of Quantel). The excitation spectra were recorded in the 30690-30750 cm^{-1} spectral region by focusing the total LIF from the interaction region on the cathode of a photomultiplier (PM) tube (9893QB/350, Electron Tubes). During data acquisition phase, for each laser frequency (tuning realized in 0.06-cm^{-1}-step mode) the signal from PM was averaged in the oscilloscope (for 64 laser shots) and the resulting waveform was saved in a computer. The final spectrum was determined from collected waveforms after selecting proper size of time-integration window (the selection of time-gating window had an impact on which type of molecules from supersonic beam contributed to the final spectrum). It is important, that selection of time gating-window takes place in data analysis phase of the experiment, so different type of spectra can be obtained from one set of waveforms (see Fig.2 below)

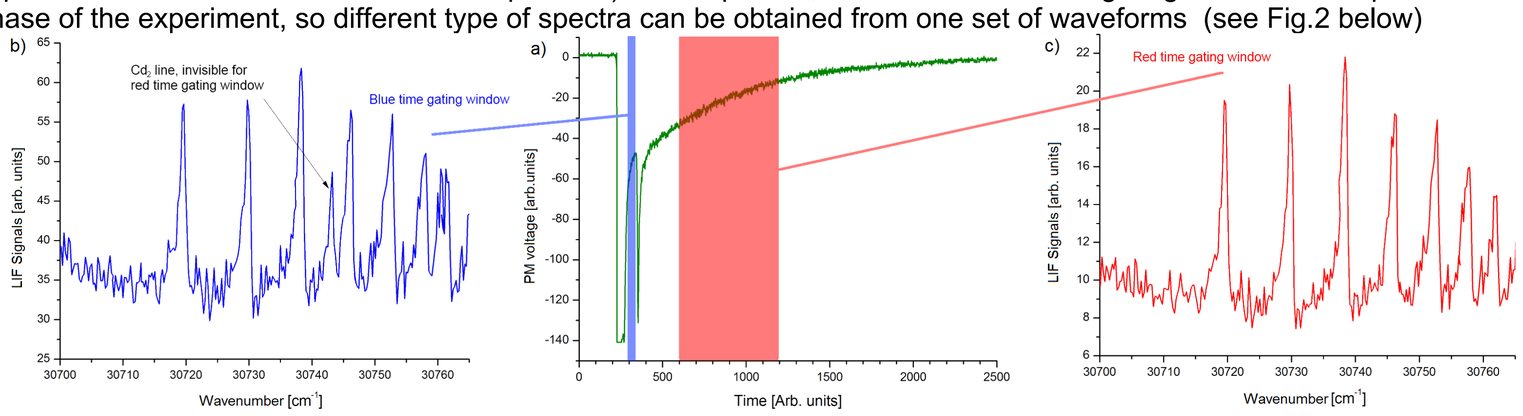
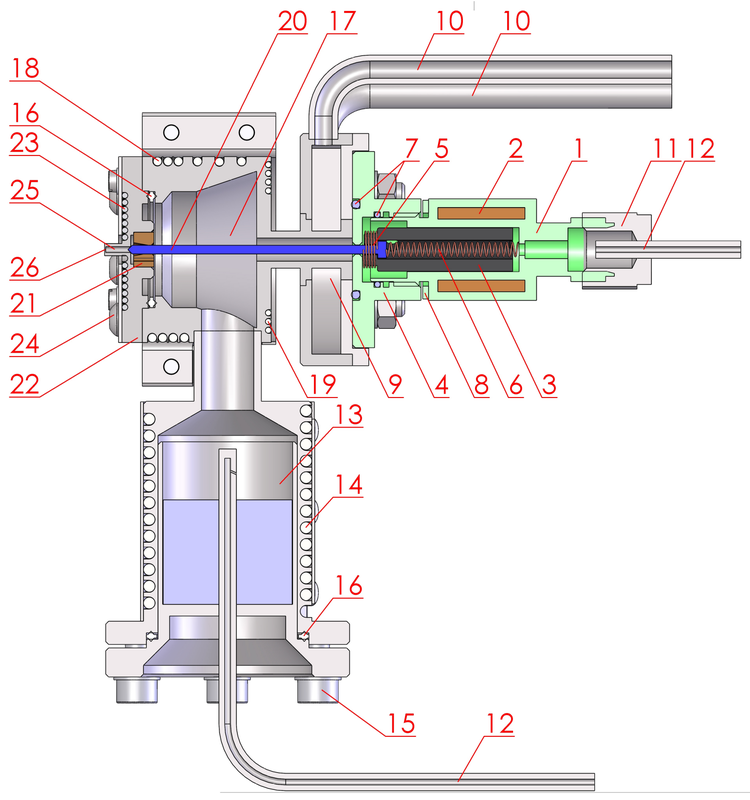
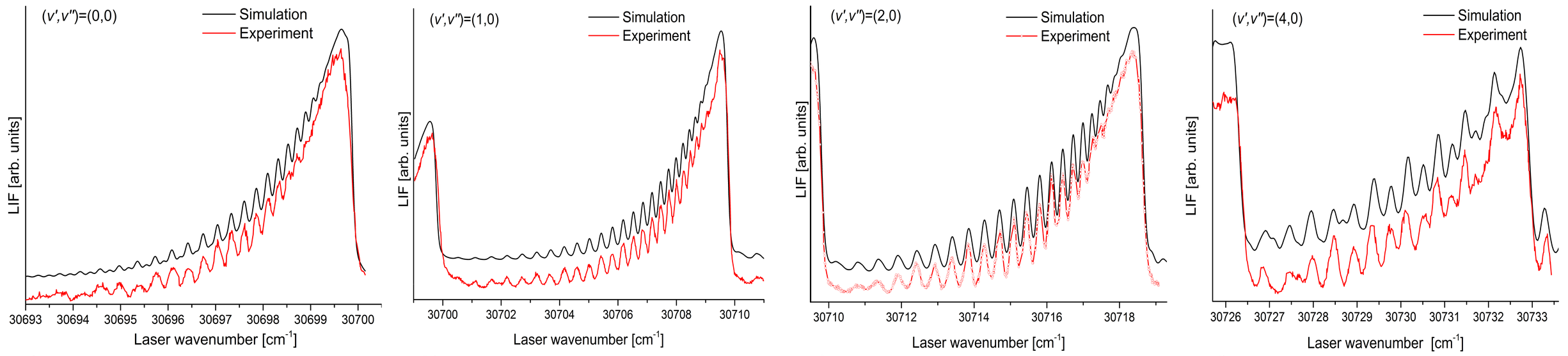


