Calculating vibration-rotation spectrum intensities of laser-induced fluorescence for the $B^1\Pi – X^1\Sigma^+$ electronic transition in a LiCs molecule

To cite this article: A D Smirnov and V S Boldyrev 2017 *J. Phys.: Conf. Ser.* **918** 012007

Calculating vibration-rotation spectrum intensities of laser-induced fluorescence for the $B^1\Pi - X^1\Sigma^+$ electronic transition in a LiCs molecule

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Abstract. The purpose of this study was to calculate the intensities of the vibration-rotation spectrum of laser-induced fluorescence for the $B^1\Pi - X^1\Sigma^+$ electronic transition in a LiCs molecule. We find vibration-rotation energies and wave functions as a result of numerically solving the radial wave equation based on potential energy curves plotted in the present work for the ground and excited states. We compare calculated and experimental intensities.

1. Introduction

Over the last decade, the number of experimental and theoretical publications dealing with heteronuclear alkali dimers in ground and excited electronic states has considerably grown. A feature that distinguishes heteronuclear alkali dimers from homonuclear ones is the presence of a permanent electric dipole moment. Work [1] remarks that polar alkali metal dimers are promising candidates for creation of quantum computers. In [2-6] we calculated energetic and radiative parameters for heteronuclear alkali dimers (CsK, CsLi, RbLi, NaK, NaRb, NaCs, KRb, RbCs, KLi). In the present work we calculated vibration-rotation spectrum intensities of laser-induced fluorescence for the $B^1\Pi - X^1\Sigma^+$ electronic transition in a $^7Li^{133}Cs$ molecule. Out of all mixed alkali dimers LiCs has the biggest permanent electric dipole moment [7]. Publications [8, 9] used laser techniques and high resolution equipment to conduct experimental studies of the LiCs molecule spectrum. These studies derived vibration and rotation spectroscopic constants for the ground and excited electronic states of the $B^1\Pi - X^1\Sigma^+$ transition in a LiCs molecule.

2. Calculation

We calculated the intensity for a spontaneous emission on an electric dipole transition $e'v'j' \to e''v''j''$ using an equation from [10]

$$I(e'v'j' \to e''v''j'') = \frac{64\pi^4}{3c^3} N_{e'v'j'} \frac{S_{J'J''}}{2J'+1} \nu_{v'j,v''j''}^{4} \left| \int \psi_{v'j'}(r)\, R_e(r)\, \psi_{v''j''}(r)\, dr \right|^2$$

where $N_{e''v''j''}$ is the energy level population of the excited state; $S_{J'J''}$ is the rotational line strength; $\nu_{v'j',v''j''}$ is the wavenumber of a vibration-rotation line; $\psi_{v'j'}(r)$ and $\psi_{v''j''}(r)$ are rovibrational wave functions for the excited and ground electronic states; $R_e(r)$ is the dependence of the electronic transition dipole moment on internuclear distance. We used the following expression to calculate wavenumbers of a vibration-rotation line:

$$\nu_{v'j',v''j'} = T_e^{'} + E(v',j') - E(v'',j''),$$

where $T_e^{'}$ is electronic energy of the excited state; $E(v',j')$, $E(v'',j'')$ are vibration-rotational energies of the excited and ground electronic states.

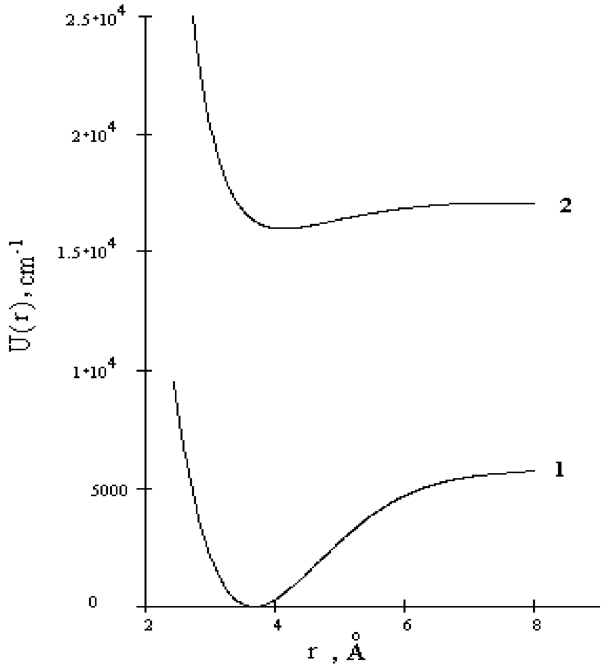

Figure 1. Potential energy curves for the ground (1) and excited (2) electronic states for the $B^1\Pi - X^1\Sigma^+$ transition in a LiCs molecule.

We derived the values of $E(v',j')$, $E(v'',j'')$, $\psi_{v'j'}(r)$ and $\psi_{v''j''}(r)$ as a result of solving the radial wave equation numerically using the Rydberg – Klein – Rees (RKR) potential energy curves, plotted in the present work. Figure 1 shows potential energy curves for the ground and excited electronic states for the $B^1\Pi - X^1\Sigma^+$ transition in a LiCs molecule. We took the function $R_e(r)$ from the publication [11]. We calculated wavenumbers for 77 vibration-rotation lines. Table 1 presents part of the calculated values and compares them with experimental data.

