

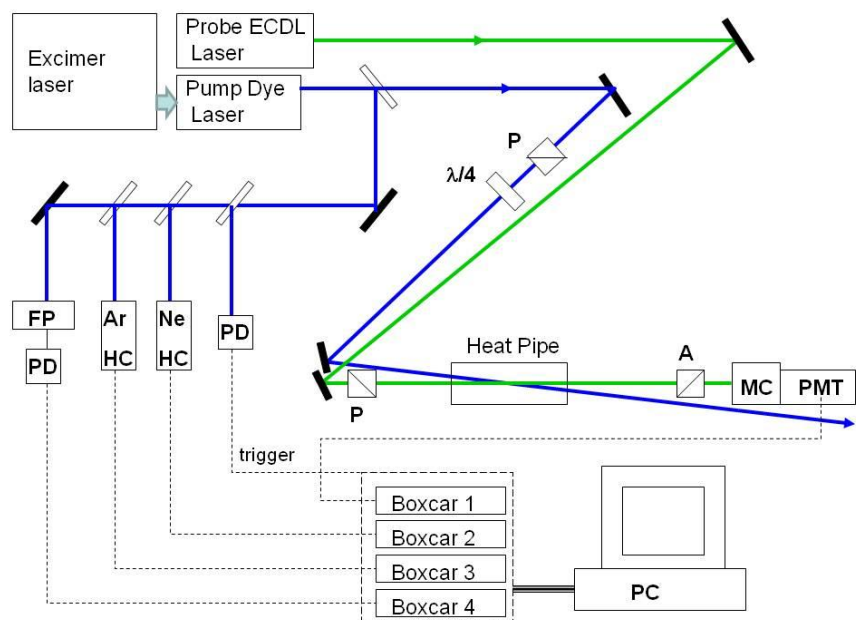


The $3^1\Pi_u$ state in caesium dimer

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Experiment



P – polariser, *A* – analyser

$\lambda/4$ – quarter-wave plate, *FP* – Fabry-Pérot interferometer

Ar HC / *Ne HC* – argon / neon hollow-cathode lamp

MC – monochromator, *PD* – photodiode

PMT – photomultiplier tube

- The copropagating pump and probe laser beams are crossed in the molecular sample.

- The probe laser is set at a fixed wavelength in the $B^1\Pi_u \leftarrow X^1\Sigma_g^+$ band system of Cs_2 molecule, resonant with a few known rovibronic transitions, thus labelling the involved rovibrational levels in the ground state.

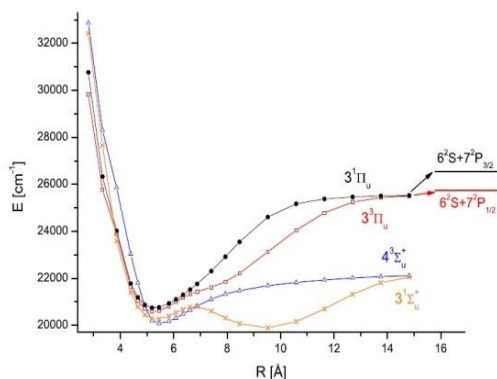
The pump laser is tuned across the investigated band system - 20400 - 21600 cm^{-1} .

- The information about the excitation spectrum of the molecules is contained in the transmitted intensity of the probe light.

Analysis

- Our study reveals that instead of regular ladder of levels belonging solely to the $3^1\Pi_u$ state we deal with an intricate system of highly perturbed levels belonging to more electronic states.

- This can be inferred from a picture of theoretical potential energy curves for the related energy region

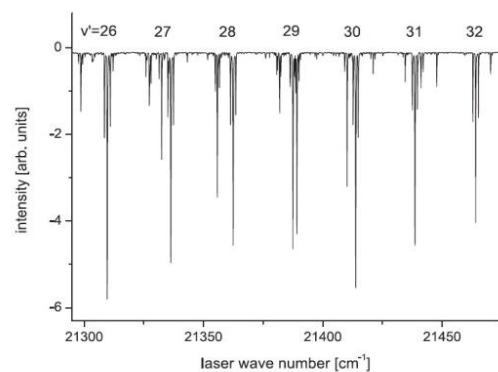


Theoretical potential curves of the four electronic states of Cs_2 related to the present experiment

- All vibrational levels of the $3^1\Pi_u$ state starting from $v = 4$ are heavily perturbed.

