The double minimum $E^1\Sigma^+_u$ state in Cs_2

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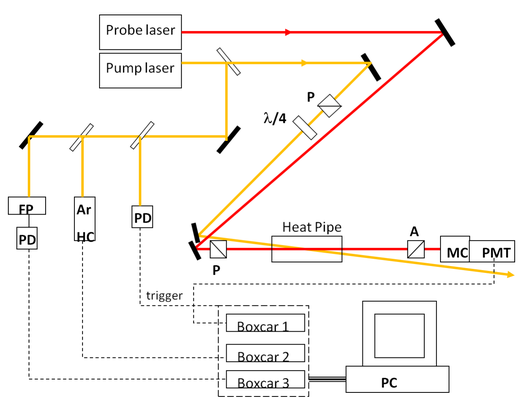
Motivation

Electronic states with two minima in the potential energy curve are particularly difficult for experimental characterisation because positions of rovibrational levels are irregular in the region close to the internal barrier. In addition, the outer potential well is usually inaccessible for excitation from the ground electronic state which makes absolute numbering of vibrational levels confusing. In recent years the double minimum states have raised additional interest in view of cold physics experiments, since their unusually broad potential curves provide favourable conditions for photoassociation of molecules from ultracold atoms [1].

Experimental setup

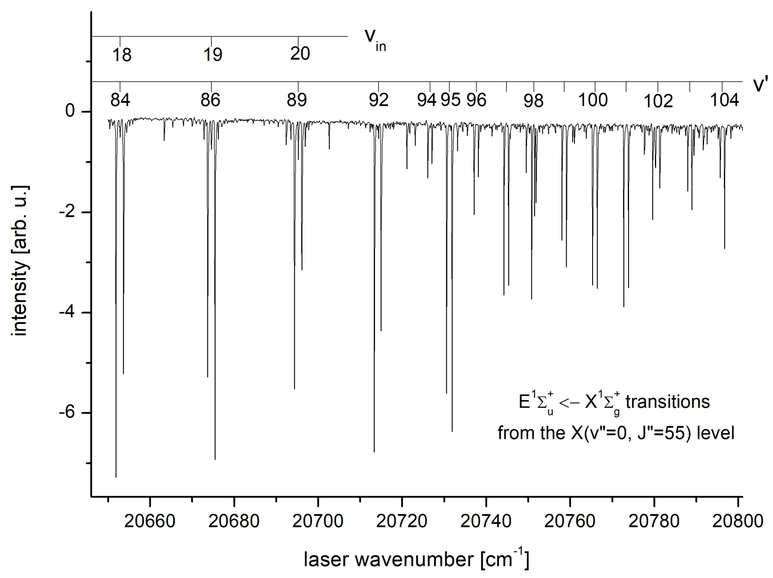


Polarisation labelling spectroscopy

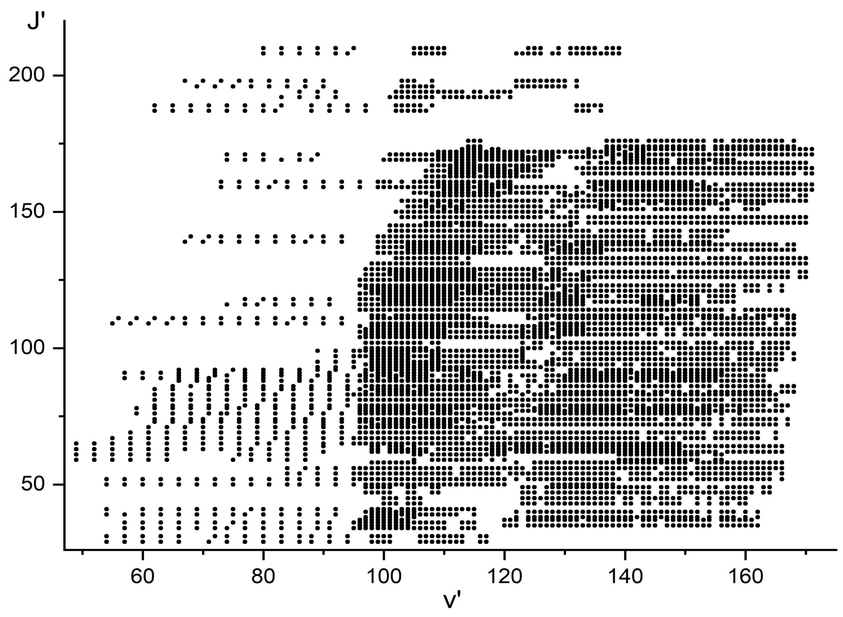
P - polariser,
A - analyzer,
λ/4 - quarter-wave plate,
FP - Fabry-Pérot interferometer,
Ar HC - argon hollow-cathode lamp,
MC -monochromator,
PMT - photomultiplier tube,
PD - photodiode.

The copropagating pump and probe laser beams are crossed in the molecular sample. The probe laser is set at a fixed wavelength resonant with a few known rovibronic transitions $B^1\Pi_u$ (v', J') ← $X^1\Sigma^+_g$ (v", J"), thus labelling the involved rovibrational levels in the ground state. Because of high density of rovibrational levels, a single-mode external cavity diode laser is used as a probe. The pump laser (an excimer laser pumped pulsed dye laser) is tuned across the investigated band system, in the region 20200-21300 cm^{-1}. The information about the excitation spectrum of the molecules is contained in the transmitted intensity of the probe light.

