

# Analysis of the $\text{Na}_2 4^3\Sigma_g^+$ state above and below the $3s + 3d$ atomic limit

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## Abstract

The experimental ro-vibrational term values of the  $\text{Na}_2 4^3\Sigma_g^+$  state both below and above the  $3s + 3d$  atomic limit are analyzed. The multiparameter (double-well modified Lennard-Jones—DWMLJ) model function is proposed to fit a double-well potential. The earlier reported vibrational numbering of the predissociated terms (above  $3s + 3d$ ) is corrected and the final DWMLJ potential function for the  $\text{Na}_2 4^3\Sigma_g^+$  state is reported.

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## 1. Introduction

Observations and analysis of excited triplet states of alkali metal diatomic molecules, which have singlet ground state, are very interesting and important experimental and theoretical subjects. Accurate quantitative description of these states, besides being of pure theoretical interest, is also of great importance to the analysis of properties of Bose–Einstein and Fermi condensates of alkali metals, to the development of systems of coherent control over physical and chemical processes, etc.

One of the most powerful techniques allowing to perform a study of such states in detail is the perturbation facilitated optical–optical double resonance (PFOODR) method proposed in [1]. This method has been widely applied to observe spectroscopically the triplet states of the alkali metal dimers including the  $\text{Na}_2$  molecule (see [2–24] and references therein). There also exist high quality

ab initio computations of the  $\text{Na}_2$  singlet and triplet state potential energy curves and dipole transition moments performed by one of the authors of the current article S. Magnier with the methods described in [25].

Liu et al. [11] reported the first observation of the strong predissociation in the system  $\text{Na}_2 2^3\Pi_g \sim 3^3\Pi_g \sim 4^3\Sigma_g^+$ . Both  $3^3\Pi_g$  and  $4^3\Sigma_g^+$  states dissociate to the  $3s + 4p$  atomic limit, which is about  $1100 \text{ cm}^{-1}$  higher than the  $3s + 3d$  dissociation limit of the  $2^3\Pi_g$  state. Due to strong non-adiabatic interactions, ro-vibrational levels of the  $3^3\Pi_g$  and  $4^3\Sigma_g^+$  states between the  $3s + 3d$  and  $3s + 4p$  limits predissociate.

The excitation spectra into the ro-vibrational levels above the  $3s + 3d$  limit by detecting  $3d \rightarrow 3p$  atomic fluorescence [11] (see Fig. 5 below), exhibited very wide overlapped profiles originating from the predissociation of the  $3^3\Pi_g$  levels, and narrower peaks embedded onto the latter ones originating from the predissociation of the  $4^3\Sigma_g^+$  levels. Some dips and peaks in the spectra remained unassigned.

In our previous studies [17–19], we performed a simulation of the  $\text{Na}_2 2^3\Pi_g \sim 3^3\Pi_g$  predissociation based on the

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ab initio potential curves using the multichannel split operator computational technique [26–28]. The resulting simulated spectrum possessed a reasonable resemblance with the experimental spectrum [11], although, of course, peaks of the  $4^3\Sigma_g^+$  predissociated lines as well as unassigned features were not reproduced. Later [22] additional spectra of the  $\text{Na}_2$   $2^3\Pi_g \sim 3^3\Pi_g \sim 4^3\Sigma_g^+$  predissociation were observed and simulated within the similar model and the similar characteristic quality, however, with a quite different computational method of the complex scaling (see [29–31]). In recent work [23] the method of the complex scaling was applied to simulate the spectrum of [11] using a more elaborated model including interactions with the  $4^3\Sigma_g^+$  state. To finalize those efforts the fitting of the potential energy curves of the  $\text{Na}_2$   $2^3\Pi_g, 3^3\Pi_g, 4^3\Sigma_g^+$  states and other parameters ruling the process (interaction matrix elements, dipole moments) to the experimental data is needed. In the end the quality of simulations should become comparable with the quality of the experiments.

It is well known that the effectiveness and correctness of the fitting procedures depend crucially on the quality of the zeroth order approximation for the fitted parameters. Such a zeroth order approximation can be the potential energy curves of the  $\text{Na}_2$   $2^3\Pi_g, 3^3\Pi_g, 4^3\Sigma_g^+$  states in the adiabatic or diabatic representation (i.e., non-interacting), which are able to reproduce the experimental data that are weakly influenced by the non-adiabatic effects.

