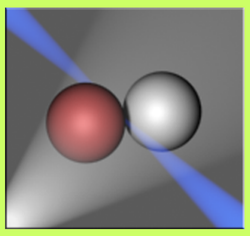

Molecular Spectroscopy and Quantum Information

Transition dipole moment and the ambiguity of determination of interatomic potential in diatomic molecule

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Introduction: correlation between potential parameters

In case of a Morse representation of the interatomic potential, a Birge-Sponer (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 corellated. 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, which provide simulation consistent with the experimental spectrum. To emphasize the problem let us consider two-dimensional contour graph (so called agreement plot [1], [2]) 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, one can use – for example – the formula below. Figure 2 shows, that simulated spectra A,B,C (which correspond to vibrational constants A,B,C in Figure 1) provide satisfactory agreement with the experimental spectrum (Expt).

$$P = \frac{1}{\left(0.01 + \sum_{i \in measured\ v} \left[\left(E_i^{exp} - E_{v\ best}^{exp}\right) - \left(E_i^{sim} - E_{v\ best}^{sim}\right)\right]^2\right)}$$

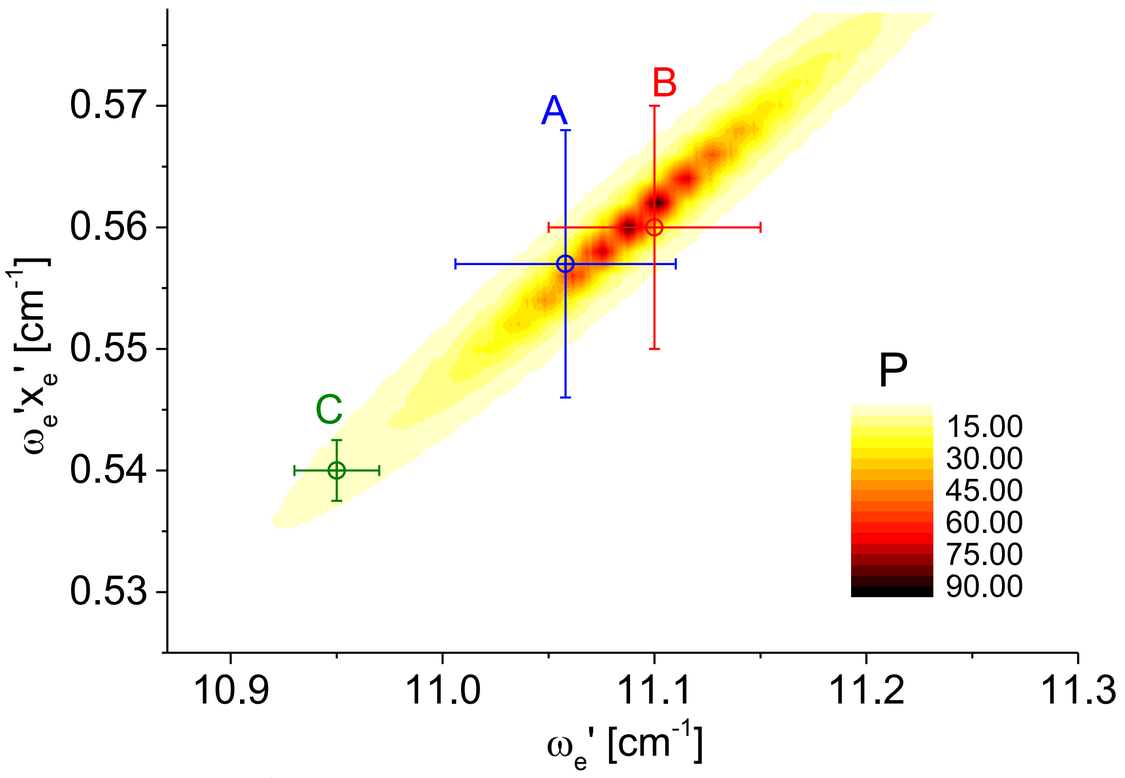

Fig.1. Example of the agreement plot.
Correlation plot of the $B^3\Pi(5^3P_1) \leftarrow X^1\Sigma^+(5^1S_0)$ transition in CdAr [2]. A: result of B-S analysis. B: result of the agreement plot analysis. C: example of vibrational constants beyond error range resulted from B-S analysis which provides a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

