

# Investigation of a highly excited electronic $^1\Pi$ state of NaLi molecule

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We report on our investigation of the excitation spectra of the NaLi molecule in the energy range 31000–33900 cm<sup>-1</sup>. A polarisation labelling technique is used to ensure rotational resolution of the spectra and to enable unambiguous assignment of the NaLi transitions. A hitherto unknown electronic state of  $^1\Pi$  symmetry is observed. Major molecular constants of the state are determined and its potential curve constructed using the inverted perturbation approach method.

Keywords: NaLi molecule, laser spectroscopy, electronic states, potential energy curves.

## 1. Introduction

The technique of polarisation labelling spectroscopy (PLS) [1, 2] provides a powerful tool for investigation of the excitation spectra of molecules under rotational resolution. It elegantly surmounts the difficulty of analysing spectra otherwise highly congested: with a proper choice of the frequencies and polarisation of two laser beams, interacting with a given molecular sample, only transitions from a few known rovibrational levels in the ground state are observed. This usually results in spectra with easily resolved and understandable rotational structure.

A variety of states in both homonuclear and heteronuclear alkali dimers have been observed by our group with the PLS technique (see, *e.g.*, [3–7] and references therein), to gain information about their electronic structure. Among the molecular species under investigation, the NaLi belongs to the most difficult to deal with because of the problems with generating molecular vapour at high enough and stable concentration, as well as simultaneous presence of Na<sub>2</sub> and Li<sub>2</sub> molecules, both of which absorb light in the same spectral regions as NaLi. In recent years, however, we succeeded to observe and characterise the  $E(4)^1\Sigma^+$  state of NaLi [8, 9]. The aim of

this paper is to give a resume of the experimental observation of a hitherto unknown excited state of  ${}^1\Pi$  symmetry in this molecule, located about  $31180\text{ cm}^{-1}$  above the bottom of the ground state potential well.

## 2. Experimental

The experimental set-up is similar to that employed in our previous experiment [8], except for the use of a tuneable optical parametric oscillator in place of the dye laser. The known level ( $\nu'' = 0, J'' = 30$ ) of the ground state of  $\text{Na}^7\text{Li}$  was labelled with a light of an  $\text{Ar}^+$  laser ("probe" beam) operated on a  $496.5\text{ nm}$  line (100 mW power). Transitions from the labelled level were excited in a V-type optical-optical double resonance polarisation scheme, using pulsed light from a parametric oscillator/amplifier system (OPO/OPA) provided with a frequency doubler ("pump" beam) and pumped with the third harmonic of an injection seeded Nd:YAG laser. The system delivered UV pulses of 5 mJ energy, 10 ns duration and  $0.16\text{ cm}^{-1}$  spectral width. Both light beams co-propagated at a small angle, crossing in the molecular sample. Vapour containing NaLi was produced by heating metallic sodium and lithium to about  $400^\circ\text{C}$  and  $610^\circ\text{C}$ , respectively, in a dual-temperature heat-pipe oven [10]. A total pressure of 4 torr was established in the oven using helium as a buffer gas. The intensity of the argon ion laser beam was monitored through a polariser-analyser system (Glan-Thompson prisms placed either side of the heat-pipe) so that double resonance signals appeared on a black background. Spectra were recorded as the frequency doubled OPO/OPA light was tuned from  $31000$  to  $33900\text{ cm}^{-1}$ . The wave number calibration was achieved by taking optogalvanic spectra of argon and by additional sampling of the pump light with a  $0.5\text{ cm}$  long Fabry-Pérot interferometer (both auxiliary signals being observed at a fundamental frequency of tuneable OPO/OPA radiation). The accuracy of wave number measurements was better than  $0.1\text{ cm}^{-1}$ .

