High resolution spectroscopy of the $^{13}_g (b) \leftarrow ^{13}_u (x)$ transition of Na$_2$

A. Färbert, J. Lutz, T. Platz, W. Demtröder

Fachbereich Physik, Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-67663 Kaiserslautern, Germany

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Abstract. Rotational-vibrational transitions of the triplet system $^{13}_g \leftarrow ^{13}_u$ of the Na$_2$ molecule have been investigated around $\nu = 13970$ cm$^{-1}$ by Doppler-free polarization spectroscopy in a heat pipe and by resonant two-step photoionization in a collimated cold argon beam, seeded with sodium vapor. The fine- and hyperfine structure of the transitions is partly resolved. The analysis of the measured spectra and a theoretical discussion of the expected multiplet structure yields the rotational constants $B'_g(v' = 17) = 0.0866(4)$ cm$^{-1}$ for the upper and $B'_u(v'' = 0) = 0.0533(4)$ cm$^{-1}$ for the lower state. The difference $\Delta b = b(^3\Sigma_u^+) - b(^3\Sigma_g^+)$ of the hyperfine coupling constants $b$ turns out to be $\Delta b = 80$ MHz.

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1 Introduction

The investigation of triplet transitions in alkali dimers, starting from the loosely bound lowest $^{13}_u$ state with a shallow potential has found increasing interest because of its relevance to the trapping of optically cooled alkali atoms in a magneto-optical trap [1, 2]. The trapped atoms all have parallel electron spins and the cross sections for elastic collisions between these trapped cold atoms depend on the long range part of the $^{13}_u$ potential [3]. In the molecular model spin-flip collisions correspond to transitions between the $^{13}_u$-potential and the $X^1\Sigma_g^+$-potential. Because of symmetry selection rules these transitions are only made allowed by hyperfine interactions, causing an indirect electron spin-nuclear spin-electron spin coupling [4]. These “symmetry breaking” interactions cause a mixing of the singlet and triplet states at large internuclear distances, where the energy separation of the two potentials is of the order of the atomic hyperfine splitting, which is 1.7 GHz for the case of the Na $(^3\Sigma_{1/2})$ groundstate. From high resolution laser spectroscopy the rotational energy levels, their fine structure (spin-rotation-interaction) and their hyperfine structure can be deduced for both, the lower and the upper state of the $^{13}_g \leftarrow ^{13}_u$ transition (we follow here the recently adapted nomenclature to label the gerade and ungerade states separately, starting from the lowest state as number 1. In the old nomenclature the $^{13}_g$-state is named $a^3\Sigma_u^+$, (Fig. 1)).

In order to resolve the rotational structure and in particular the hyperfine structure, sub-Doppler resolution is demanded. We have used two different Doppler-free spectroscopic techniques: polarization spectroscopy in a sodium vapor heat pipe and resonant two-photon two-color ionization spectroscopy in a collimated cold supersonic argon beam seeded with sodium vapor. In this beam Na$_2$-molecules are formed during the adiabatic expansion of the Ar/Na-mixture and the population of $(v', J')$-vibration-rotation levels in the $^{13}_u$ state depends on the number of collisions, which can produce $^{13}_u$-Na$_2$ dimers, but can also depopulate the $(v'', J'')$ levels by collision-induced transitions into levels of the lower $X^1\Sigma_g^+$ state. The $^{13}_g \leftarrow ^{13}_u$ transition of Na$_2$ is partly overlapped by the $A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ system. Transitions to these perturbed levels also show hyperfine splittings [6-8] and it is not obvious, how to distinguish those transitions from the wanted $^{13}_g \leftarrow ^{13}_u$ triplet transitions. It is therefore necessary to take a more detailed look at the expected hyperfine patterns and to outline the differences between the two types of transitions. We therefore start with a section on basic theoretical considerations.

2 Theoretical background

2.1 Rotational structure

The rotational structure of the $^{13}_g \leftarrow ^{13}_u$ system of Na$_2$ consists of $P$- and $R$-lines with wave numbers:

$P$: $\tilde{v}(N) = v_0 - (B'_u + B''_u)N + (B'_u - B''_u)N^2$  \hspace{1cm} (1a)

$R$: $\tilde{v}(N) = v_0 + 2B'_u + (3B'_u - B''_u)N + (B'_u - B''_u)N^2$  \hspace{1cm} (1b)
where \( N = N'' \) is the rotational quantum number of the lower level and centrifugal distortion has been neglected. Ab-initio calculations show [9], that the equilibrium internuclear distance \( r_e \) is smaller in the upper \( 1^3\Sigma_u^+ \) state than in the lower \( 1^3\Sigma_g^+ \) state. This implies that \( B' > B'' \) and contains the \( P \)-branch shows a band head, shaded towards the blue. The \( A^1\Sigma_u^- \)-state, on the other hand, has a rotational constant \( B' \) which is smaller than \( B''(X^1\Sigma_g^+) \), resulting in a red shaded \( R \)-branch for the \( A^1\Sigma_u^- \) transitions. This is one of several features to distinguish between triplet transitions and perturbed singlet transitions, provided that the rotational analysis is possible for many \( N \)-values around the band head.

