

The $6^1\Pi_u$ state of Na_2 molecule

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Excitation spectra of sodium dimer were analysed within the range 34200–36400 cm^{-1} . The experiment was done using polarisation labelling spectroscopy technique. In the spectral region under investigation we found several vibrational progressions belonging to a single band system having the ground state of Na_2 as the lower state. The upper state was of $^1\Pi_u$ symmetry as indicated by the presence of Q lines in the spectrum and basing on theoretical calculations it was identified as the $6^1\Pi_u (3s+4f)$ state. The Dunham coefficients and potential curve characterising this state were deduced from the observed spectra.

Keywords: Na_2 molecule, laser spectroscopy, electronic states, potential energy curves.

1. Introduction

Alkali metal dimers are workhorses in molecular spectroscopy of diatomic species, attracting considerable interest of both experimentalists and theoreticians. The sodium dimer is unquestionably the most popular of them and has been investigated for a long time basing on numerous spectroscopic methods. Among its electronic states of singlet ungerade symmetry accessible with one photon transitions from the ground $X^1\Sigma_g^+$ state, the $D(4)^1\Pi_u$ state is the highest one that has been thoroughly characterised in experiments thus far [1–3]. Some rovibronic levels of still higher energy were reported by Li *et al.* [4] but their assignment is still only tentative. On the theoretical side, calculations extend to higher excitation energies and reach up to $8^1\Sigma_u^+$ and $7^1\Pi_u^+$ states [5, 6]. This disparity between theoretical and experimental results led us to experimental investigation of excitation spectrum of the Na_2 molecule within the range 34200–36400 cm^{-1} . In this paper we report the first observation of the $6^1\Pi_u$ state located in this range.

2. Experimental

The polarisation labelling spectroscopy (PLS) method used in our experiment was described in detail in our previous papers (see, *e.g.*, [7, 8]). The method is based on

optical–optical double resonance. A strong pump beam of laser light, circularly or linearly polarised, creates optical anisotropy in the molecular sample under investigation. This anisotropy may be detected through a change of polarisation of a much weaker, initially linearly polarised probe beam, originating from a second laser. The condition is that molecular transitions induced by both beams should start from the same rovibrational level in the lower state which in our case was the ground state of Na_2 . The key of the method is that the probe beam is of a fixed frequency being resonant with a few transitions originating from the known rovibrational levels in the ground state (the “labelled” levels), whereas the pump beam is tuned across the investigated spectral range. When examining changes in polarisation of the probe beam, only these transitions induced by the pump light are detected which start from the levels labelled by the probe laser. Owing to significant decrease of a number of spectral lines observed in this way in comparison with the corresponding absorption spectrum of the molecule, the PLS technique enables significant simplification of the spectra and resolving of individual lines despite their Doppler broadening.

In our experiment the optical parametric oscillator and amplifier (OPO/OPA) system with a frequency doubler (Sunlite Ex, Continuum) was employed as the pump beam source. The OPO was pumped by a third harmonic of the injection seeded Nd:YAG laser (Powerlite 8000). The system provided UV pulses with a spectral width of about 0.16 cm^{-1} and energy up to 5 mJ, with frequency tuned between 34200 and 36400 cm^{-1} . The probe beam originated from an Ar^+ laser (Carl Zeiss ILM120) working at one of five wavelengths: 476.5, 488.0, 496.5, 501.7 or 514.5 nm with the power ranging from 20 to 150 mW. The Na_2 molecules were generated in a heat-pipe

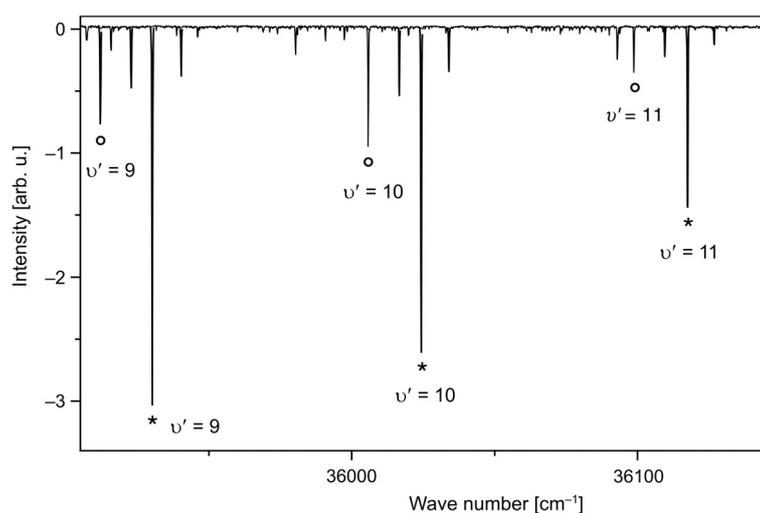


Fig. 1. A part of the $6^1\Pi_u \leftarrow X^1\Sigma_g^+$ polarisation spectrum of Na_2 recorded with the 501.7 nm line of the Ar^+ laser as the probe and linearly polarised pump light. The Q lines of two prominent vibrational progressions are marked: $(v', J' = 43) \leftarrow (v'' = 2, J'' = 43)$ by asterisks, $(v', J' = 47) \leftarrow (v'' = 2, J'' = 47)$ by circles.

oven filled with 4 mbar of helium as a buffer gas and heated up to 730 K. Two reference signals were recorded alongside the excitation spectra of Na_2 : an optogalvanic spectrum of argon and a transmission spectrum of the Fabry–Pérot interferometer with $\text{FSR} = 1 \text{ cm}^{-1}$ enabled calibration of the molecular spectra with an accuracy of 0.1 cm^{-1} .

