

The ambiguity in determination of interatomic potential of diatomic molecule

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Abstract. A method of estimation of errors of interatomic potential parameters is presented. It can be employed in order to obtain errors of parameters of analytical potentials. The method works even for correlated parameters of the interatomic potential *e. g.*, parameters dependent on the vibrational frequency ω_e' and anharmonicity $\omega_e'x_e'$. Exemplary results of application of the method to interatomic potential represented by a Morse function are presented.

1. Introduction

The main goal of this study is to show a method for assessment of errors of interatomic potentials of diatomic molecules. For a simplicity, here we consider molecular states which potentials can be described using a Morse function. The inspiration for this work lays in observation that for a given molecular spectrum (especially without resolved rotational structure) there exist a large number of significantly different combination of molecular constants: vibrational frequency ω_e' and anharmonicity $\omega_e'x_e'$ (or equivalently large numbers of Morse potentials with different parameters D_e' and β') for which we can obtain an appropriate simulation of the experimental spectrum [1]. Figure 1 presents values of so-called agreement parameter P , which describes an agreement between simulated and experimental spectra in function of the ω_e' and $\omega_e'x_e'$ for the $B^3\Gamma(5^3P_1) \leftarrow X^1\Delta^+(5^1S_0)$ transition in CdAr complex [2]. Detailed description of the procedure of constructing of the plot can be found in Ref. [3]. It was observed that each combination of molecular constants for which parameter P is larger than 15, leads to a simulation which satisfactorily agrees with the result of experiment. To demonstrate the fact, in Fig. 2 we present the experimental spectrum and three exemplary simulations that were conducted for pairs of values of molecular constants ω_e' and $\omega_e'x_e'$ depicted in Fig. 1 with points A, B and C. One can see that each of these simulations reconstructs satisfactorily the experimental spectrum, especially if we neglect the rotational structure. It is also worth to mention that during the analysis of molecular spectra one should also consider a correlation between value of the equilibrium distance R_e' and the transition dipole moment (TDM) in case when the TDM is included in the simulation as both the factors have influence on the intensities of vibrational transitions.



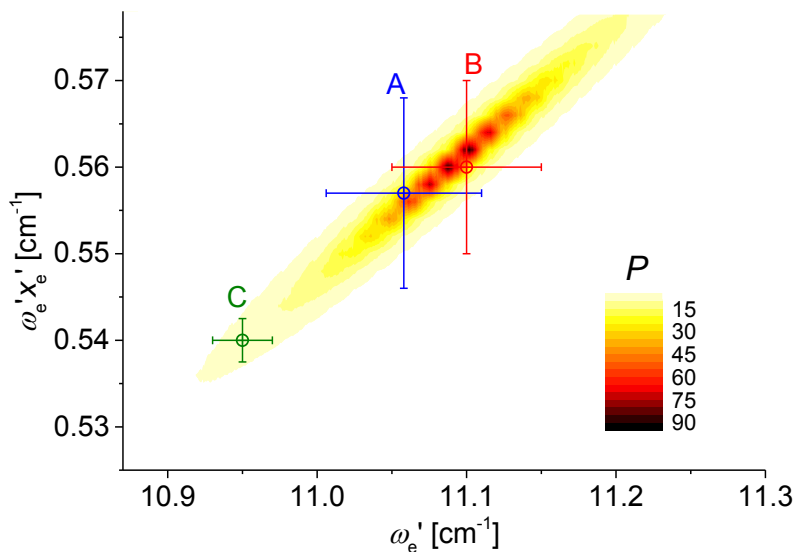


Figure 1. Agreement plot for the $B^31(5^3P_1)\leftarrow X^10^+(5^1S_0)$ transition in CdAr. A (red): the result of Birge-Sponer (B-S) analysis, B (blue): the result of correlation plot analysis, C (green): an example of vibrational constants ω_e' and $\omega_e'x_e'$ beyond the error bars resulted from the B-S analysis which provides a high simulation-to-experiment agreement; compare with Fig. 2.

