Separation of overlapped spectral profiles originated from different complexes excited in a supersonic expansion beam experiment

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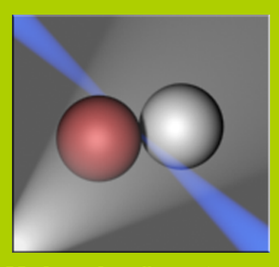

Molecular Spectroscopy and Quantum Information

Atomic Scale Science for Innovative Economy

Introduction

We present a method, which can be used to separate of overlapped profiles of molecular spectra originated from different laser-excited complexes in supersonic beam experiment [1,2] (for experimental details see Fig.1, for example of overlapped spectrum see trace a in Fig. 4). The method, is based on two ideas: selecting of proper time-gating window and subtraction of spectra obtained for different time-gating windows.

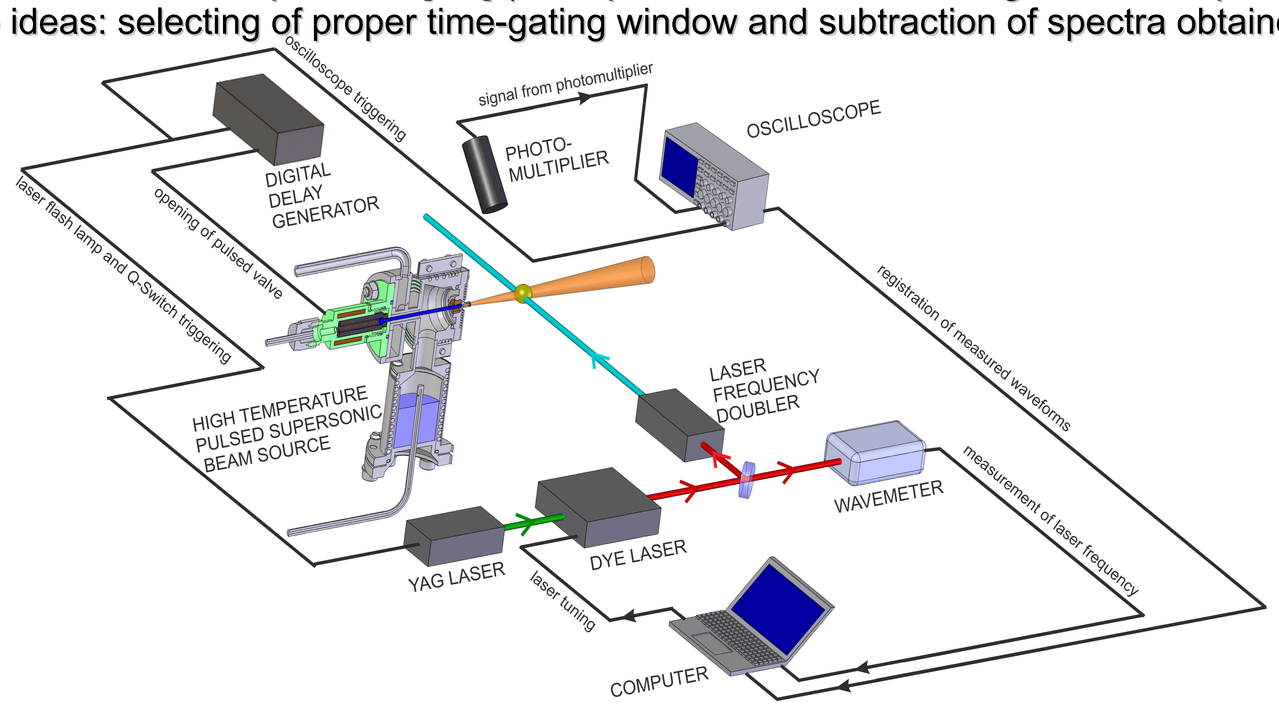

Fig.1. Experimental set up

A digital delay generator (DG645 Stanford Research Systems) is used to synchronize the pulses of high-temperature, supersonic molecular beam source and YAG-laser-pumped-dye laser (YG981C and TDL90 of Quantel). In a vacuum chamber (pumped down to 10^{-3} mbar) the molecular beam is irradiated by the frequency doubled dye laser beam. The LIF signal from interaction region is focused on a cathode of a photomultiplier (PM). For each laser wavelength, the signal from PM is averaged on the digital oscilloscope for several (e.g. 64) laser shots and finally, the whole waveform from the oscilloscope is saved in the computer memory for further analysis. Moreover, for each laser tuning step, the laser frequency and bandwidth are measured using wavemeter (WSU30 of High Finese) as well as other important experimental parameters (e.g. pressure in vacuum chamber) are registered.

Selection of proper time gating window

Raw experimental data collected in our experiment are in the forms of waveforms. Each wavform is a collection of photomultiplier voltages measured by the osciloscope with specific time interval after triggering. To obtain the useful spectrum from these raw data it is necessary to determine the limits (so called time gating window) over which the waveforms are integrated. Because the different molecules usually have different lifetimes in excited states selecting of proper time gating window is powerful method in the process of the separation of overlapped spectra (see Fig.2).