Table 1. Comparison between experimental and calculated wavenumbers of the vibration-rotation lines for the $B^1\Pi - X^1\Sigma^+$ transition in a LiCs molecule.

v''	j''	$\nu^{calc}_{v'j',v''j''}$, cm^{-1}	$\nu^{\exp}_{v'j',v''j''}$, cm^{-1}	v''	j''	$\nu^{calc}_{v'j',v''j''}$, cm^{-1}	$\nu^{\exp}_{v'j',v''j''}$, cm^{-1}
				$v' = 0$	$j' = 76$		
1	76	15545.091	15545.154	7	76	14539.353	14539.402
2	76	15372.122	15372.169	8	76	14379.407	14379.456
3	76	15201.236	15201.297	9	76	14221.731	14221.785

4	76	15032.505	15032.562	10	76	14066.366	14066.418
5	76	14865.931	14865.982	11	76	13913.349	13913.392
6	76	14701.538	14701.582	12	76	13762.722	13762.767
				$v' = 2$	$j' = 38$		
0	37	16112.333	16112.391	8	37	14722.903	14722.925
0	39	16083.821	16083.889	8	39	14696.039	14696.071
3	37	15575.746	15575.788	9	37	14558.726	14558.747
3	39	15547.833	15547.886	9	39	14532.081	14532.113
4	37	15400.987	15401.025	10	37	14396.741	14396.757
4	39	15373.279	15373.326	10	39	14370.319	14370.345
5	37	15228.300	15228.336	11	37	14236.971	14236.983
5	39	15200.798	15200.844	11	39	14210.777	14210.798
6	37	15057.709	15057.741	12	37	14079.450	14079.448
6	39	15030.417	15030.459	12	39	14053.504	14053.486

Figures 2 and 3 show the results of calculating relative intensities of vibration-rotation lines in the spectrum for the $B^1\Pi - X^1\Sigma^+$ electronic transition in a LiCs molecule and a comparison with an experimental spectrum [9].

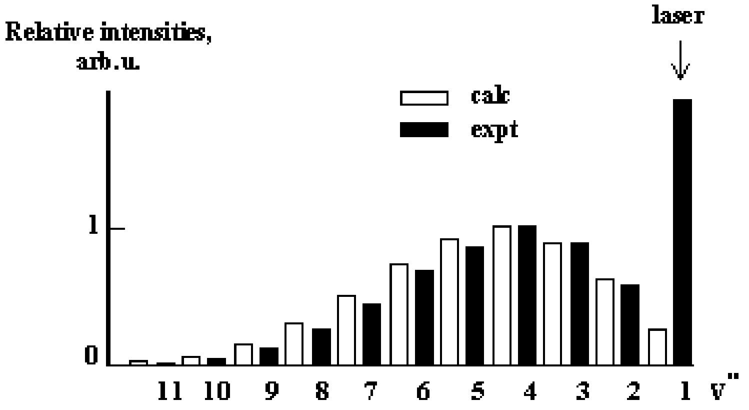

Figure 2. Comparison between experimental and calculated relative intensities of vibration-rotation lines ($v' = 0, j' = 76$; $v'', j'' = 76$) for the $B^1\Pi - X^1\Sigma^+$ electronic transition in a LiCs molecule. Calculated and experimental intensities are normalized to be equal for the strongest spectral line, $\nu_{(laser)} = 15545.158$ cm^{-1}.

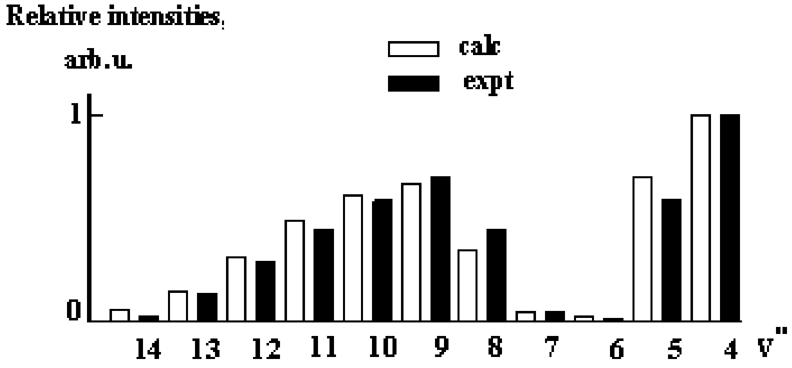

Figure 3. Same as figure 2 for the $v' = 2, j' = 38$; $v'', j'' = 39$ lines.

3. Discussion of results

Good agreement between the calculated and experimental wavenumbers of the vibration – rotation lines confirms the accuracy of the potential curves plotted in this work and the wave functions computed for the ground and excited states of the $B^1\Pi - X^1\Sigma^+$ electronic transition in a LiCs molecule. The calculated wavenumbers deviate from experimental values by less than 0.1 cm^{-1}, which makes for approximately 0.0005 %.

Figures 2 and 3 demonstrate that the intensity distributions of vibration-rotation lines of the calculated spectrum are in good agreement with the experimental laser-induced fluorescence spectrum of the $B^1\Pi - X^1\Sigma^+$ electronic transition in a LiCs molecule.

4. Conclusion

The results show that the wavenumbers and vibration-rotation line intensities calculated using the potential curves plotted in the present paper for the ground and excited electronic states of a LiCs molecule closely agree with the experimental data.

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