POPULATION DISTRIBUTION OF VIBRATIONAL LEVELS OF THE $2^1\Pi$ STATE OF NaLi

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Abstract. *We studied population distribution of vibrational levels for the $2^1\Pi$ of NaLi molecule from $v' = 0$ to $v' = 16$. The population of the levels was calculated numerically by solving the radial Schrodinger equation with an experimental potential extrapolated to the dissociation limit via a long range potential. We found that, for each highly excited level its population distribution is favorable around the right turning-point. The results provide important information for choosing convenient experimental parameters and explaining dynamical processes in the molecule.*

Keywords: diatomic molecules, laser spectroscopy.

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I. INTRODUCTION

The advent of femto-second laser spectroscopy techniques opens ways to explore dynamical processes in molecules after optical excitations. The molecular dynamics has been now an interesting field for spectroscopists, biologists, and chemists in order to understand intermolecular transitions. In experiments for investigation of molecular dynamics, the population distribution of vibrational levels is crucial information for setting parameters [1]. Recently, alkali-metal diatomic molecules are particular interested for this kind of spectroscopic experiment because of their simple electronic structure and their spectra lying in UV-VIS region, which is easily excited by commercial laser sources. Therefore, there is a need of information for population distribution of vibrational levels in this kind of molecules.

Finding ways of interpretation spectra, which consist of spectroscopic terms and intensity distribution, is an indispensable stage in and spectroscopic research. The usual way, which is

based on the adiabatic approximation, is to represent spectroscopic term with eigenvalues of the so-called Radial Schrödinger Equation (RSE) as [1]

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

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 wave function; and $U(R)$- potential energy of the molecule.

II. THE POTENTIAL ENERGY 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 obtained by the polarization labeling spectroscopy technique [7] corresponding to 0.1 cm^{-1} experimental uncertainty in fig.1. The characteristic feature of spectra was that all the recorded progressions terminated abruptly at $v' \leq 16$, independently of the starting v level, although the vibrational separations had not converged.
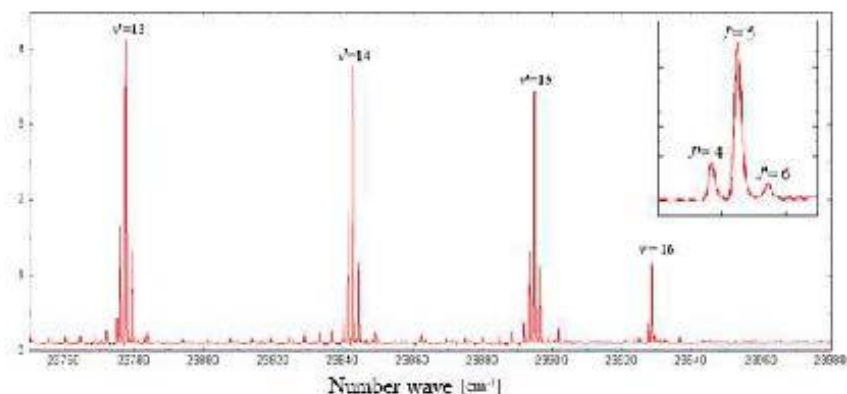

Fig. 1. A fragment of PLS spectrum near the dissociation limit observed in the case of linear pump polarization and 15594.71 c^{-1} probe wavenumber, which labels level (0, 9) in the ground state. The vibrational quantum number is indicated in this figure.

In the first stage of the analysis we tried to fit in a least squares sense all the experimentally determined energies of vibrational levels in the $2^1\Pi$ state with the well known Dunham expansion. In the final analysis 17 molecular constants were fitted to 732 spectral lines [7]. These molecular constants were used to calculate a preliminary rotationless RKR potential curve of the $2^1\Pi$ state in Table 1.

Table 1. The RKR potential curve of the $2^1\Pi$ state of NaLi.

v'	R_{min}[Å]	R_{max}[Å]	U [cm^{-1}]
-.49976281	3.7289730		0.0
0	3.5369809	3.9453877	75.357
1	3.4088748	4.1223776	223.970
2	3.3253822	4.2557618	369.224
3	3.2598828	4.3733415	510.638
4	3.2049632	4.4837627	647.787
5	3.1574617	4.5915015	780.279
6	3.1157854	4.6995907	907.730
7	3.0790579	4.8105339	1029.733
8	3.0467620	4.9267526	1145.837
9	3.0185588	5.0509041	1255.515
10	2.9941729	5.1862115	1358.146
11	2.9732968	5.3369173	1452.981
12	2.9554741	5.5090384	1539.121
13	2.9399017	5.7118044	1615.491
14	2.9250067	5.9608047	1680.812
15	2.9073285	6.2861890	1733.575
16	2.8773205	6.7625462	1771.861

We used the Inverted Perturbation Approach (IPA) method in which the short range potential (for $R < R_{out}$) is represented by a set of grid points $[R_i, U_i]$ whereas in the long range an analytical expression

$$U_{LR} = U_\infty - \frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} \text{ for } R > R_{out} \tag{2}$$

is employed [10]. In general, the values U_i, C_n, U_∞ and R_{out} are fitting parameters to be adjusted in such a way that the difference between the measured level energies and their counterparts calculated from the molecular potential is minimum in a least squares sense. The final potential curve is defined in the range 2 Å$\leq R \leq 11.92928$ Å by 37 parameters $U(R)$ and for $R > 11.92928$ Å by 4 long range parameters $[U_\infty, C_n]$, all of them are listed in Table 2 [7].

Table 2. Parameters defining the IPA potential energy curve of the$2^1\Pi$ state of NaLi.