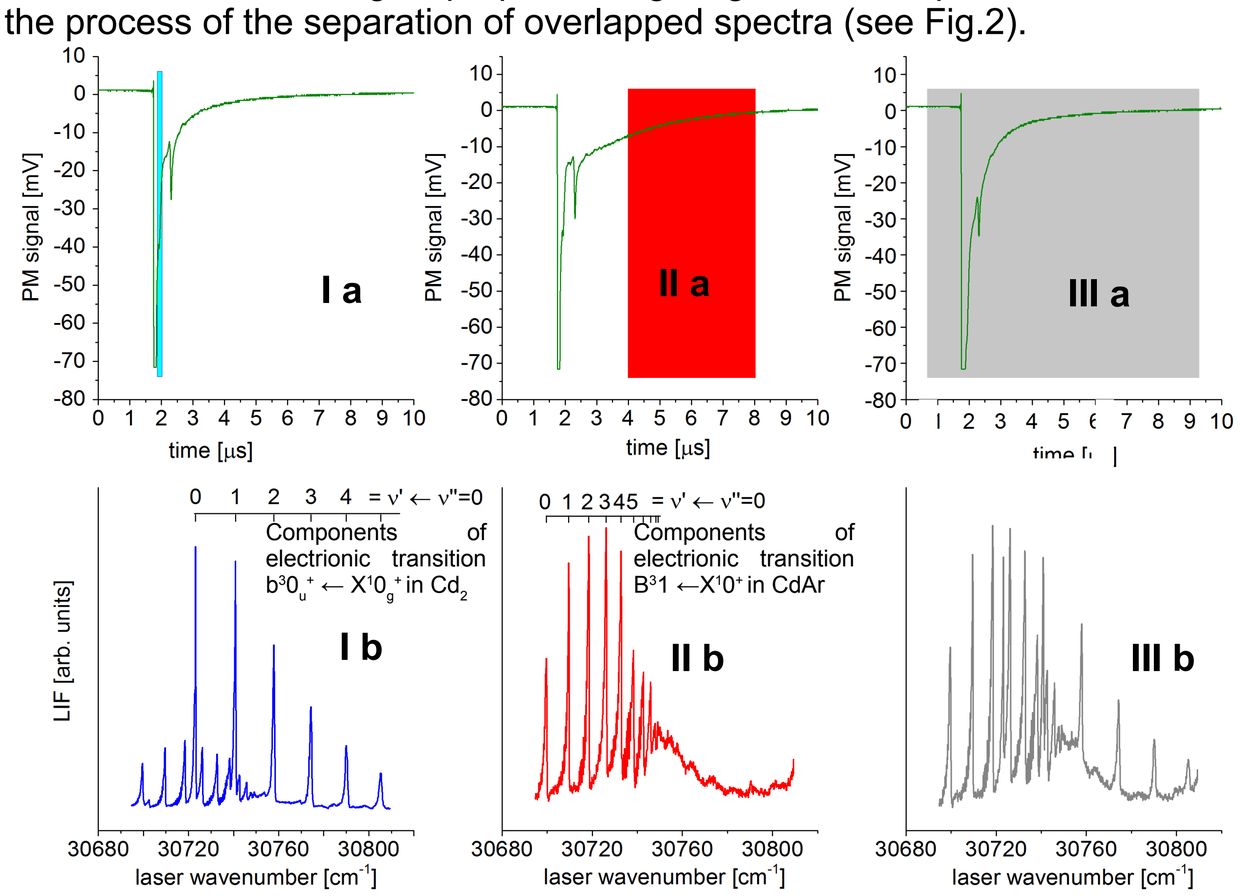

Fig.2. Influence of a time gating window on the obtained spectrum

Figure above shows blue, red and gray spectra (part Ib, IIb and IIIb respectively) that were obtained using blue, red and gray time-gating windows, respectively (colored rectangles presented in Ia, IIa and IIIa - the colors of rectangles correspond to the colors of spectra). As can be seen, the short time-gating window (blue, Ia), that starts immediately after the laser pulse, prefers selection of spectrum of Cd_2 molecule, while the longer one (red, IIa), that starts adequately later, prefers selection of spectrum originating from CdAr molecule. It is consistent with the observation that lifetime of the $B^3 1$-state of CdAr is longer than that of the $b^3 0_u^+$-state of Cd_2 [3,4].

Spectra subtraction procedure

The second method, which allow much better separation of overlapped spectra is based on a subtraction of spectra obtained for different time -gating windows. The spectra obtained using different time gating-windows have different contribution of signals originating from different complexes, so reciprocal subtraction of these spectra multiplied by carefully chosen numerical factors can lead to the final spectrum in which admixture from unwanted molecule is considerably reduced (see traces e) and f) in Figure bellow in comparison with traces c) and d) in the same Figure, or traces Ib and IIb in Figure1).

