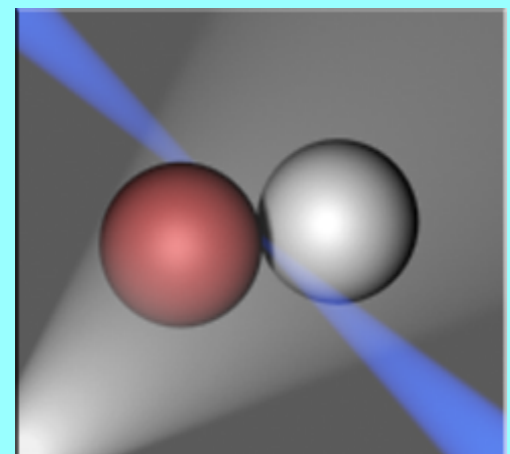


SUBVIBRATIONAL LIF SPECTROSCOPY OF THE $B^3(5^3P_1) \leftarrow X^1(5^1S_0)$ TRANSITION IN EXCITATION SPECTRUM OF CdNe VAN DER WAALS COMPLEX

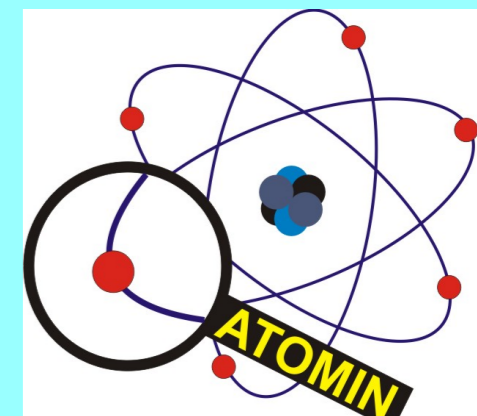


Molecular Spectroscopy
and Quantum Information



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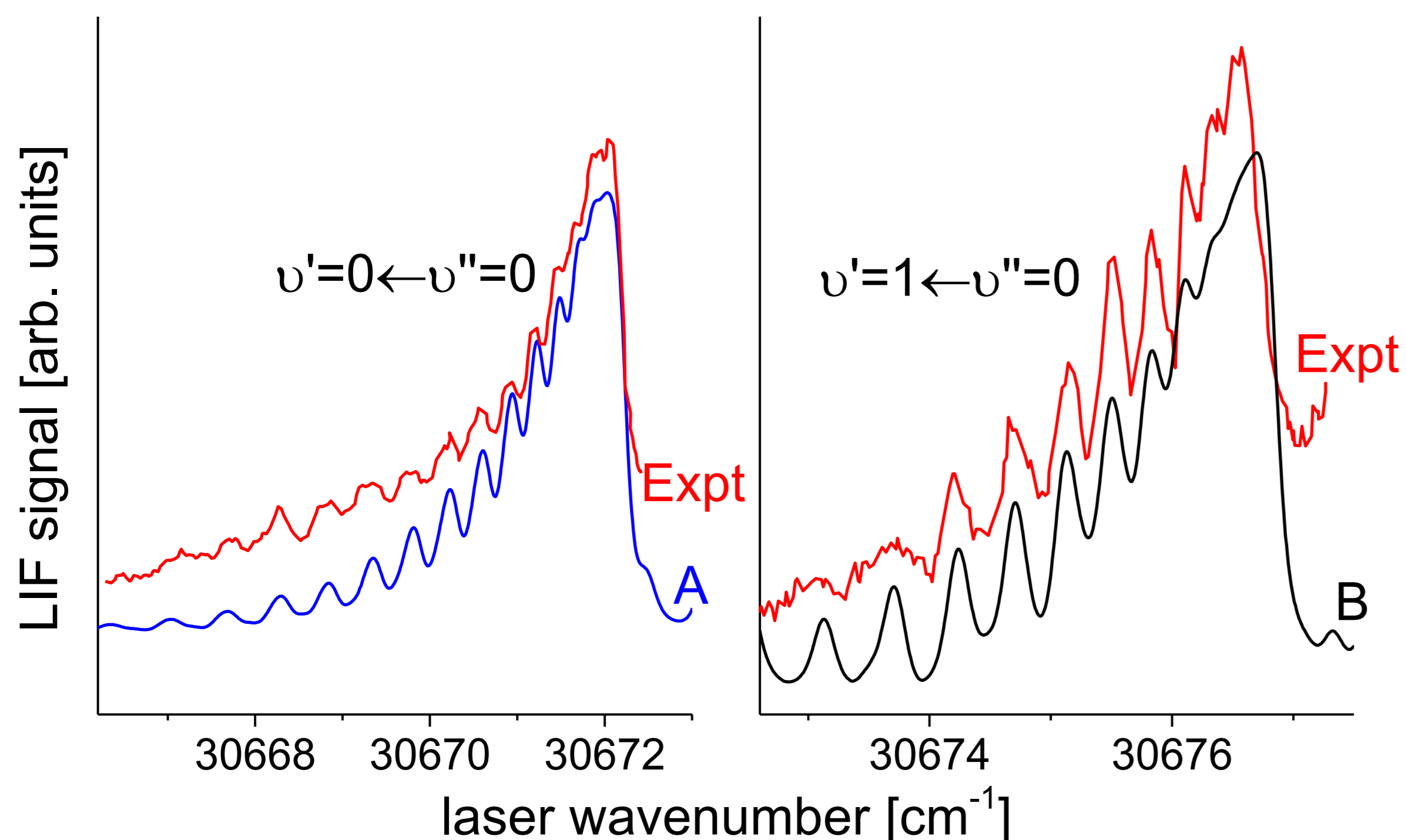