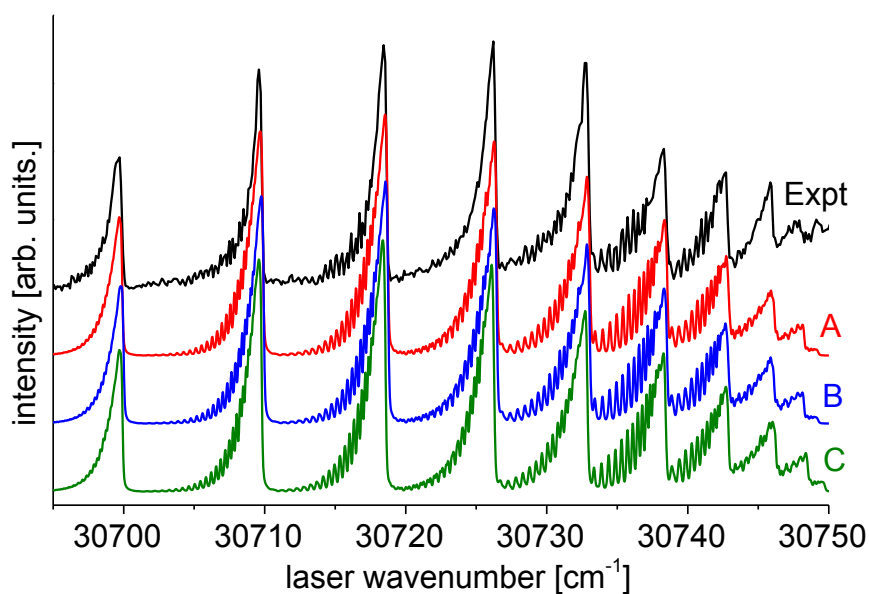


Figure 2. Simulation of the $B^31(5^3P_1)\leftarrow X^10^+(5^1S_0)$ transition in CdAr. Experimental (Expt: black) and simulated (A: red, B: blue and C: green) spectra of the transition under consideration. The simulated spectra A, B and C were obtained for values of vibrational constants ω_e' and $\omega_e'x_e'$ depicted in Fig.1 with points A, B and C, respectively.

2. Estimation of errors of interatomic potential parameters

To estimate an error of a given potential parameter of interatomic potential, we propose the following approach. In the first step, one of the initial parameters of the potential (the one for which we search

for the error) is changed by a small fraction (*i.e.*, a proposed error) and then fixed. In the second step, all other parameters of the potential are refitted (using a gradient descent method) to obtain the best possible agreement between the new simulation (performed using LEVEL program [4]) and the experimental spectrum. In the last step, an assessment of the agreement between new, temporary simulation and the experimental spectrum is performed. The result of the assessment is described by an χ^2 coefficient:

$$\chi^2 = \frac{1}{N} \sum_{i=1}^N (I_i^{sim} - I_i^{expt}), \quad (1)$$

where I_i^{sim} and I_i^{expt} are intensities of the simulated and the experimental spectra, respectively, measured for the i -th point of the spectrum, and N is the total number of points in the spectrum. If the χ^2 calculated according to Eq. (1) is not significantly different from the coefficient χ_0^2 calculated for initial parameters of the potential (*e.g.*, $\chi^2 \leq 1.2\chi_0^2$), we assume that the error should be larger, so we repeat the whole procedure until the χ^2 exceeds certain limit. As an example, we tried to assess the uncertainty of a Morse potential parameters for the excited state of the $A^30^+(5^3P_1) \leftarrow X^10^+(5^1S_0)$ transition in CdAr. To do this, we simulated the reference spectrum for parameters of a Morse potential from Ref. [5] ($R_e'=3.510[\text{\AA}]$, $D_e'=314.88[\text{cm}^{-1}]$, $\beta'=1.4632[\text{\AA}^{-1}]$). In the error estimation procedure, we used the reference spectrum instead of the real experimental spectrum to perform the proposed calculations. The results of the error assessment are presented in Table 1.

Table 1. Estimated values of errors of parameters of a Morse potential representing the $A^30^+(5^3P_1)$ state in CdAr. Performing the estimation we assumed that the temporary simulation is indistinguishable from the reference spectrum if $\chi^2 \leq 1.2\chi_0^2$.

Parameter	Value	Estimated error
$R_e' [\text{\AA}]$	3.510	0.005
$D_e' [\text{cm}^{-1}]$	314.88	0.35
$\beta' [\text{\AA}^{-1}]$	1.4632	0.0025

3. Conclusions

In this work we present a method for estimation of errors of analytical interatomic potential parameters which can be used even when the potential parameters are correlated. Possibly, after small modifications, the method can be used for pointwise interatomic potentials.

Acknowledgements

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