The ro-vibrational terms of the  $\text{Na}_2$   $4^3\Sigma_g^+$  state have been observed and reported in [2,3,7,9–12,24]. In total they include 408 term values lying in the energy range [32275.219, 36197.722]  $\text{cm}^{-1}$  and spanning the rotational quantum numbers  $N$  from 3 to 47. Among them 212 terms (vibrational states  $v \in [0, 27]$ ) are below the  $3s + 3d$  atomic limit, and 196 terms (assigned in the original works as  $v \in [27, 55]$ ) are above the  $3s + 3d$  dissociation limit (i.e., predissociated). Some of the low lying observed terms were classified as perturbed by levels of the  $2^3\Pi_g$  and  $3^3\Pi_g$  states, and their deperturbation was performed [9]. The accuracy of the experimental measurements of the term values varied from  $\sim 0.02$  to  $\sim 0.2$   $\text{cm}^{-1}$  depending on the experimental techniques implemented in the corresponding work.

The term values reported in the previous publications were used to construct the following empirical potential functions of the  $\text{Na}_2$   $4^3\Sigma_g^+$  state: the RKR potential in [7], hybrid RKR-ab initio potential in [12], RKR potential in [24]. The latest RKR potential [24] only spanned the part of the state below the  $3s + 3d$  dissociation limit. The hybrid potential [12] spanned a wider range up to the highest terms observed, however, in its construction the later experimental data had not been used. This hybrid potential exhibits a reasonable similarity to the ab initio potential in the lower part, but deviates from it more significantly in the upper part (see Fig. 5 in [12]). Partially, the long-distance second (shallow) well found in the ab initio computations (see Fig. 3 below) was not reproduced.

The purpose of the current work is to construct the best adiabatic potential energy function of the  $\text{Na}_2$   $4^3\Sigma_g^+$  based

on all the experimental ro-vibrational term values available for today and spanning the range from the bottom of the state to the closest vicinity of its dissociation limit. This potential can be used later as a zero-th order approximation in the analysis of the interacting states  $2^3\Pi_g \sim 3^3\Pi_g \sim 4^3\Sigma_g^+$ . The multiparameter double-well modified Lennard-Jones (DWMLJ) function has been proposed and used as a model for this potential. The previous vibrational numbering of the levels above the  $3s + 3p$  atomic limit has been revised so that according the new assignment the observed experimental levels span the range up to  $v = 65$ . The final DWMLJ potential is much closer to the ab initio function than the hybrid potential of [12] and allows us to classify some of the earlier unassigned features in the predissociation spectra [11] as the intermediate levels of the  $4^3\Sigma_g^+$  state.

## 2. Method

One of the ways to describe a potential energy function of a molecule in a wide range of interatomic distances and energies is via a utilization of the multiparameter model functions [32,33]. We adopted such an approach in our recent works [20,34] devoted to the analysis of the  $a^3\Sigma_u^+$  state of the molecules  $\text{Na}_2$  and  $\text{K}_2$ , respectively. Partially, the potential function of [34] was reported in the form of a modified Lennard-Jones potential. The modified Lennard-Jones (MLJ) function [35]  $U_{\text{MLJ}}(R)$  is defined by the equation

$$U_{\text{MLJ}}(R) = T_e + D_e[1 - (R_e/R)^N e^{-\beta(y)^2}]^2, \quad (1)$$

where:

$$\beta(y) = \beta^{(0)} + \beta^{(1)}y + \beta^{(2)}y^2 + \beta^{(3)}y^3 + \dots,$$

$$y = \frac{R^p - R_e^p}{R^p + R_e^p},$$

where  $R$  is the interatomic distance,  $R_e$  is the equilibrium interatomic distance,  $D_e$  is the dissociation energy,  $T_e \equiv U_{\text{MLJ}}(R_e)$  is the energy at the bottom of the well,  $N$  is the leading power of the theoretically predicted inverse-power long-range asymptotic behavior  $U_{\text{MLJ}}(R) \sim T_e + D_e - C_N/R^N$ , and  $p$  is a Šurkus parameter (positive integer as a rule, see [36,33]). We decided to apply the analogous approach to the current analysis of the  $\text{Na}_2$   $4^3\Sigma_g^+$  state.

One of the significant features of the  $\text{Na}_2$   $4^3\Sigma_g^+$  state, differentiating it from the  $a^3\Sigma_u^+$  state, is that, according to the ab initio computations, it has a second (shallow) well at long distances (see Fig. 3 below). In principle, the function (1) is capable of reproducing some non-trivial potential functions including those with a double well. However, our attempt to use it to reproduce the ab initio potential function of the  $\text{Na}_2$   $4^3\Sigma_g^+$  with a single  $\beta(y)$  was unsuccessful. The error of this representation remained large and decreased slowly as the power of the  $\beta(y)$  polynomial was increased.

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