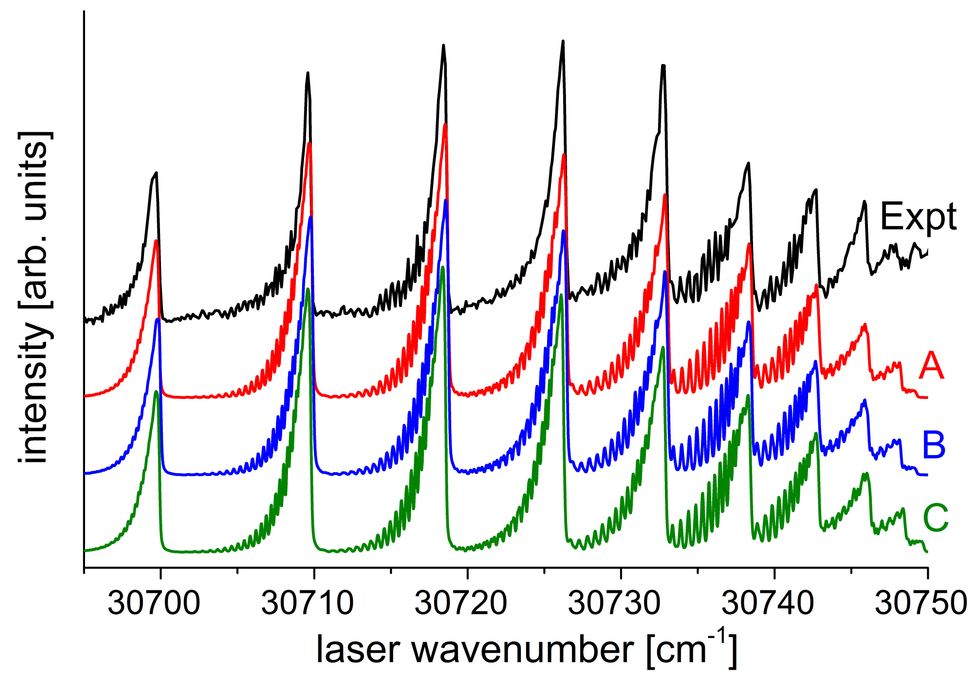

Fig.2. Simulation of the $B^3\Pi(5^3P_1) \leftarrow X^1\Sigma^+(5^1S_0)$ transition in CdAr.
Experimental (black, trace Expt) and simulated spectra (red, blue and green traces A, B and C) of the $B^3\Pi(5^3P_1) \leftarrow X^1\Sigma^+(5^1S_0)$ transition in CdAr. Simulated spectra obtained for values of vibrational constants ω_e and $\omega_e x_e$ presented in Figure 1.

Estimation of errors of parameter of interatomic potential

To estimate an error of given potential parameter, we propose the following approach. In the first step, the parameter for which we search the error, is changed by a small fraction (proposed error) and then fixed. In the second step, all other parameters of potential are reffited (using *gradient descent* method) to obtain the best possible agreement between the new simulation and the experimental spectrum. In the last step, an assessment of accordance between new simulation and experimental spectrum is made, which is described by a χ^2 coefficient. If the new χ^2 is not signifficantly different from coefficient calculated for initial parameters (e.g. $\chi^2 < 1.2\ \chi_0^2$), we assume that error should be larger, so we repeat the whole procedure until the χ^2 exceed certain limit.