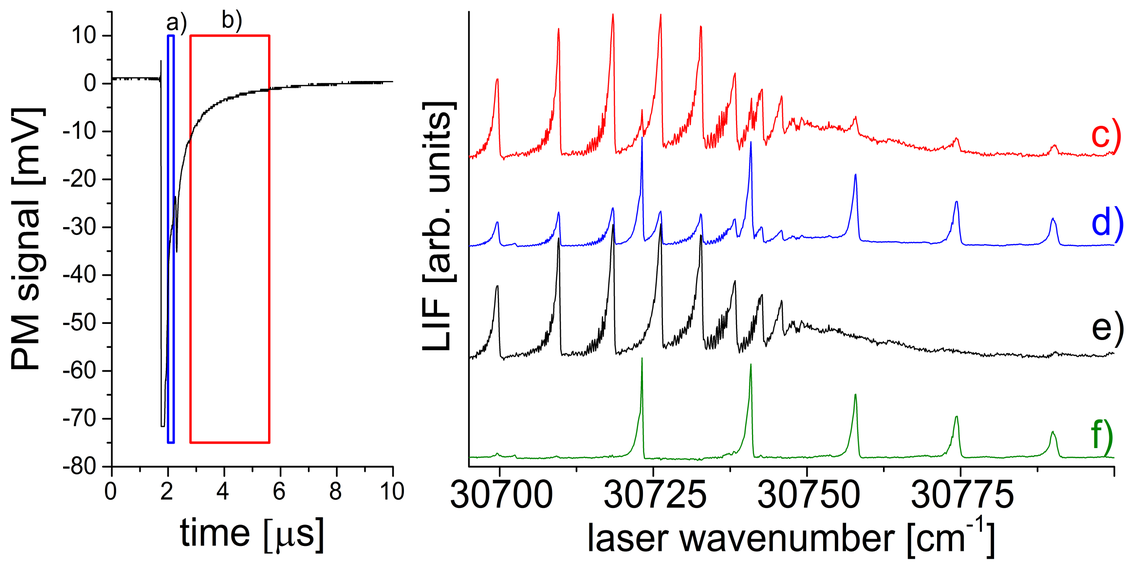

Fig.3. Spectra subtraction procedure

Traces c) and d) were obtained using red and blue time-gating windows (rectangles a) and b) on the left side of the Figure). The red spectrum in trace c) consists of a large contribution from the $B^3 1 \leftarrow X^1 0^+$ transitionin CdAr with small admixture from the $b^3 0_u^+ \leftarrow X^1 0_g^+$ transition in Cd_2. Contrary, the blue spectrum in trace d) consists of large contribution from transition in Cd_2 and small admixture of CdAr. The black spectrum (trace e) is a result of subtraction of spectrum d) from spectrum c), while the green spectrum (trace f) is a result of subtraction of spectrum c) from spectrum d).

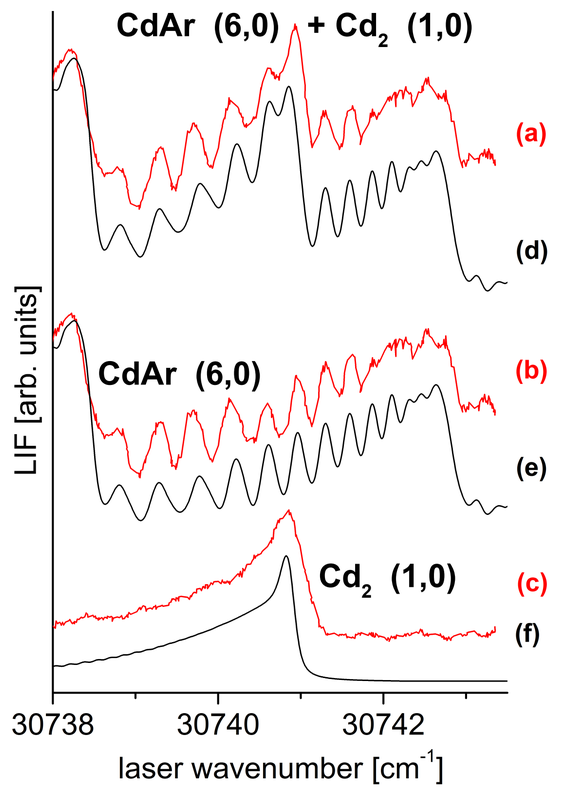

Fig.4. Spectra separation example

Trace a) presents overlapped rotational profiles originated from transition $B^3 1 \leftarrow X^1 0^+ (\upsilon'=6; \upsilon''=0)$ in CdAr and $b^3 0_u^+ \leftarrow X^1 0_g^+ (\upsilon'=1; \upsilon''=0)$ in Cd_2 measured with higher spectral resolution than that in Fig.3. Traces b) and c) present separated spectra. (d), (e), (f) simulations performed with a Pgopher [5] program.

References

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