## 3. Appearance of the spectra and molecular constants of the excited state

The labelling of the initial level for the observed spectra is obtained via the  $P$  line  $B^1\Pi(\nu = 1, J = 29) \leftarrow X^1\Sigma^+(\nu'' = 0, J'' = 30)$  [11]. According to the selection rules specific to the PLS [12] in such a case one can observe polarisation spectra with both circularly and linearly polarised pump light. For circularly polarised pump, only vibrational progressions containing  $P$  and  $R$  doublets are allowed, whereas for linear polarisation of the pump light the spectra may consist of series of either  $P, Q, R$  triplets (for  ${}^1\Pi \leftarrow {}^1\Sigma^+$  bands) or  $P, R$  doublets (for  ${}^1\Sigma^+ \leftarrow {}^1\Sigma^+$  transitions). Part of the recorded spectrum shown in Fig. 1 and containing  $Q$  lines indicates that the symmetry of the upper state in the observed transitions is  ${}^1\Pi$ .

The observed lines span the range  $\nu' = 0-19$  of the upper state. The vibrational numbering of levels in the  ${}^1\Pi$  state has been established by assuming that the lowest

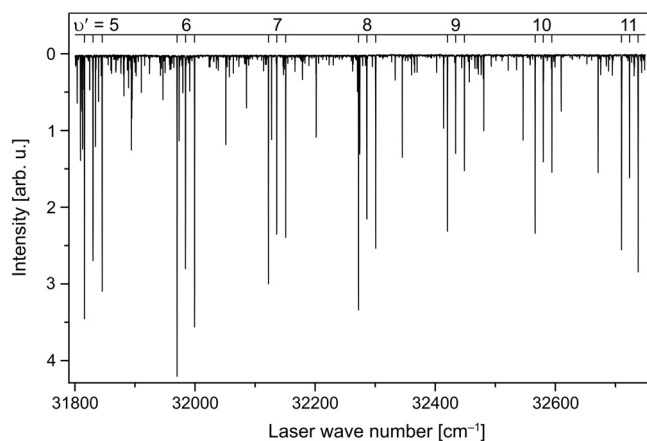


Fig. 1. A part of the polarisation spectrum of Na<sup>7</sup>Li observed for linear polarisation of pump light. The assigned progression corresponds to transitions  ${}^1\Pi(v', J' = 29, 30, 31) \leftarrow X^1\Sigma^+(v'' = 0, J'' = 30)$ .

level recorded corresponds to  $v' = 0$ . Unfortunately, the observed pattern of line intensities could not be used to verify this assumption, as we recorded only transitions originating from  $v'' = 0$ . Therefore, the vibrational numbering proposed by us should be treated with some caution.

The wave numbers of spectral lines were converted to energies of levels in the upper state referred to the bottom of the  $X^1\Sigma^+$  state using the precisely known term value of the ground state  $T''(v'' = 0, J'' = 30)$  [13]. The level energies were then fitted with the conventional Dunham expansion

$$T(v, J) = T_e + \sum_{m,n} Y_{mn} \left( v + \frac{1}{2} \right)^m \left[ J(J+1) - 1 \right]^n$$

where the symbols  $T_e$  and  $Y_{mn}$  have their usual meaning. The above expression is valid for the  $f$  parity levels, whereas for the levels of  $e$  parity the term  $qJ(J+1)$  was

T a b l e 1. Dunham coefficients for the observed  ${}^1\Pi$  state in Na<sup>7</sup>Li (all units in cm<sup>-1</sup>).

Coefficient	Value	Error* [%]
$T_e$	31180.46	0.001
$Y_{10}$	169.388	0.021
$Y_{20}$	-1.1382	0.48
$Y_{30}$	$0.913 \times 10^{-2}$	4.5
$Y_{40}$	$-0.28 \times 10^{-3}$	3.7
$Y_{01}$	0.25567	0.11
$Y_{11}$	$-0.260 \times 10^{-2}$	0.91
$q$	$0.27 \times 10^{-3}$	6.5

\*The quoted error of a constant is one standard deviation.

appended in order to describe the lambda doubling interactions. The constants for the  $^1I$  state under investigation, derived from a simultaneous fit to 55 lines in which the standard deviation was  $0.052 \text{ cm}^{-1}$ , are given in Tab. 1.

