Molecular Constants of the $2^1\Pi$ State of NaLi Molecule

Nguyen Tien Dung, Le Canh Trung, Dinh Xuan Khoa, and Nguyen Huy Bang
Vinh University, 182 Le Duan Street, Vinh City, Vietnam
E-mail: bangvinhuni@gmail.com

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Abstract. We report our determination of the molecular constants for the $2^1\Pi$ state of NaLi from a set of 732 spectral lines. Using the linear least-squares fitting method, an optimum set of molecular constants, which corresponds to dimensionless root mean of squares of deviation $\sigma = 0.62$ within $0.1\,\text{cm}^{-1}$ experimental uncertainty, have been derived.

I. INTRODUCTION

The alkali-metal diatomic molecules with their main absorption bands in the UV-VIS region are very appropriated for modern laser spectroscopy techniques. Experimental investigations for these molecules have further promoted since the emergence of molecular Bose-Einstein condensates (see [1] and references therein). As several experimental techniques related to cold molecules involve optical excitation either in the formation and/or detection stages, a precise spectroscopic characterization of excited molecular states is necessary.

Among alkali-metal diatomic molecules NaLi is particularly interested because it is the lightest hetero-nuclear type and has permanent dipole moment, thus can be manipulated with external electric fields. Several experimental investigations for the $1^1\Sigma^+$ and $1^1\Pi$ symmetric types were performed to study up to the $9^1\Sigma^+$ and $7^1\Pi$ excited states [2-7]. Among those, the $2^1\Pi$ state was still known only at vibrational resolution [4].

In this paper we determine the molecular constants for the $2^1\Pi$ state of NaLi based our recent experimental data [8].

II. MOLECULAR CONSTANTS OF THE $2^1\Pi$ STATE

The experimental data used in this work consist of 732 spectral lines in the $2^1\Pi \leftarrow 1^1\Sigma^+$ band. The data were obtained by the polarization labeling spectroscopy technique [8] within to $0.1\,\text{cm}^{-1}$ experimental uncertainty. Distribution of the data field corresponding
Fig. 1. Distribution of data field with the corresponding vibrational and rotational quantum numbers in the $2^1\Pi$ state.

to rotational and vibrational quantum numbers in the $2^1\Pi$ state is presented in detail in Fig. 1.

Once spectral lines had been assigned quantum numbers, their wave number $\tilde{v}$ were fitted to the following relation:

$$\tilde{v} = T'(v', J') - T''(v'', J'') + \delta.$$  \hspace{1cm} (1)

In the Eq. (1), $T'$ and $T''$ represent term values of the upper and lower states, respectively; $\delta$ describes the $\Lambda$-doubling in the $2^1\Pi$ state, given by

$$\delta = q_e[J(J + 1) - 1],$$  \hspace{1cm} (2)

where, $q_e$ represents lambda-doubling coefficient for $\epsilon$-parity levels which gives rise to $P$ and $Q$ transitions. The spectroscopic term value $T(v, J)$ is represented with the conventional Dunham expansion:

$$T(v, J) = T_e + \sum_k \sum_l Y_{kl}(v + \frac{1}{2})^k [J(J + 1) - 1]^l,$$  \hspace{1cm} (3)
where $T_e$ and $Y_{kl}$ stand for electronic energy and Dunham coefficient, respectively. The term values for the labelled levels were calculated by using Dunham coefficients obtained from [2] and fixed during the fitting procedure. The final optimum set of Dunham coefficients for the $2^1\Pi$ state corresponding to a dimensionless root mean of squares of deviation $\sigma = 0.62$ has been obtained, and listed in Table 2.

**Table 1.** Molecular constants of the $2^1\Pi$ state of NaLi

<table>
<thead>
<tr>
<th>Constants</th>
<th>Value [cm$^{-1}$]</th>
<th>Error [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_{00}$ ($T_e$)</td>
<td>22296.72539</td>
<td>0.001</td>
</tr>
<tr>
<td>$Y_{10}$ ($\omega_e$)</td>
<td>151.3553669</td>
<td>0.061</td>
</tr>
<tr>
<td>$Y_{20}$ ($-\omega_e x_e$)</td>
<td>-1.212648477</td>
<td>2.097</td>
</tr>
<tr>
<td>$Y_{30}$</td>
<td>-0.1163013955</td>
<td>2.874</td>
</tr>
<tr>
<td>$Y_{40}$</td>
<td>0.5415371$\times 10^2$</td>
<td>3.810</td>
</tr>
<tr>
<td>$Y_{50}$</td>
<td>-0.2242726086$\times 10^3$</td>
<td>2.138</td>
</tr>
<tr>
<td>$Y_{01}$ ($B_e$)</td>
<td>0.2255917721</td>
<td>0.004</td>
</tr>
<tr>
<td>$Y_{11}$</td>
<td>-0.2459652022$\times 10^2$</td>
<td>2.44</td>
</tr>
<tr>
<td>$Y_{21}$</td>
<td>0.8423599232$\times 10^4$</td>
<td>9.029</td>
</tr>
<tr>
<td>$Y_{31}$</td>
<td>-0.204878997$\times 10^4$</td>
<td>1.444</td>
</tr>
<tr>
<td>$Y_{42}$</td>
<td>-0.178619694$\times 10^5$</td>
<td>2.102</td>
</tr>
<tr>
<td>$Y_{12}$</td>
<td>-0.653086282$\times 10^7$</td>
<td>16.828</td>
</tr>
<tr>
<td>$Y_{22}$</td>
<td>-0.1843230918$\times 10^7$</td>
<td>4.254</td>
</tr>
<tr>
<td>$q_e$</td>
<td>-0.9339851354$\times 10^4$</td>
<td>5.715</td>
</tr>
<tr>
<td>$D_e$</td>
<td>17620</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Since the $2^1\Pi$ state associates to Na(3P)-Li(2S) atomic asymptotes, its dissociation energy can be determined by

$$D_e[2^1\Pi] = \Delta + D_e[1^1\Sigma^+] - T_e[2^1\Pi],$$

(4)

where, $\Delta$ is energy separation between the Na(3P) and Na(3S) atomic states, $D_e[1^1\Sigma^+]$ is dissociation energy of the ground electronic state $1^1\Sigma^+$. Taking electronic energy $T_e[2^1\Pi]$ from this work; $\Delta = 16965$ cm$^{-1}$ from [9]; and $D_e[1^1\Sigma^+] = 7105$ cm$^{-1}$ from [2]; the dissociation energy of the $2^1\Pi$ state is estimated to be $D_e = 1760$ cm$^{-1}$.

From the experimental data and the dissociation energy determined above, the highest vibrational level observed here is only 17 cm$^{-1}$ below the dissociation limit, thus the experimental data cover about 99% depth of the potential well.

Having the molecular constants, we calculated bond length $R_e$ between the Na and Li atoms based on the following conventional relation:

$$R_e = \sqrt{\frac{\hbar}{B_e 4\pi\mu c}},$$

(5)

where $\mu$ is reduced mass of NaLi, $c$ is the light speed in vacuum. Taking the value of $B_e$ in Table 2, the bond length is determined to be $R_e = 3.728438$ Å.
III. CONCLUSIONS

Spectroscopic structure of the $2^1\Pi$ state of NaLi has been characterized to rotational resolution for the first time. A set of molecular constants was determined based on the experimental data up to near the dissociation limit. The results give comprehensive spectroscopic characterization of the state and provide a benchmark to check reliability of modern theoretical calculations.

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