Fig.1. Simulation of the $B^3(5^3P_1) \leftarrow X^1(5^1S_0)$ transition in CdNe.

Experimental (red traces Expt) and simulated spectra (blue A and black B traces) of the $B^3(5^3P_1) \leftarrow X^1(5^1S_0)$ transition in CdNe. Parameters of the simulations: $T_{rot}=4K$, $\Delta_{Lor}=0.1cm^{-1}$, $\Delta_{Gauss}=0.12cm^{-1}$, rotational constants from Table 1.

Analysis of the $B^3(5^3P_1) \leftarrow X^1(5^1S_0)$ transition in excitation spectrum of CdNe

We present newly recorded laser induced fluorescence (LIF) excitation spectra with partially resolved rotational structure and corresponding simulations of two vibrational components of the $B^3(5^3P_1) \leftarrow X^1(5^1S_0)$ transition in CdNe complex. The CdNe were produced using a high temperature pulsed supersonic source of van der Waals diatomic complexes. Table 1 presents vibrational and rotational characteristics that provide satisfactory simulation-to-experiment agreement.

$B^3(5^3P_1)$		
$\omega_e[cm^{-1}]$	6.8 ± 0.1	
$\omega_e x_e[cm^{-1}]$	1.08 ± 0.02	
$R_e[\text{\AA}]$	5.12 ± 0.05	
$D_e[cm^{-1}]$	10.7 ± 0.2	
	$v=0$	$v=1$
$B_v[cm^{-1}]$	0.0300	0.0282
$D_v[10^{-6}cm^{-1}]$	5.84	10.51

Table.1. Vibrational and rotational characteristics of the $B^3(5^3P_1)$ state in CdNe.

Correlation plot of the ω_e and $\omega_e x_e$ vibrational constants

In case of a Morse representation of interatomic potentials, Birge Spomer (B-S) analysis that is based on experimentally measured distances between energies of consecutive vibrational transitions, provides the method to obtain values of vibrational constants ω_e and $\omega_e x_e$ as well as values of their errors. Unfortunately, the B-S method does not take into consideration the fact, that values of the ω_e and $\omega_e x_e$ are strongly correlated. It means, that for given experimental data, it is possible to find a number of pairs of the ω_e and $\omega_e x_e$ far beyond the error range provided by the B-S method. The ω_e and $\omega_e x_e$ pairs, after using them in simulations, provide ladders of vibrational energies consistent with the experimental data. This problem is especially essential in case of "pure" vibrational spectra (i.e., spectra with unresolved rotational energies), where rotational structure cannot be employed to determine values of vibrational constants.