#### 4. Determination of the potential energy curve

Once the coefficients in the Dunham expansion had been found, we applied the Rydberg–Klein–Rees (RKR) method to obtain the rotationless potential energy curve for the  $^1I$  state. However, in view of a limited span of the data field in rotational quantum numbers ( $J' = 29\text{--}31$ ), precision of the potential curve constructed that way was rather questionable. Therefore, it was further refined by the inverted perturbation approach (IPA) technique [14], using the RKR curve as a starting point. The final potential curve is shown in Fig. 2 and tabulated in Tab. 2 in a grid of 22 points. For interpolation of the potential to an arbitrary middle point, a natural cubic spline [15] should be used (*i.e.*, the second derivative at the first and the last point should be set to zero). An error analysis specific to the IPA method [16] shows that the observed levels determine the potential curve reliably only between about  $2.7$  and  $5.3 \text{ \AA}$ . Points beyond this range are given in Tab. 2 mostly to ensure proper boundary conditions for solving the Schrödinger equation. However, these points have some influence on the values of the potential for  $2.7 \text{ \AA} < R < 5.3 \text{ \AA}$  because of the properties of the cubic spline interpolation. In the lack of theoretical calculations related to electronic states of NaLi in this energy range (the most extensive of them covering excitation energies only up to  $30000 \text{ cm}^{-1}$  [17]) it is impossible to determine correlation between the observed state and atomic asymptotes.

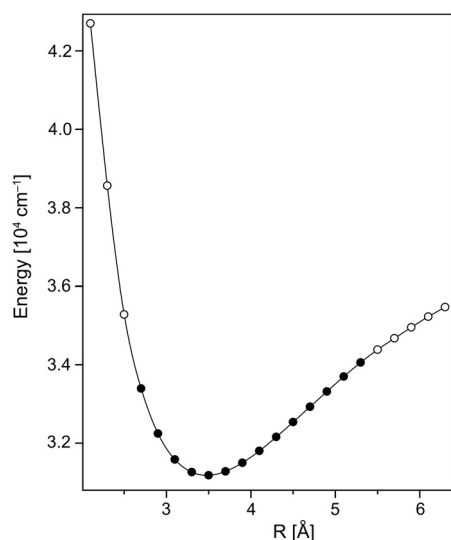


Fig. 2. The IPA potential curve of the  $^1I$  state of Na $^7$ Li under investigation. Full circles denote the reliably determined points (see the text).

Table 2. Rotationless IPA potential energy curve for the  $^1\Pi$  state in Na $^7$ Li.

$R$ [Å]	$U$ [cm $^{-1}$ ]	$R$ [Å]	$U$ [cm $^{-1}$ ]
2.1	42700.239	4.3	32157.203
2.3	38560.408	4.5	32537.040
2.5	35281.660	4.7	32927.674
2.7	33392.799	4.9	33318.457
2.9	32244.581	5.1	33698.893
3.1	31581.452	5.3	34057.816
3.3	31259.964	5.5	34384.377
3.5	31180.639	5.7	34676.678
3.7	31277.644	5.9	34955.918
3.9	31499.353	6.1	35228.114
4.1	31803.420	6.3	35469.898

When solving the Schrödinger equation with the potential from Tab. 2 by means of the Numerov–Cooley method [18] with 0.0007 Å grid space, the experimentally derived energies of 55 rovibronic levels in the  $^1\Pi$  state under investigation are reproduced with a dimensionless standard deviation of 0.4. It must be stressed that because of limited rotational data, the potential energy curve is likely to give better predictions of energies of unobserved levels than the Dunham coefficients.

## 5. Conclusions

In the range of 31180–34500 cm $^{-1}$  above the bottom of the ground state of NaLi we have observed a previously unknown state of  $^1\Pi$  symmetry. The Dunham coefficients and potential energy curve were determined for this state. Theoretical calculations of potential curves for electronic states of NaLi located in the energy range mentioned above are highly desirable as they could be helpful in determination of the dissociation limit of the observed state and stimulate further experimental research on this molecule.

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