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INTENSITY DISTRIBUTION OF THE $3^1\Pi \leftarrow 1^1\Sigma^+$ BAND SYSTEM OF NaLi

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Abstract. *In the framework of adiabatic approximation we perform numerical calculations of intensity distribution for the* $3^1\Pi \leftarrow 1^1\Sigma^+$ *band system of NaLi based on the Franck-Condon (FC) principle. In addition, the internuclear distances at which the most favorable transitions occurred are predicted. Comparing the calculated FC factors and the corresponding spectral lines observed recently reveals a good agreement, particularly, at node of envelop of the FC factors. Some local deviations in spectral intensity between the calculated results and experimental data indicate local perturbations in the* $3^1\Pi$ *state. This result requires further investigations in details.*

I. INTRODUCTION

The alkali-metal diatomic molecules are very attractive for both theoreticians and experimentalists because of their relatively simple electronic structure, that is frequently considered as a simple model that could be expanded for more complex molecular systems by addition an appropriated approximations. From the experimental point of view the alkali-metal diatomic molecules visible and UV absorption band are suitable objects used in modern laser spectroscopy techniques. Investigations of alkali-metal molecules have recently increased an additional impetus after obtaining Bose-Einstein condensate in dilute alkali-metal vapors and the ultra-cold molecules and molecular condensates consisting of different alkali-metal mixtures created. This helps spectroscopists to have the precision data, which are crucial for planning and interpretation of the new class of experiments. The NaLi, as well as other heteronuclear alkali-metal molecules, is considered to be particularly interesting throw away because its permanent dipole moment, thus can therefore be manipulated with external electric fields.

Finding ways for interpretation of spectra, which consist of spectroscopic terms and intensity distribution, is an indispensable stage in any spectroscopic research. The usual way based on the adiabatic approximation is to represent spectroscopic terms with eigenvalues in form of Radial Schrödinger Equation (RSE) as [1]

$$\left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\hbar^2}{2\mu r^2}[J(J+1) - \Lambda^2] + U(r)\right]\chi_{v,J}(r) = E_{v,J}\chi_{v,J}(r), \tag{1}$$

where μ - reduced mass of the two atoms; v and J are vibrational and rotational quantum numbers, respectively; Λ - quantum number of the project of total angular momentum on the internuclear axis ($\Lambda = 0,\ 1,\ 2\ \ldots$); r - internuclear distance; χ - vibrational wavefunction; and $U(r)$ - potential energy of the molecule. The vibrational intensity distribution is presented by FC factors in terms as [1]

$$q_{v''v'} = \left| \int\limits_0^{+\infty} \chi_{v''}(r)\chi_{v'}(r)dr \right|^2 , \tag{2}$$

where $\chi_{v"}(r)$ and $\chi_{v'}(r)$ are vibrational wavefunctions associated to the lower and upper vibrational levels, respectively.

FC factors gives us possibility of knowing additional informations on chemical bonding as well as transition channels in intramolecular dynamical processes [2]. From experimental point of view the FC factors also give a useful way to check the accuracy of determination for vibrational quantum numbers in analysing spectra [3]. In this work we present our numerical calculations for FC factors of the $3^1\Pi \leftarrow 1^1\Sigma^+$ band system of NaLi based on adiabatic experimental potential energy curves.

II. FC-FACTOR CALCULATION

In order to calculate FC factor for the $3^1\Pi \leftarrow 1^1\Sigma^+$ band system of NaLi we first created vibrational wavefunctions by numerically solving the RSE (1). Here, we used potential energy curve of $1^1\Sigma^+$ and $3^1\Pi$ states constructed in work [4]. The RSE was solved in a grid 0.0001Å of internuclear distance by Numerow-Cooley method [5]. On this way we obtained two wavefunctions at levels $v^{''} = 0$ and 1 in the $1^1\Sigma^+$, and eighteen wavefunctions at the levels $v^{'} = 0 \div 17$ in the $3^1\Pi$. The choice of these levels was reasoned to be coherent with experimental observation in [6].

Based on the wavefunctions we then calculated FC factors for the $3^1\Pi(v^{'} = 0 \div 17) \leftarrow 1^1\Sigma^+(v^{''} = 0)$ and $3^1\Pi(v^{'} = 0 \div 17) \leftarrow 1^1\Sigma^+(v^{''} = 1)$ bands. The integration in (2) was carried out in the same grid above. Finally, we obtained values of FC factors as presented in Tables 1 and 2, and schemed in Fig. 1.

