ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Spectroscopy 234 (2005) 264–269

Journal of MOLECULAR SPECTROSCOPY

www.elsevier.com/locate/jms

Λ-Doubling investigation of the $5^1\Pi_g$ Rydberg state of Na_2 using optical–optical double resonance spectroscopy

Chin-Chun Tsai [a,b,*], Ray-Yuan Chang [a], Thou-Jen Whang [b,c]

[a] Department of Physics, National Cheng-Kung University, Tainan 70101, Taiwan
[b] Institute of Electro-Optical Science and Engineering, National Cheng-Kung University, Tainan 70101, Taiwan
[c] Department of Chemistry, National Cheng-Kung University, Tainan 70101, Taiwan

Received 18 August 2005; in revised form 18 September 2005
Available online 2 November 2005

Abstract

The splitting of Λ-doubling in the $5^1\Pi_g$ Rydberg state of Na_2, which dissociates to Na(3*s*) + Na(4*d*), has been measured using the high-resolution cw optical–optical double resonance technique. The observed data are in the range of $0 \leqslant v \leqslant 22$ and $11 \leqslant J \leqslant 83$ with Λ-doubling revealed. A set of Dunham coefficients with Λ-doubling constants has been obtained from the experimental results. The splitting of Λ-doubling increases quadratically with the rotational quantum number J and weakly depends on the vibrational quantum number v. These splitting constants are much larger than those in the Na_2 $B^1\Pi_u$ state, which dissociates to Na(3*s*) + Na(3*p*). This indicates that the splitting of Λ-doubling in the $5^1\Pi_g$ state is affected by both the perturbations by adjacent Σ states and the L-uncoupling.

© 2005 Elsevier Inc. All rights reserved.

Keywords: Λ-Doubling; L-Uncoupling; Laser spectroscopy; Excited states; Multiple resonances; Diatomic molecules; Sodium

1. Introduction

In a diatomic molecule, the precession of electronic angular momentum L takes place along its internuclear axis with constant component M_L where M_L can take the values $M_L = L, L-1, \ldots, -L$ [1]. However, reversing the direction of precession does not change the energy of the state but does change M_L to $-M_L$. States with different M_L have in general a larger energy separation since the electric field which causes the separation is very strong. It is common to classify the electronic states of diatomic molecules according to the value of $|M_L|$ and let $\Lambda = |M_L|$. The corresponding angular momentum vector Λ represents the component of the electronic orbital angular momentum L along the internuclear axis. For a given L, the quantum number Λ can take the values $\Lambda = 0, 1, 2, \ldots, L$, corresponding to the designation of molecular states $\Sigma, \Pi, \Delta, \ldots$, respectively. States $\Pi, \Delta, \ldots$ are doubly degenerate since M_L can have two values $+\Lambda$ and $-\Lambda$, while states Σ are non-degenerate. When interaction with other electronic states is also considered, these doubly degenerate states are split by so-called Λ-doubling. Mathematically, the wavefunctions of these doubly degenerate states can be written as a phase factor $e^{\pm i\Lambda\phi}$, where ϕ is the azimuthal angle rotating around the internuclear axis. The different angular momenta in the molecule—electron spin S, electronic angular momentum L, and angular momentum of nuclear rotation N^+—form a resultant that is always designated as J, the total angular momentum. The mutual interactions of these angular momenta are coupled in different ways according to their interaction strength and have been classified by Hund [2]. However, Hund's coupling cases represent only idealized limiting cases. In molecule, the rotation of nuclei N^+ disturbs the energy of the states. For a larger speed of rotation, each total angular momentum J in the state of $\Lambda \neq 0$ will split into two components. This splitting is called Λ-doubling and increases quadratically with J. This phenomenon of diatomic molecular spectra was experimentally and theoretically studied in the early years by Van Vleck [3] and Mulliken and Christy [4].

---

[*] Corresponding author. Fax: +886 6 2747995.
E-mail address: chintsai@mail.ncku.edu.tw (C.-C. Tsai).

0022-2852/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2005.09.013

For a molecule in a Rydberg state correlating with an atomic asymptote with smaller principal quantum number n, the electronic states with different Λ value are far apart in energy since the coupling of angular momentum to its internuclear axis is large and L precesses very rapidly. Each electronic state has its own set of rotational and vibrational energy levels. If one considers a series of orbits with increasing principal quantum number n, the influence of the internuclear axis on its electronic energy rapidly decreases when the orbit gets larger. The rate of precession of L and the energy interval between different Λ states diminishes quickly as the size of the orbit increases. Finally, the precession of L around the internuclear axis breaks down and Λ is no longer a good quantum number. In the Hund's coupling cases, transition occurs from case (a) or case (b) to case (d) while the coupling of L breaks down. This transition between Hund's coupling cases is shown in Fig. 1. Therefore, the degeneracy will be removed and the Λ-doubling splitting becomes larger as the size of the orbit increases. The transition between the Hund's coupling cases of the molecule NO has been reported by Klisch et al. [5]. To analyze the Λ-doubling splitting, the regular perturbation is applied by coupling the state of interest to the nearby electronic states whose Λ value differs by one [6]. The observations of Λ-doubling have been reported for molecules such as, NO, H_2, Li_2, and NaK [7,8,9]. In the sodium dimer, Λ-doubling has been reported only in the $B^1\Pi_u$ state with the first-order splitting constant $q_0 = 0.115 \times 10^{-4}\ \mathrm{cm}^{-1}$. In this report, the separation between the e/f levels of Λ-doubling in the $5^1\Pi_g$ state has been measured by using high-resolution cw optical–optical double resonance (OODR) spectroscopy. The first-order splitting constant is 15 times larger than that in the $B^1\Pi_u$ state. The Λ-doubling splitting increases as a quadratic function of rotational quantum number J and the dependence on the vibrational quantum number v is weak. The large Λ-doubling splitting constants indicate that the effects are from the perturbations between the adjacent electronic states as well as the uncoupling of orbital angular momentum L.