R [Å]	U [cm^{-1}]	R [Å]	U [cm^{-1}]	R [Å]	U [cm^{-1}]
2.0	34823.8882	3.3	22729.4579	5.0	23505.3076
2.1	33119.5763	3.4	22552.3012	5.2	23661.1771
2.2	31371.8651	3.5	22426.0730	5.4	23781.7714
2.3	29719.2695	3.6	22346.0999	5.6	23872.6004
2.4	28348.6429	3.7	22306.4918	5.8	23938.3475
2.5	27167.4940	3.8	22302.8516	6.2	24018.6258
2.6	26176.3919	3.9	2333.1360	7.1	24065.9534
2.7	25347.6186	4.0	22395.1989	8.6	24068.1703
2.8	24655.4021	4.1	22483.6399	10.1	24065.9715
2.9	24111.3227	4.2	22590.8287	12.4	24062.9823
3.0	23650.2503	4.4	22834.8481	16.0	24061.1800
3.1	23266.4208	4.6	23084.1882		
3.2	22965.2520	4.8	23311.9381		

$R_{out} = 11.92928$ Å,
$U_\infty = 24059.6$ cm^{-1},
$C_6 = -2.538.10^7$ cm^{-1} (Å)^6,
$C_8 = 1.902.10^9$(Å)^8,
$C_{10} = 1.556.10^{10}$(Å)^{10}

III. CALCULATION OF THE WAVE FUNCTION

We used the potential energy and the eigenvalues corresponding to the vibrational levels from $v' = 0$ to $v' = 16$of the NaLi in $2^1\Pi$ state. The RSE was solved in a grid 0.0001Å of the internuclear distance by means of Numerow - Cooley method [2], the wavefunction of NaLi in $2^1\Pi$ state calculated the R internuclear distance from $2A^0$ to $16A^0$. Where, we found the wave function of vibrational levels from $v' = 0$ to $v' = 16$. The wavefunctions of the vibrational levels take the form of numbers. We take the wavefunction squares to determine the population distribution of vibrational states. Fig. 2 discribes the population distribution of a number of vibrational levels by distance R.

From Fig 2 shows that the population is distributed unequally among the vibrational levels, the lower level vibrational amplitude is greater. In the same vibrational level, the population distribution is uneven residence with distance R between two turning points. Furthermore, corresponding to vibrational quantum number$v' = m$, the distribution function of residence have $m + 1$ maximum.
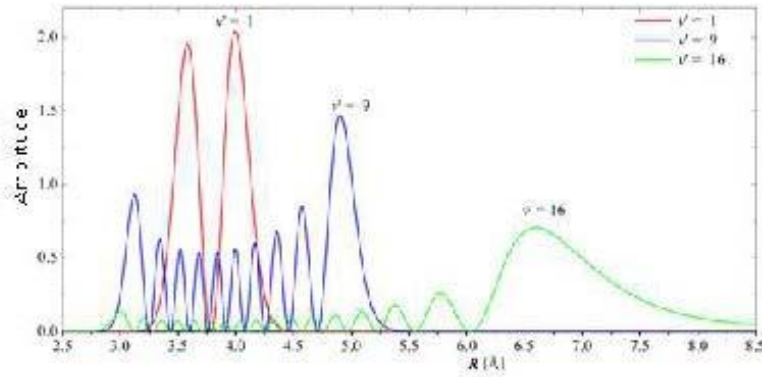
Fig. 2. The population distribution of vibrational levels $v' = 1$, $v' = 9$, $v' = 16$.

To see the localization of the vibrational states on the potential curve, we draw a graph of the population distribution of vibrational level $v' = 1$, $v' = 5$, $v' = 9$, $v' = 16$ with the IPA curve as in Fig 3.
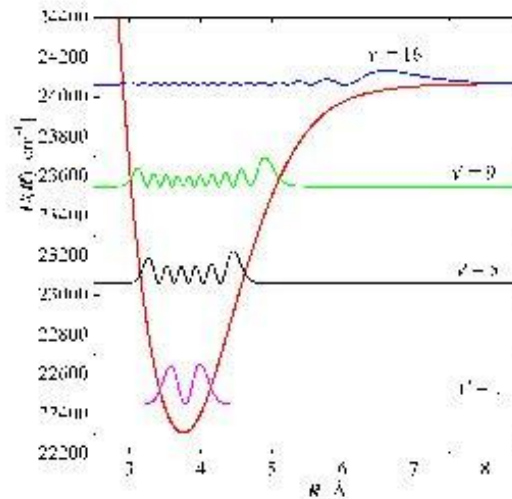

Fig. 3. The population distribution of vibrational levels $v' = 1$, $v' = 5$, $v' = 9$, $v' = 16$ with the IPA curve.

From Fig. 3 shows that the population at outside turning points decreases rapidly but still greater than zero. The population distribution does not eliminate reside turning points as a consequence of quantum mechanics on the continuity of the wave function. On the other hand, in the same vibrational level, the population distribution is the largest near the turning points. The high vibrational levels (ex at level $v' = 16$), the population distribution are mainly concentrated near the right turning point. Physically, this is explained by the force between two atoms at the turning point left more than at the right turning-point so that the time be available at the right turning-point more than at the left turning-point.

IV. CONCLUSIONS

We have studied population distribution of vibratioal levels in the $2^1\Pi$ state of NaLi molecule up to near dissociation limit. It has been shown that the population is distributed unequally among the vibratioanal levels. On the other hand, in each vibrational level with quantum number m node has m +1 maximum. Furthermore, the population distribution drops rapidly but not vanished. These behaviors provide important information for choosing convenient experimental parameter and explaining dynamical processes in the molecule.

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