Fig. 2 a) Sample of the waveform (averaged signal from PM for one laser frequency), red and blue rectangles illustrate the time gate interval applied for left and right spectra, respectively. b) The LIF spectrum with Cd_2 and CdAr vibrational components determined with blue time gate window. c) The LIF spectrum determined with red time gate window. The Cd_2 vibrational components are now invisible, as the fluorescence from Cd_2 lives shorter than that from CdAr (*i.e.*, Cd_2 fluoresce before opening of the integration window).



c)

Fig.1. Cross section of the high-temperature high-pressure pulsed source of vdW dimers developed in our laboratory. Parker-General Valve Series 9 commercial solenoid valve (green): 1, coil assembly; 2, solenoid coil; 3, armature; 4, flange mount; 5, buffer spring; 6, main spring; 7, Kalrez orings of DuPont™; 8, shim. Parts of the pulsed source: 9, water shield; 10, water pipes; 11, Swagelok® connection; 12, carrier gas supplies; 13, Cd reservoir; 14, reservoir heater; 15, reservoir screw; 16, iron washer; 17, source chamber; 18, source body heater; 19, source body back heater; 20, titanium plunger; 21, brass slide bearing; 22, nozzle cartridge; 23, nozzle cartridge heater; 24, nozzle cartridge screw; 25, nozzle channel; 26, orifice.



v'	$B_{v'}$ [cm^{-1}]	$D_{v'}$ [cm^{-1}]
0	0.02215	4.0114e-7
1	0.02105	4.4367e-7
2	0.01994	4.8620e-7
4	0.01735	6.1289e-7
5	0.01616	6.6467e-7
6	0.01497	7.1645e-7

Tab.1. Rotational constants of several vibrational levels of the $B^31(5^3P_1)$ state for the most abundant $^{114}Cd^{40}Ar$ isotopologue.

Fig.3 a-f: Excitation spectra (red) recorded using the $B^31(5^3P_1) \leftarrow X^10^+(5^1S_0)$ transition in CdAr with corresponding Pgopher simulations (black). Simulations that include all isotopologues were performed for $B_{v'}$ and $D_{v'}$ values from Tab.1 (constants for different isotopologues were recalculated considering differences between masses of isotopologues [3]). In the simulations, the rotational temperature T_R, laser bandwidth Δ_L, and gaussian broadening Δ_G were as follow: a) (7.5K, 0.06cm^{-1}, 0.11cm^{-1}), b) (7.1K, 0.06cm^{-1}, 0.15cm^{-1}), c) (8K, 0.06cm^{-1}, 0.15cm^{-1}), d) (9K, 0.06cm^{-1}, 0.12cm^{-1}), e) (8K, 0.06cm^{-1}, 0.15cm^{-1}), f) (8K, 0.06cm^{-1}, 0.15cm^{-1}).

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References

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[2] PGOPHER, a Program for Simulating Rotational Structure, C. M. Western, University of Bristol, http://pgopher.chm.bris.ac.uk .
[3] T. Urbanczyk, J. Koperski, „Pulsed supersonic source of vdW complexes for high-temperature applications: Spectroscopy and beam characteristics”, *Eur. Phys. J. - Special Topics* (2013), in print.