Observed spectra and preliminary analysis



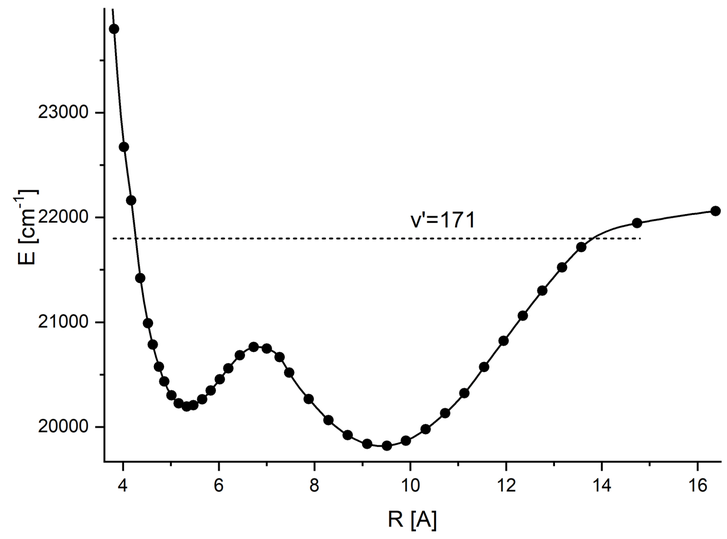
Transitions to the regions below and above the internal potential barrier can be easily distinguished by a distance of consecutive PR doublets. Quantum numbers v′ denote absolute numbering of the vibrational levels, whereas labels v_{in} correspond to independent numbering only of levels supported by the inner well.



Distribution of the experimental data in the field of vibrational and rotational quantum numbers of the $E^1\Sigma^+_u$ state of Cs_2 molecule (in total 6727 transitions observed). The numbering of vibrational levels is the absolute numbering.

Fitting potential curve of the $E^1\Sigma^+_u$ state

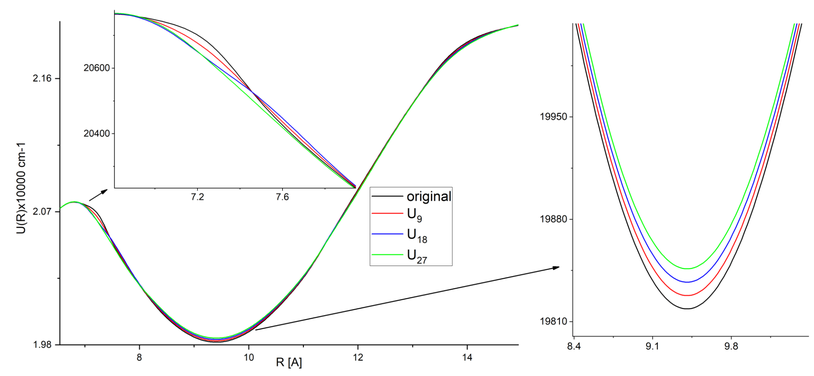
The potential energy curve (PEC) of the $E^1\Sigma^+_u$ state was constructed numerically in a pointwise form by fitting it to the experimental energy levels. As transitions from the ground X state to the outer well of the double minimum potential could not be observed, we had to rely on theoretical calculations by Spies [2] for this region. For the inner well and the region above the barrier we applied the single channel version of the Fourier Grid Hamiltonian (FGH) code from Ref. [3] combined with the nearest-energy strategy for assigning molecular levels. The final potential is defined by 54 grid points between 1.8 and 50 Å (although the experimental data define only the region 4.3 Å < R < 13.8 Å, except of the outer well between 7.47 and 11.54 Å taken from Spies [2]). This potential allows to reproduce energies of the rovibrational levels involved in the observed transitions with 0.05 cm^{-1} accuracy.



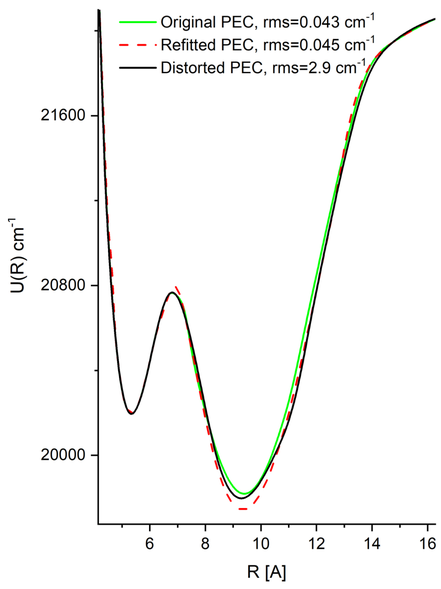
Is the fitted potential curve unique?

We performed some numerical tests to determine whether the shape of the constructed PEC is unique in and around the outer well. For this purpose we fitted the numerical potential to the experimental data starting from various initial potentials, different from the 'original' one displayed above.

In the first test we added to the original potential small distortions resulting in upward shifts of the minimum of the outer well approximately by 9, 18 and 27 cm^{-1}. Then we refitted the potentials to the same experimental data. As a result we obtained three PECs with slightly different outer wells, different vibrational numbering and the same quality regarding the experimental data.



In the second test not only the shape of the outer well but also the rest of the potential were changed more severely by shifting some of the original points by up to 150 cm^{-1}. The subsequently refitted potential is different from the original one in the outer well, but also in the outer limb beyond this well.



Consequently, a shape of the outer well remains uncertain as its determination would require observation of levels supported by it, inaccessible by the experimental technique of the present study. Nevertheless, this problem does not affect precise description of levels in the regions covered by our experiment.

References

[1] M. Pichler, W. C. Stwalley, R. Beuc and G. Pichler, Phys. Rev. A69, 013403 (2004).

[2] N. Spies, PhD Thesis, Universität Kaiserslautern, 1990.

[3] A. Pashov, P. Kowalczyk, A. Grochola, J. Szczepkowski, and W. Jastrzebski, J. Quant. Spectrosc. Radiat. Transfer, 22, 225–232 (2018).