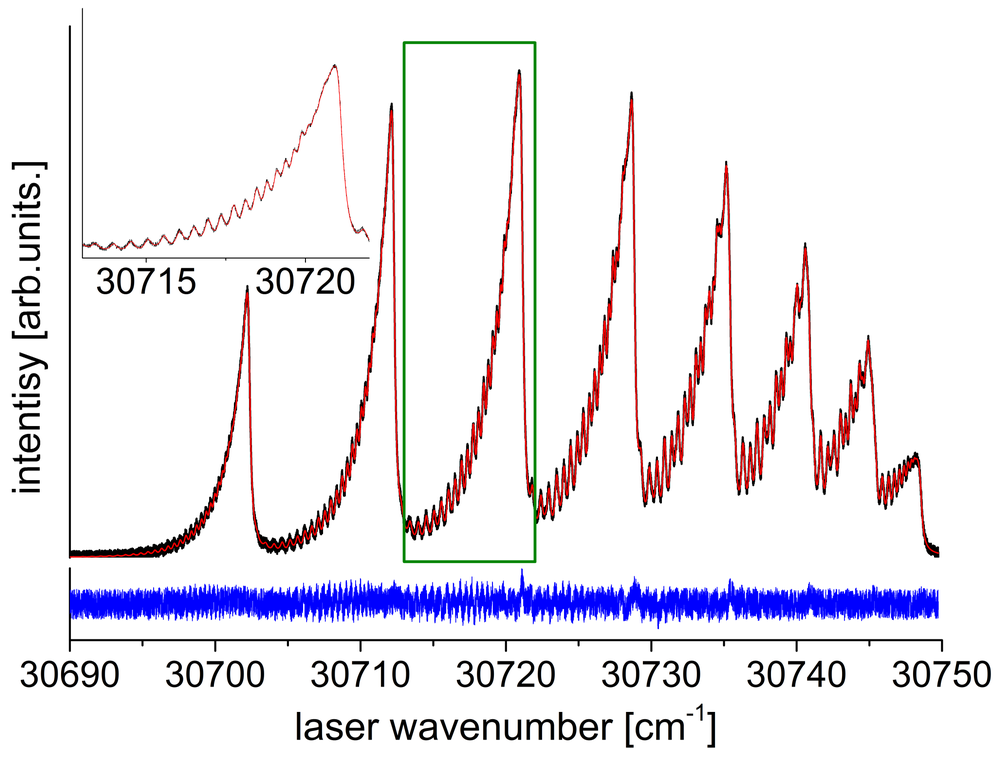

Figure 1. Experimental spectrum (black) and its simulation (red) performed for fixed R_e=5.045 Å which corresponds to the χ^2 near the acceptance threshold. The reference spectrum was computed for Δ_{Lor}=0.3 cm-1. Trace below (blue) shows the residual plot. The parameters of the reference spectrum were chosen to make its similar to the $B^3\Pi(5^3P_1) \leftarrow X^1\Sigma^+(5^1S_0)(\upsilon' \leftarrow \upsilon'' = 0)$ transition in CdAr. Inset shows details of the spectra for the $\upsilon' = 2 \leftarrow \upsilon'' = 0$ band.

Parameter P_i	Value of P_i	Uncertainty at Δ_{Lor}=1.0 cm-1	Uncertainty at Δ_{Lor}=0.3 cm-1
R_e [Å]	5.0500	0.013(0.0031)	0.0044(0.0026)
D_e [cm-1]	55.000	0.040(0.041)	0.019(0.020)
β [Å-1]	0.9880	0.0015(0.0016)	0.0005(0.0006)
TDM (R=2 Å)	1	0.24	0.082
TDM (R=3 Å)	1	0.20	0.045
TDM (R=5 Å)	1	0	0
TDM (R=8 Å)	1	0.34	0.019

Table 1. Uncertainties of a Morse potential parameters for two different resolutions of the experimental spectrum. Uncertainties in parentheses were computed without fitting of transition dipole moments (TDM). One can see, that due to a signifficant interparameter correlation between R_e and TDM, taking into account the TDM signifficantly increases the uncertainty of R_e.

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