### 2.2 Fine structure

The fine- and hyperfine structure of levels in \( 3\Sigma \)-states depend on the relative magnitudes of the different coupling strength between rotational angular momentum \( N \), electron spin \( S \) and nuclear spin \( I \). Since the electronic angular momentum \( L \) in \( \Sigma \)-states has the projection-quantum number \( \lambda = 0 \), Hund’s coupling case \( b \) applies. If the coupling between \( N \) and \( S \) is stronger than that between \( S \) and \( I \), the levels are best described by Hund’s coupling case \( b_{RI} \) (Fig. 2a), where the electron spin \( S \) couples with the rotational angular momentum \( N \) forming the resultant vector \( J \). The nuclear spin \( I \) couples with \( J \), yielding the total angular momentum \( F \). In this case the spin-rotation-interaction is larger than the hyperfine-interaction. The three fine structure components are split by electron spin-rotation-interaction \( \Delta W_{SR} = \gamma SN \) and by spin-spin-interaction between the two non-paired electrons, characterized by the spin-spin-interaction constant \( \lambda \).

The term values of the resulting three fine structure components of a rotational level \( |N\rangle \) are [10]

\[
F_1(J = N + 1) = B_N(N + 1) - \gamma + (2/3)\lambda
\]

\[
+ B_c(2N + 3) - \gamma/2 - \lambda
\]

\[
- [(2N + 3)^2(B_c - \gamma/2)^2
\]

\[
- 2\lambda(B_c - \gamma/2 + \lambda^2)^{1/2}
\]

(2a)

It is difficult to calculate the magnitude of the constants \( \gamma \) and \( \lambda \) for the \( \text{Na}_2 \) \( 1^3\Sigma_u^+ \) and \( 1^3\Sigma_g^+ \) states, since this would require a more detailed knowledge of the spin density functions of the two unpaired electrons and also of the spin polarization of the core by the valence electrons.

A crude estimation of the magnitude of \( \gamma \) for the \( 1^3\Sigma_u^+ \)-state can be obtained from measurements of the magnetic hyperfine coupling constant \( \gamma_1 = 0.3 \text{ kHz} \) in the \( X^1\Sigma_g^+ \) ground state of \( \text{Na}_2 \) [11], which yields a nuclear spin-molecular rotation splitting of

\[
\Delta W_{IN} = \gamma_1 IN
\]

(3)

of a rotational level \( |N\rangle \) due to the interaction of the nuclear magnetic moment \( \mu_N = g_I\mu_N \) with the magnetic field produced by the molecular rotation. If we assume, that the electron spin-rotation splitting in the \( 1^3\Sigma_u^+ \) state with two \( 3s \)-electrons is about

\[
\Delta W_{SN} \approx (g_S\mu_B)/(g_I\mu_N) \Delta W_{IN} = 2/(3/2)\cdot \mu_S/\mu_N \Delta W_{IN}
\]

(4)

we obtain a spin-rotation constant of \( \gamma \approx 0.75 \text{ MHz} \). For a rotational level with \( N = 20 \) this would result in a spin-rotation splitting of \( \Delta W_{SN}(N = 20) \approx 15 \text{ MHz} \), which is still smaller than the hyperfine splittings (see below).

If spin-rotation interaction would be the only cause of the fine structure splitting, then Hund’s base \( b_{PS} \) (Fig. 2b) should apply to the \( 1^3\Sigma_u^+ \)-state. In this case the electron spin \( S \) and nuclear spin \( I \) couple at first to form the vector \( G = S + I \), which then couples less strongly to \( N \) and forms a resultant angular momentum \( F = N + G \). This coupling case has been confirmed by Field et al. [12] who have measured the hyperfine structure of triplet Rydberg-levels of \( \text{Na}_2 \) and who could explain the observed hfs-patterns very well by Hund’s case \( b_{PS} \). In their case the hyperfine splittings are mainly due to the Fermi-contact interaction of the single electron in the \( 3\sigma_g \) orbital and electron-spin-spin interaction between the valence and the Rydberg electron is negligible.

In our case the spin-spin interaction in the \( 1^3\Sigma_u^+ \)-state between the two electrons in the \( 3\sigma_g \) and \( 3\sigma_u \) orbital respectively, which varies with \( 1/r_{12}^3 \), is much larger. A comparison with other molecules might be useful. For the \( 3\Sigma_g^+ \) ground state of \( \text{O}_2 \), which has been studied in detail by microwave spectroscopy [13] the spin-rotation constant \( \gamma = -0.0085 \text{ cm}^{-1} \) is mainly caused by...