

Calculation of Vibrational Intensity Distribution for the $4^1\Pi \leftarrow 1^1\Sigma^+$ Band System of NaLi

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Abstract: In the framework of adiabatic approximation we perform numerical calculations of intensity distribution for the $4^1\Pi \leftarrow 1^1\Sigma^+$ band system of NaLi based on the Franck-Condon (FC) principle. Comparison between the calculated FC factors and the corresponding spectral lines observed recently reveals a good agreement. In addition, the internuclear distances at which the most favorable transitions occurred are calculated.

Key words: diatomic molecules, Franck-Condon principle

I. INTRODUCTION

The alkali-metal diatomic molecules are very attractive for both theoreticians and experimentalists because they have a relatively simple electronic structure. Their electronic structure is frequently considered by theoreticians as a very convenient model for introducing several approximations which can be further applied to more complex molecular systems. From the experimental point of view, alkali-metal diatomic molecules with their main absorption bands placed in the visible and UV regions are very convenient objects for investigations with modern laser spectroscopy techniques. Investigations of alkali-metal molecules have recently experienced additional impetus since Bose-Einstein condensate in dilute alkali-metal vapors was obtained, and presently there are many efforts to create ultra-cold molecules and molecular condensates consisting of different alkali-metal mixtures. This makes the precision data delivered by spectroscopists crucial for planning and interpretation of this new class of experiments. The NaLi, as well as other heteronuclear alkali-metal molecules, is considered to be particularly interesting here because it has a permanent dipole moment, thus can be manipulated with external electric fields.

Finding ways of interpretation spectra, which consist of spectroscopic terms and intensity distribution, is an indispensable stage in spectroscopic research. The usual way, which is based on the adiabatic approximation, is to

represent the spectroscopic term with eigenvalues of the so-called Radial Schrödinger Equation (RSE) as [1]

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

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

$$q_{v''v'} = \left| \int_0^{+\infty} \chi_{v''}(r) \chi_{v'}(r) dr \right|^2, \quad (2)$$

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

Knowing of FC factors gives information on chemical bonding as well as transition channels which are crucial for intramolecular dynamical processes [2]. From the experimental point of view, the FC factors also give a useful way of testing of accurate determination for vibrational quan-

tum numbers in analysing spectra. In this work we present our numerical calculations of FC factors of the $4^1\Pi \leftarrow 1^1\Sigma^+$ band system of NaLi.

II. CALCULATION OF FC FACTORS

The FC factors for the $4^1\Pi \leftarrow 1^1\Sigma^+$ band system of NaLi are calculated according to (2). In the first step, we created vibrational wavefunctions by numerically solving the RSE (1) with the potential curved of the $1^1\Sigma^+$ and $4^1\Pi$ states. Here we employed potential energy curve of the $1^1\Sigma^+$ state determined in [3], and of the $4^1\Pi$ state determined in [4]. However, in order to ensure proper boundary conditions when solving the RSE we extrapolated the potential of the $4^1\Pi$ to both sides by using the Hulbert-Hirschfelder potential model [5]. The RSE was solved in a grid 0.0001 Å of internuclear distance by means of the Numerow-Cooley method [6]. This way we obtained two wavefunctions for levels $v'' = 0$ and 1 of the $1^1\Sigma^+$, and twenty wavefunctions for the levels $v' = 0 \div 19$ of the $4^1\Pi$. The choice of these levels was reasoned to be coherent with experimental observation in [4].

Having the wavefunctions we then performed calculations of FC factors for the $4^1\Pi (v' = 0 \div 19) \leftarrow 1^1\Sigma^+ (v'' = 0)$ and $4^1\Pi (v' = 0 \div 19) \leftarrow 1^1\Sigma^+ (v'' = 1)$ bands. We performed integrations in (2) in the same grid above. Finally, we obtained values of FC factors as tabulated in Tables 1 and 2, and schemed in Fig. 1.

Table 1. FC factors of the $4^1\Pi (v' = 0 \div 19) \leftarrow 1^1\Sigma^+ (v'' = 0)$ band

v'	FC factors	v'	FC factors	v'	FC factors	v'	FC factors
0	.32764E-02	5	0.12007E+00	10	0.65928E-01	15	0.10008E-01
1	.15708E-01	6	0.12610E+00	11	0.48457E-01	16	0.63505E-02
2	.39775E-01	7	0.11959E+00	12	0.34193E-01	17	0.39523E-02
3	.70961E-01	8	0.10453E+00	13	0.23322E-01	18	0.24195E-02
4	.10042E+00	9	0.85432E-01	14	0.15457E-01	19	0.14644E-02

Table 2. FC factors of the $4^1\Pi (v' = 0 \div 19) \leftarrow 1^1\Sigma^+ (v'' = 1)$ band

v'	FC factors	v'	FC factors	v'	FC factors	v'	FC factors
0	0.21873E-01	5	0.41807E-01	10	0.56397E-01	15	0.45312E-01
1	0.71544E-01	6	0.82434E-02	11	0.68241E-01	16	0.34771E-01
2	0.11669E+00	7	0.45581E-03	12	0.70626E-01	17	0.25574E-01
3	0.12303E+00	8	0.13807E-01	13	0.65594E-01	18	0.18160E-01
4	0.89333E-01	9	0.36183E-01	14	0.56217E-01	19	0.12555E-01