It is seen from Fig. 1 the intensity of the band of $v^{''} = 0$ rises to a maximum at $v^{'} = 3$ and then falls down gradually. However, intensity distribution of the band of $v^{''} = 1$ is apparently different. It rises from $v^{'} = 0$ to a maximum at $v^{'} = 1$, falls down to a minimum (very small compared to the maximum) at $v^{'} = 4$, then rises to another maximum at $v^{'} = 8$ and finally falls down gradually. This means that in the former band there is a maximum overlap between wave functions at $\{v^{''}, v^{'}\} = \{0, 3\}$ whereas in the later there are two local maxima corresponding to $\{v^{''}, v^{'}\} = \{1, 1\}$ and $\{v^{''}, v^{'}\} = \{1, 8\}$, respectively. We then determined value of internuclear distance at which the favorable transitions take place by using the following argument. According to the Franck-Condon principle the transitions take place quickly so that the nuclear kinetic energy must remain unchanged. Therefore, from the energy conservation the transitions take place at a particular internuclear distances $r = r^*$ satisfying the following equation [7]:

$$V(r^*) = E(v'') \tag{3}$$

where

$$V(r) = U''(r) + E(v') - U'(r). \tag{4}$$

Taking $E(v^{''})$and $U^{''}(r)$ from [4], $E(v^{'})$ from [7], and $U^{'}(r)$ from [5] the values of r^{*} were determined to be:

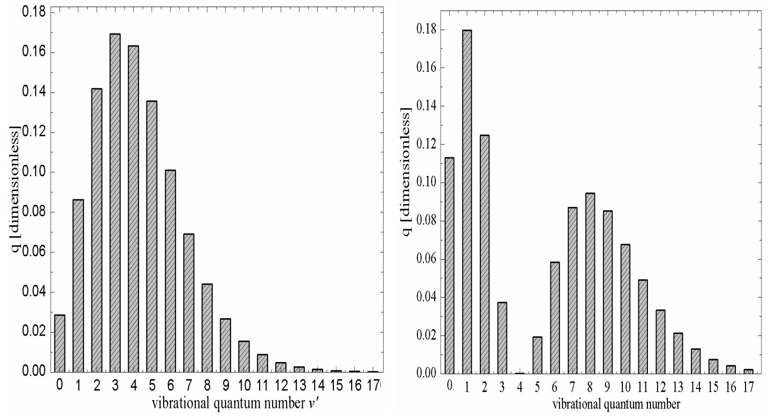
- For $v' = 3 \leftarrow \quad v'' = 0$: r^{*}= 2.95 Å
- For $v' = 1 \leftarrow \quad v'' = 1$: r^{*}= 3.15 Å
- For $v' = 8 \leftarrow \quad v'' = 1$: r^{*}= 2.82 Å.

Table 1. FC factors of the $3^1\Pi$ $(v' = 0 \div 17) \leftarrow 1^1\Sigma^{+}(v'' = 0)$ band.

$v^{'}$	**FC factors**	$v^{'}$	**FC factors**	$v^{'}$	**FC factors**	$v^{'}$	**FC factors**
0	0.28543×10^{1}	5	0.13560	10	0.15451×10^{1}	15	0.63968×10^{3}
1	0.86281×10^{1}	6	0.10104	11	0.86470×10^{2}	16	0.31545×10^{3}
2	0.14177	7	0.69097×10^{1}	12	0.46908×10^{2}	17	0.15237×10^{3}
3	0.16924	8	0.44134×10^{1}	13	0.24762×10^{2}		
4	0.16330	9	0.26671×10^{1}	14	0.12729×10^{2}		

Table 2. FC factors of the $3^1\Pi$ $(v'= 0 \div 17) \leftarrow 1^1\Sigma^{+}$ $(v'' = 1)$ band.

$v^{'}$	**FC factors**	$v^{'}$	**FC factors**	$v^{'}$	**FC factors**	$v^{'}$	**FC factors**
0	0.11299	5	0.19219×10^{1}	10	0.67637×10^{1}	15	0.75022×10^{2}
1	0.17971	6	0.58442×10^{1}	11	0.49098×10^{1}	16	0.42269×10^{2}
2	0.12475	7	0.86977×10^{1}	12	0.33195×10^{1}	17	0.23053×10^{2}
3	0.37297×10^{1}	8	0.94492×10^{1}	13	0.21193×10^{1}		
4	0.17312×10^{3}	9	0.85088×10^{1}	14	0.12875×10^{1}		



(a) (b)

Fig. 1. Chart of the calculated FC factors for transitions start from $v'' = 0$ (a) and $v'' = 1$ (b) in the ground $1^1\Sigma^{+}$ state to vibrational levels in the excited $3^1\Pi$ state of NaLi.