To clearly emphasize and partially solve the problem described above, we propose so-called *correlation plot* [1]. The plot, is in form of two dimensional contour graph plotted in function of ω_e and $\omega_e x_e$. For each combination of the ω_e and $\omega_e x_e$, the plot presents the agreement between simulated and experimental ladders of vibrational energies. To validate the agreement between simulated and experimental data we use the following formula:

$$P = \frac{1}{(0.01 + \sum_i \epsilon_{measured} v) [(E_i^{exp} - E_{v_{best}}^{exp}) - (E_i^{sim} - E_{v_{best}}^{sim})]^2}$$

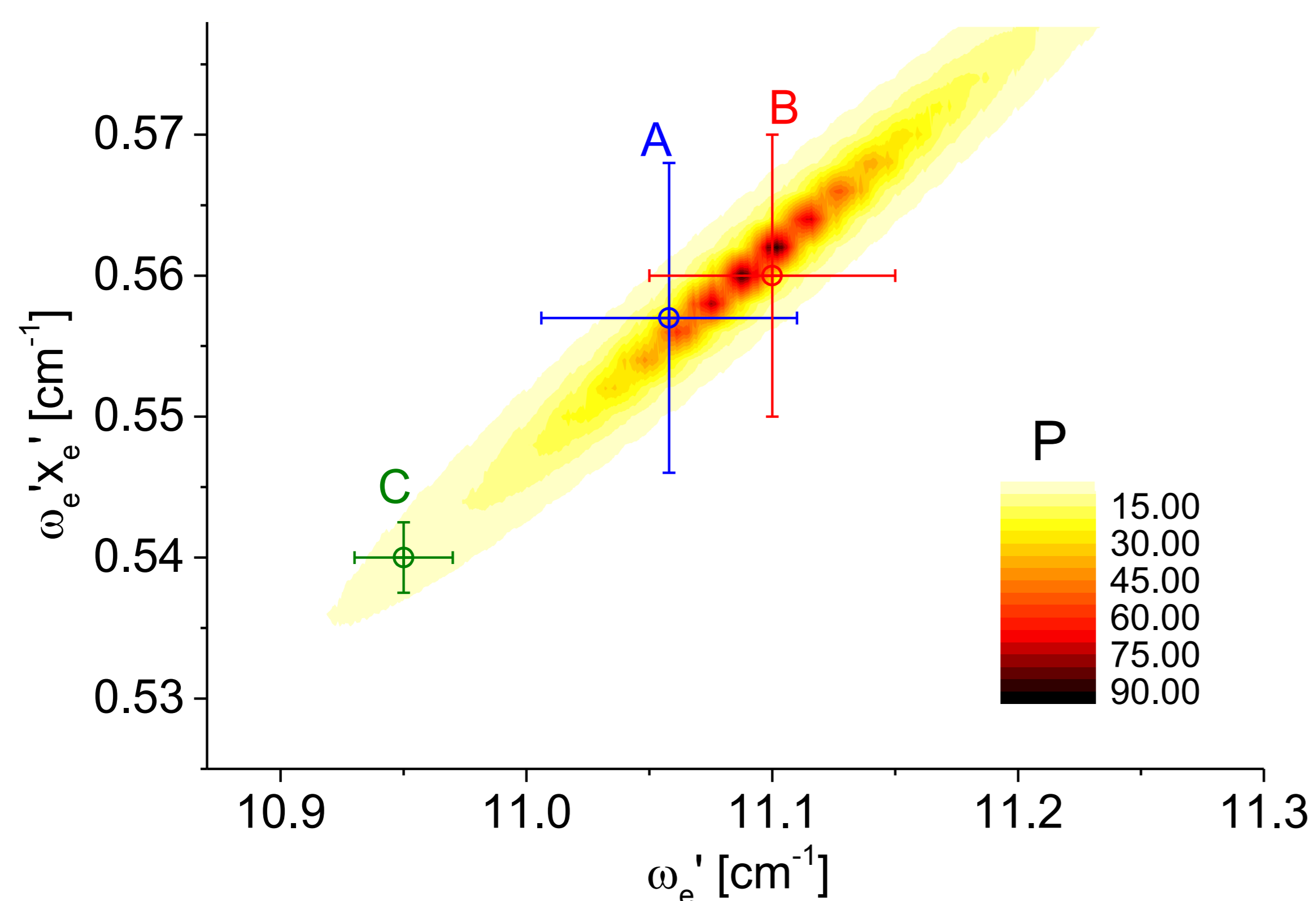


Fig.3. Example of correlation plot.

Correlation plot of the $B^3(5^3P_1) \leftarrow X^1(5^1S_0)$ transition in CdAr [2]. A: result of B-S analysis. B: result of correlation plot analysis. C: example of vibrational constants beyond error range resulted from B-S analysis which provides a high simulation to experiment agreement. Compare with Fig. 4.