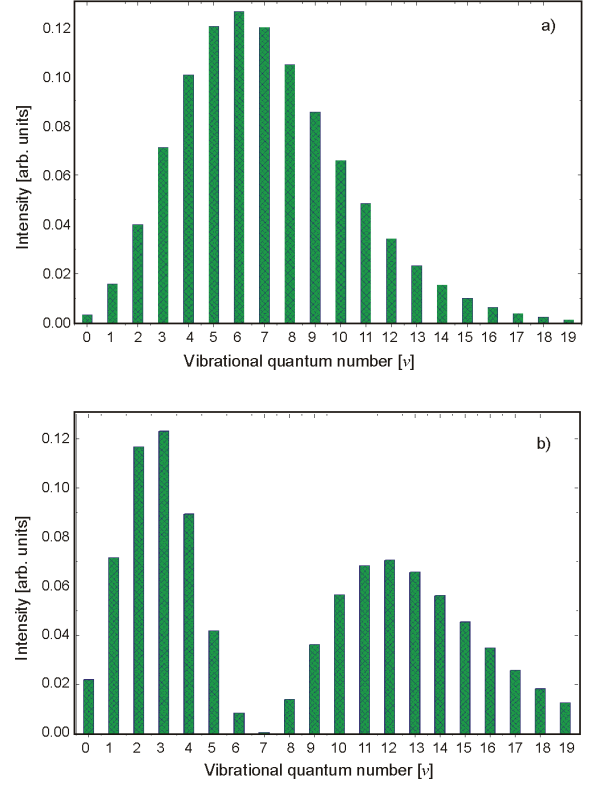


Fig. 1. Chart of the calculated FC factors for transitions start from $v'' = 0$ (a) and $v'' = 1$ (b) in the ground $1^1\Sigma^+$ state to vibrational levels in the excited $4^1\Pi$ state of NaLi

From Fig. 1 we see that intensity of the band of $v'' = 0$ rises to a maximum at $v' = 6$ 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 $v' = 3$, falls down to a minimum (very small compared to the maximum) at $v' = 7$, then rises to another maximum at $v' = 12$ and finally falls down gradually.

III. DETERMINATION OF INTERNUCLEAR DISTANCE FOR THE MOST FAVORABLE TRANSITIONS

We determined the value of internuclear distance at which the favorable transitions take place by using the following argument. We have assumed that $\bar{\nu}$ (in cm^{-1}) is the wavenumber of transition, $E(v')$ and $E(v'')$ are term energies of the upper and lower level, respectively. Owing to the energy conservation we have

$$\bar{\nu} = E(v') - E(v'') = U'(R) + T'(R) - [U''(R) + T''(R)], \quad (3)$$

where U' and T' denote potential energy and kinetic energy, respectively.

According to the Franck-Condon principle, the transition takes place quickly so that the nuclear kinetic energy must remain unchanged. Namely $T''(R^*) = T'(R^*)$ where R^* is internuclear distance at which the transition has taken place. Therefore, from (3) we have

$$\bar{v} = E(v') - E(v'') = U'(R^*) - U''(R^*). \quad (4)$$

By introducing function

$$V(R) = U''(R) + E(v') - U'(R), \quad (5)$$

we see that the transition takes place when

$$V(R^*) = E(v''). \quad (6)$$

Taking $E(v'')$ and $U''(r)$ from [3], $E(v')$ and $U'(r)$ from [4] we determined the values of R^* for the two bands are:

- For the $4^1\Pi$ ($v' = 6$) $\leftarrow 1^1\Sigma^+$ ($v'' = 0$) transition:
 $R^* = 2.933 \text{ \AA}$
- For the $4^1\Pi$ ($v' = 3$) $\leftarrow 1^1\Sigma^+$ ($v'' = 1$) transition:
 $R^* = 3.100 \text{ \AA}$
- For the $4^1\Pi$ ($v' = 7$) $\leftarrow 1^1\Sigma^+$ ($v'' = 1$) transition:
 $R^* = 2.948 \text{ \AA}$
- For the $4^1\Pi$ ($v' = 12$) $\leftarrow 1^1\Sigma^+$ ($v'' = 1$) transition:
 $R^* = 2.778 \text{ \AA}$.

IV. COMPARISON WITH EXPERIMENT OBSERVATION

The experimental data used to compare with the calculated FC factors were observed in [4]. It consists of 420 spectral lines in the $4^1\Pi \leftarrow 1^1\Sigma^+$ band system in which rotational and vibrational quantum numbers in the $4^1\Pi$

state ranging $J' = 9 \div 47$ and $v' = 0 \div 19$, whereas value of the vibrational quantum number in the ground state is $v'' = 0$ and 1. The comparison reveals general good agreement between the calculation and observation, particularly at node $v' = 7$ of the band of $v'' = 1$. At this node no spectral data occurs.]

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