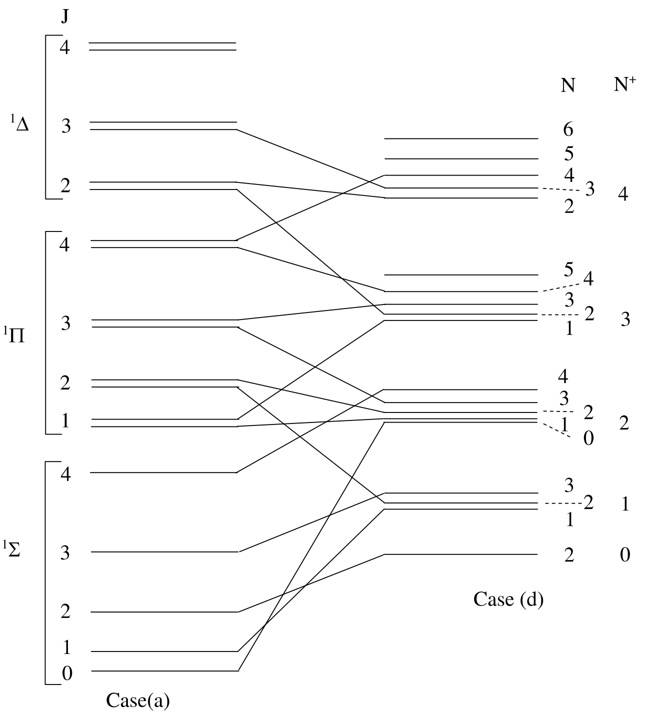

Fig. 1. Correlation diagram between Hund's coupling case (a) and case (d) for the $s + d$ atomic asymptote. In case (d), coupling of the total electronic spin to the remaining angular momentum is not significant. So, only singlet states, i.e., $S = 0$, are considered in this diagram (if $S = 0$, then $J = N$). In case (a), Σ, Π, and Δ represent the possible states and J is the rotational angular momentum. For states with $\Lambda \neq 0$, each of the rotational levels J splits into two components of e/f parities known as Λ-doubling.

2. Experiment

The experimental setup has been described in more detail in [10]; hence we only dwell on it briefly. As shown in Fig. 2, sodium metal is loaded into a five-arm stainless steal heat-pipe oven with about 1 Torr of argon buffer gas and heats to 350 °C at the center of the heat-pipe oven to generate sodium vapor. A single line Ar^+ laser (Coherent I-90, total of nine lines) is used to excite the $B^1\Pi_u(v', J') \leftarrow X^1\Sigma_g^+(v'', J'')$ transitions of Na_2. Several intermediate levels of $B^1\Pi_u$ state can be excited simultaneously by one of the lines from the Ar^+ laser. Table 1 lists the Ar^+ laser wavelength (in air), transitions, and the term values of $B^1\Pi_u$ state used in this study. The term values of the intermediate $B^1\Pi_u$ state are calculated from the set III molecular constants in Table VII of [11]. We did not add the photon energy of the pump Ar^+ laser to the term value of the ground state to form the term values of $B^1\Pi_u$ state since the Ar^+ laser frequency

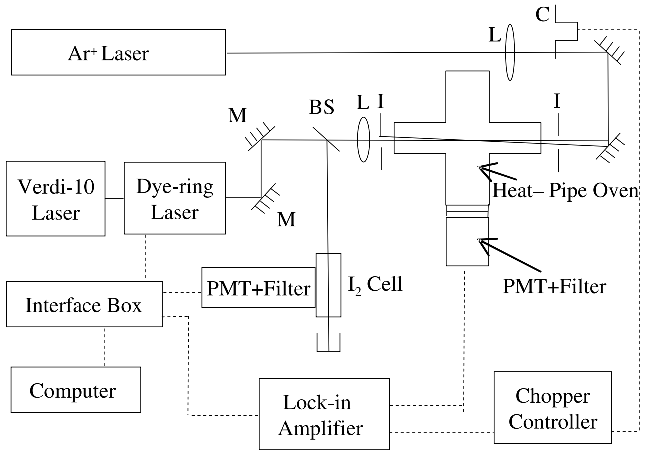

Fig. 2. The block diagram of experimental setup for OODR spectroscopy. The Ar^+ laser beam is tilted after passing through the center of the heat-pipe to avoid interference with the dye laser. (M, mirror, BS, beam-splitter, L, lens, I, iris, and C, chopper.)

Download English Version:

https://daneshyari.com/en/article/9589417

Download Persian Version:

https://daneshyari.com/article/9589417

Daneshyari.com