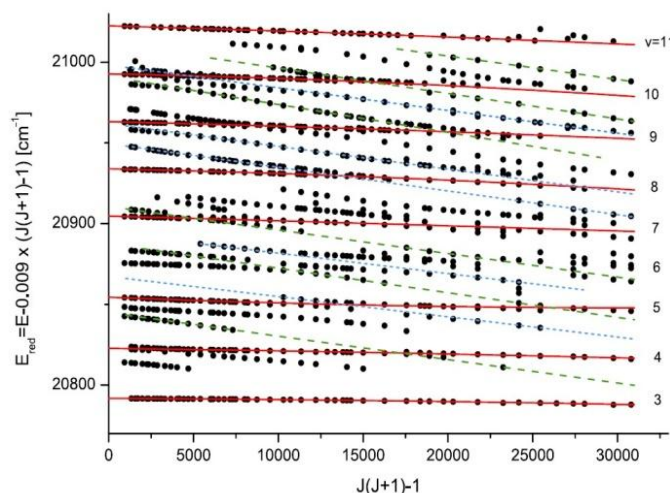
- The Figure includes both 'main' and 'extra' levels, the latter belonging to other state(s) inaccessible in direct excitation from the singlet ground state of Cs_2 and observable due to mixing of their wave functions with these of the $3^1\Pi_u$ state.

- In case of the vast majority of levels, even if strongly perturbed, we are certain about their assignment to J quantum numbers because in most spectra only a single (v'' ; J'') level in the ground state was labelled.



A part of the polarisation spectrum

- The bottom part of the $3^1\Pi_u$ state potential runs nearly in parallel with the nearby $3^3\Pi_u$ state potential, and in addition it is crossed by the $4^3\Sigma_u^+$ state curve. To simplify the analysis to some extent, we limited our analysis to f parity levels, prone to perturbations by $\Omega = 1$ components of both triplet states.



Reduced term values $E_{red} = E - 0.09 \times [J(J+1)-1]$ [cm^{-1}] of part of the observed rovibrational levels in the $3^1\Pi_u \sim 3^3\Pi_u \sim 4^3\Sigma_u^+$ complex in Cs_2 (dots) plotted against $J(J+1)-1$. The term values calculated from the band constants of the $3^1\Pi_u$ state listed in the Table presented beside are represented by red solid lines. The long dashed (green) and short dashed (blue) lines represent approximate term values of the two triplet perturbers.

Results

- We found that only the four lowest levels of the $3^1\Pi_u$ state, $v = 0 - 3$, are free of observable perturbations and only their positions can be described in a compact way by molecular constants (see Table beside).

constant	value
T_e	20684.56(3)
ω_e	30.62(1)
B_e	0.009125(30)
$\alpha_e \times 10^4$	0.3784 (32)
$D_e \times 10^8$	0.274(9)
rms	0.06
φ	4911.3(9)
$R_e[\text{\AA}]$	5.27(1)

Molecular constants (in cm^{-1}) for the $3^1\Pi_u$ state of Cs_2 representing energies of rovibrational levels in the range $v = 0 - 3$.

- For several vibrational levels of the $3^1\Pi_u$ state we tried to pick out these rotational levels which appeared to be only weakly affected by local perturbations and to determine rough band constants by fitting their energies to the formula:

$$E(v, J) = T_v + B_v[J(J+1) - 1] - D_v[J(J+1) - 1]^2$$

- The results are presented in the Table below.

v	T_v	B_v	$D_v \times 10^9$	rms
4	20822.86	0.00885	1.6	0.09
5	20854.72	0.00850	-10.1	0.07
...				
7	20904.72	0.00873	2.0	0.11
8	20933.89	0.00878	6.4	0.03
9	20963.12	0.00878	5.0	0.09
10	20992.73	0.00880	8.1	0.06
11	21022.51	0.00871	2.6	0.07
12	21052.27	0.00861	0.6	0.10
...				
17	21193.82	0.00826	-1.7	0.11
18	21217.45	0.00857	4.5	0.09
19	21246.95	0.00836	-0.9	0.05
20	21272.30	0.00858	5.7	0.12
...				
24	21378.75	0.00834	-0.9	0.11
25	21405.74	0.00832	1.3	0.10
26	21432.60	0.00831	3.2	0.12
27	21458.81	0.00834	4.6	0.09
28	21484.35	0.00837	5.1	0.13
...				
32	21587.81	0.00809	-1.8	0.14
33	21613.53	0.00815	1.8	0.12
34	21639.75	0.00808	1.2	0.09
35	21665.53	0.00806	0.4	0.10

Approximate band constants (all values in cm^{-1}) of some vibrational levels $v > 3$ of the $3^1\Pi_u$ state (with no deperturbation attempted).

Conclusions

Full deperturbation analysis of the strongly interacting $3^1\Pi_u \sim 3^3\Pi_u \sim 4^3\Sigma_u^+$ system requires a coupled channels treatment taking into account all three interacting states and possible spin-orbit and rotational interactions between pairs of them. This is a serious numerical challenge yet it is in future plans of our group.