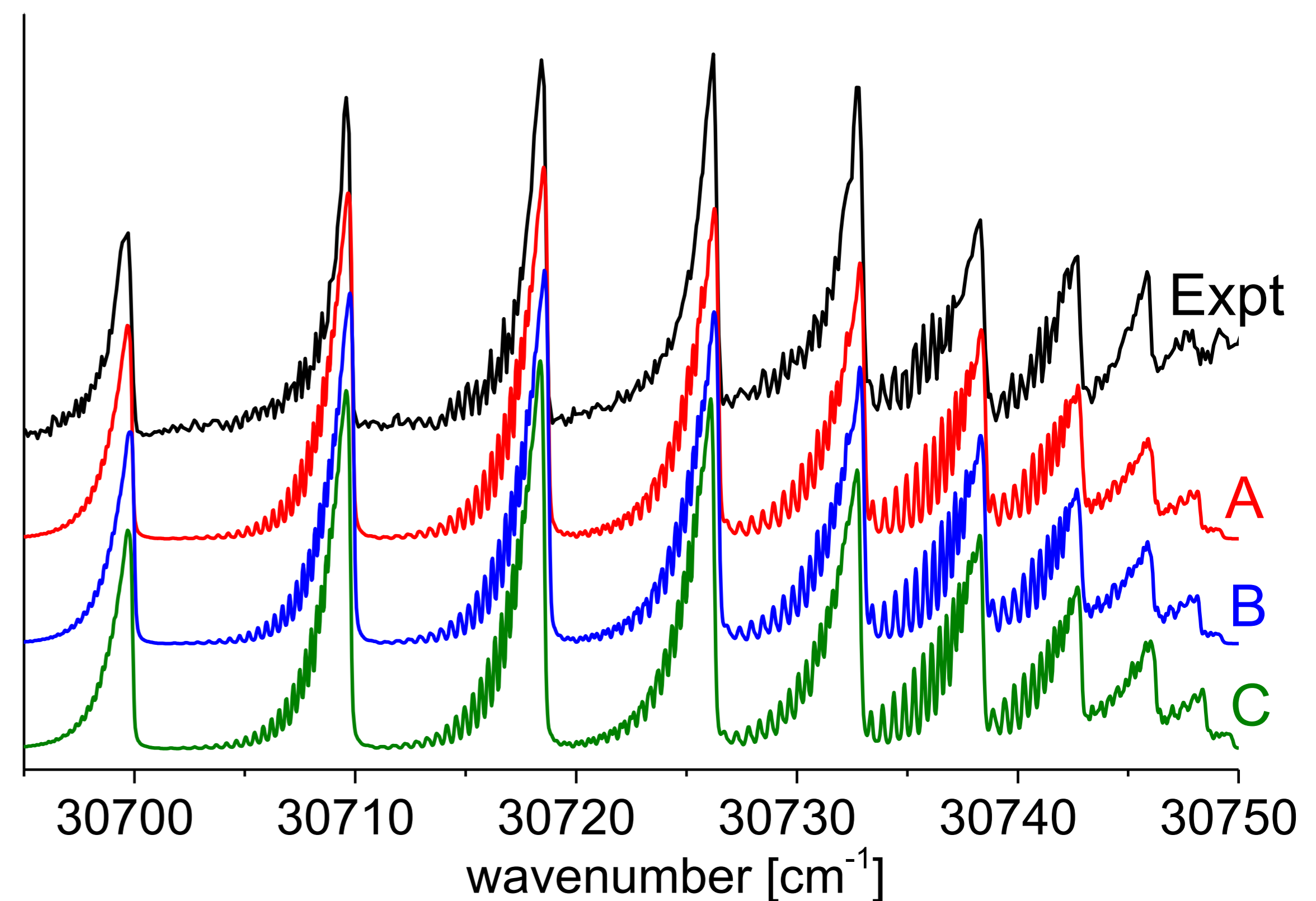


Fig.4. Simulation of the $B^3(5^3P_1) \leftarrow X^1(5^1S_0)$ transition in CdAr.

Experimental (black, trace Expt) and simulated spectra (red, blue and green traces A, B and C) of the $B^3(5^3P_1) \leftarrow X^1(5^1S_0)$ transition in CdAr. Simulated spectra obtained for values of vibrational constants presented in Fig. 3.

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- [1] T. Urbanczyk, J. Koperski, *Mol. Phys.* **112**, 2486–2494 (2014).
- [2] T. Urbanczyk, J. Koperski, *Chem. Phys. Lett.* **591**, 64–68 (2014).