3. Results

An example of the recorded spectrum of Na_2 is shown in Fig. 1. The preliminary analysis has shown that the observed spectra correspond to transitions from the ground $X^1\Sigma_g^+$ state to a state of $^1\Pi_u$ symmetry. It can be easily noticed that this state is strongly

T a b l e 1. Dunham coefficients for the $6^1\Pi_u$ state of Na_2 obtained in the present work*.

Coefficient	Value [cm^{-1}]	Uncertainty [%]
Y_{00}	35447.18	0.0001
Y_{10}	110.364	0.02
Y_{20}	-1.05793	0.45
Y_{30}	0.02138	1.3
Y_{01}	0.111790	0.02
Y_{11}	-1.2191×10^{-3}	0.45
Y_{21}	2.108×10^{-5}	2.2
Y_{02}	-4.622×10^{-7}	0.50

*The quoted uncertainty of a constant is one standard deviation. To reproduce the original data, the parameters are given with more significant figures than are required by the associated standard errors.

T a b l e 2. Rotationless RKR potential for the $6^1\Pi_u$ state of Na_2 .

ν	$T_e + G_\nu$ [cm^{-1}]	R_{\min} [\AA]	R_{\max} [\AA]
	35447.177		3.622*
0	35502.051	3.469	3.796
1	35611.087	3.367	3.938
2	35716.762	3.302	4.045
3	35821.361	3.251	4.136
4	35924.293	3.208	4.219
5	36025.686	3.171	4.296
6	36125.669	3.139	4.368
7	36224.371	3.109	4.437
8	36321.918	3.082	4.503
9	36418.440	3.057	4.566
10	36514.064	3.034	4.627

*The first line refers to the bottom of the potential curve; R is the equilibrium distance.

perturbed and only Q lines in the spectra (corresponding to transitions to f -parity levels in the upper state) form regular vibrational progressions; therefore only Q lines were used in further analysis.

Altogether 153 Q lines were identified. They correspond to transitions to rovibrational levels of the ${}^1\Pi_u$ state with vibrational quantum number ν ranging from 0 to 10 and rotational quantum number J from 13 to 76. The Dunham coefficients were used to describe the observed levels in a standard way and the results are shown in Tab. 1. The root mean square deviation of the final fit equals to 0.08 cm^{-1} , in agreement with the precision of the measurements. Basing on the obtained Dunham coefficients, the potential energy curve for the ${}^1\Pi_u$ state was constructed using the semiclassical Rydberg–Klein–Rees (RKR) method [9]. The results are listed in Tab. 2 which contains the vibrational term values G_ν as well as the RKR turning points.

4. Discussion and conclusions

The experimental potential of the investigated ${}^1\Pi_u$ state is displayed in Fig. 2 together with theoretical curves for the $5{}^1\Pi_u$ and $6{}^1\Pi_u$ states calculated by MAGNIER *et al.* [5, 6]. A comparison of experimental potentials of the lower states of the same symmetry, $C(2){}^1\Pi_u$ [8], $3{}^1\Pi_u$ [10] and $D(4){}^1\Pi_u$ [2, 3], investigated by us previously with the corresponding potentials originating from the same calculation shows that the theoretical work underestimates the term energies T_e of these states by 200–230 cm^{-1} . Therefore we assign the electronic state observed in this experiment as the $6{}^1\Pi_u$ state correlated with the $\text{Na}(3^2S) + \text{Na}(4^2F)$ atomic asymptote, as its experimental $T_e = 35447.18\text{ cm}^{-1}$ exceeds then the theoretical value by 258 cm^{-1} . Moreover, strong perturbation of the e -parity levels in the observed state is consistent with the predicted presence of the $6{}^1\Sigma_u^+$ state very close to $6{}^1\Pi_u$. This assignment would mean, however, that the $5{}^1\Pi_u(3s+4d)$ is missing in the spectra, with the only plausible explanation

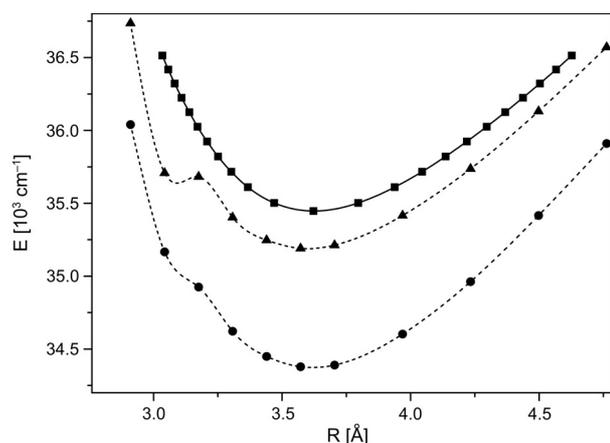


Fig. 2. The potential energy curve of the investigated $6{}^1\Pi_u$ state (squares) compared with theoretical calculations of MAGNIER *et al.* [5, 6] for the $5{}^1\Pi_u$ (circles) and $6{}^1\Pi_u$ (triangles) states.

being a much lower transition dipole moment for the $5^1\Pi_u \leftarrow X^1\Sigma_g^+$ band system. Unfortunately, to the best of our knowledge no theoretical calculation on this subject is available yet.

It must be noted that theoretical curves for both the $5^1\Pi_u$ and $6^1\Pi_u$ states display irregular shape of the inner wall (Fig. 2). The experimental potential does not confirm this prediction which may be a computational artefact connected with a limited basis set used in the calculation.

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