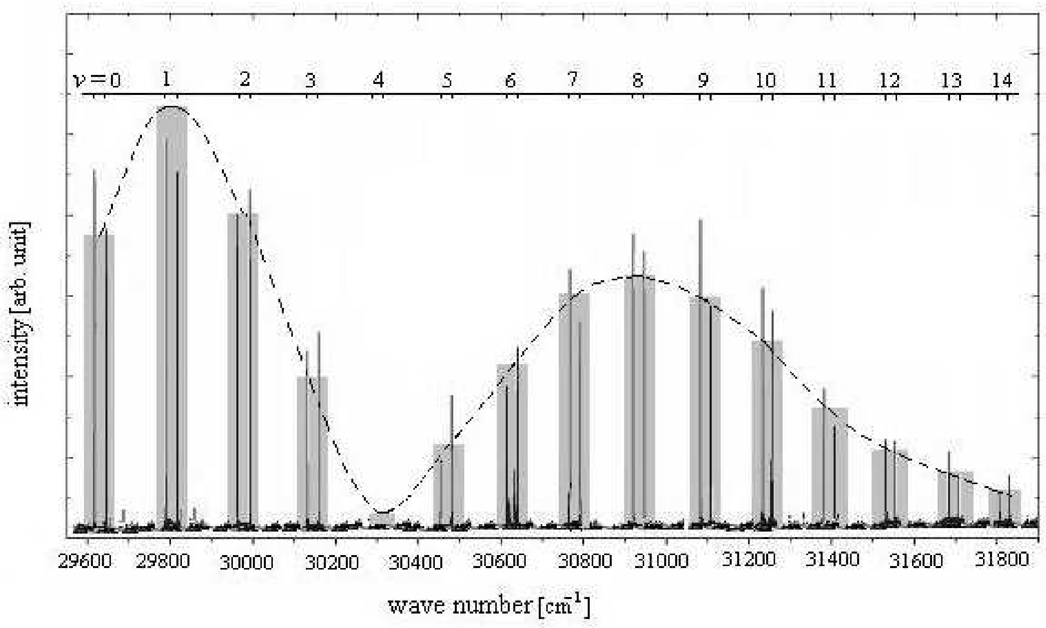


Fig. 2. The calculated FC factors (grey bars), FC envelop (dashed curve), and experimentally observed spectrum of $3\Pi \leftarrow 1^1\Sigma^+$ (v'' =1, J''= 25) band. At the node of FC envelop ($v' = 4$) no spectrum appear.

III. COMPARISON WITH EXPERIMENT AND DISCUSSION

The experimental data used to compare with the calculated FC factors were presented in work [6]. There are 381 spectral lines in the $3^1\Pi \leftarrow 1^1\Sigma^+$ band system in which rotational and vibrational quantum numbers in the $3^1\Pi$ state ranging $J^{'} = 9 \div 47$ and $v^{'} = 0 \div 17$, whereas value of the vibrational quantum number in the ground state is $v^{''}$ = 0 and 1. The comparison reveals generally a good agreement between the calculation and observation, particularly at node $v^{'} = 4$ of the band of $v^{''} = 1$. At this node there is no any spectral occurs, as illustrated in Fig. 2 for vibrational progression of P and Q transitions corresponding to $v^{''} = 1$ and $J^{''}$= 25. However, we found some local deviations between the calculated FC factors and observation, particularly for levels $v^{'} = 3$, 7, 8, and 9. This may be, possibly, attributed to following reasons. The first one is due to the measurements throw away carried out in few hours, in which experimental conditions (molecular concentration, sensitivity of detector, power of scanning laser) may be changed throw away. The second reason is due to interactions between the $3^1\Pi$ with the nearby states. By comparing positions of these spectral lines to those determined with molecular constants in [6] we found deviation values typically 0.2 - 0.7 cm^{-1}. Therefore, in order to describe adequately perturbation phenomena concerning to these levels one needs resort to deperturbation analysis, which is beyond the adiabatic approximation [2].

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