

## Studies of rotational level $\Lambda$ -doubling by rf–optical double resonance spectroscopy: application to NaK $D^1\Pi$

M. Auzinsh<sup>a</sup>, I. Klincare<sup>a,\*</sup>, O. Nikolayeva<sup>a</sup>, A.V. Stolyarov<sup>b</sup>, M. Tamanis<sup>a</sup>, R. Ferber<sup>a</sup>

<sup>a</sup>Department of Physics, University of Latvia, 19 Rainis boulevard, LV-1586 Riga, Latvia

<sup>b</sup>Department of Chemistry, Moscow State University, 119899 Moscow, Russia

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### Abstract

We report here the application of optical–radio frequency double resonance spectroscopy for individual rotational levels of the NaK  $D^1\Pi$  state. Lambda doubling constant  $q$  values for five  $v'$ ,  $J'$  levels are obtained. These data are combined with measurements of dc  $e$ - $f$  Stark-mixing-induced changes in optical spectra, and the electric dipole moment  $d_p$  in the  $D^1\Pi$  state is determined. © 1997 Elsevier Science B.V.

**Keywords:** Optical–rf double resonance; Stark effect; NaK  $\Lambda$ -doubling; Dipole moment

### 1. Introduction

The electronic–rotational interaction of the  $^1\Pi$  state with  $^1\Sigma$  states induces well known  $\Lambda$ -doubling in  $^1\Pi$  with splitting  $\Delta_{cf}^J = q[J(J+1) - \Lambda]$ ,  $q$  being the  $\Lambda$ -doubling constant. Only quantitative information for  $\Lambda$ -doubling splitting in the NaK  $D^1\Pi$  state is given in [1], where the  $q$  value for levels with large rotational quantum number  $J$  ( $J \geq 100$ ) has been deduced from level shifts. However, for this state there exists developed spectroscopic information [1–3], including lifetime measurements [4]. Numerous more-or-less pronounced local perturbations caused by the  $D^1\Pi$ – $d^3\Pi$  interaction have been revealed.

Our interest in  $q$  values for particular rotational levels was caused by an investigation of electric dipole moment performed on the NaK  $D^1\Pi$  state. The usefulness of rf (or  $\mu\omega$ ) spectroscopy in order

to determine  $\Lambda$ -doubling splitting for short-lived electronic states has been demonstrated in [5] for the ( $A^1\Pi$ ) CS molecule. In [6] Stark-effect-induced changes in laser-induced fluorescence (LIF) spectra from NaK  $D^1\Pi$  have been recorded, and the optical–rf double resonance signal on the  $v' = 7$ ,  $J' = 5$  level has been demonstrated, but only qualitative information without mentioning any  $q$  values is presented.

### 2. Method

Fig. 1 explains the methods used in this work. Due to the combination of  $\Delta J = 0, \pm 1$  and  $+ \leftrightarrow -$  selection rules, only  $P, R$  doublet emission is allowed at  $P$ - or  $R$ -type excitation of the  $^1\Sigma \rightarrow ^1\Pi$  transition, whereas only  $Q$  singlet emission is allowed at  $Q$ -type excitation. If, however, an external electric rf or dc field is applied, the  $+ \leftrightarrow -$  or  $elf$  Stark effect mixing

\* Corresponding author.

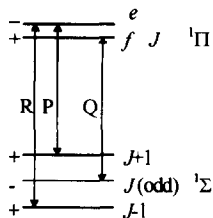


Fig. 1. Selection rules for  ${}^1\Sigma - {}^1\Pi$  transition.

in a  ${}^1\Pi$  state with fixed  $J$  gives rise to the appearance of forbidden lines. Therefore, one can observe in the LIF progression  ${}^1\Pi \rightarrow {}^1\Sigma$  the whole  $(P, Q, R)$  triplet, instead of either doublets or singlets (see Fig. 2). Two types of experiment can be performed in such a system:

1. recording the 'forbidden' line intensity as a function of rf field frequency gives an optical–rf double resonance signal, from which  $\Lambda$ -splitting  $\Delta'_{ef}$  or the  $q$  value for particular  $J$  can be deduced.
2. measuring the intensity ratio between 'forbidden' and 'parent' lines as a function of static electric field gives the ratio of  $\Lambda$ -splitting to electric dipole moment  $d_p$ :  $\Delta'_{ef} / d_p$  or  $q/d_p$

### 3. Experimental

The experimental set-up is shown in Fig. 3(a).  ${}^{23}\text{Na}{}^{39}\text{K}$  molecules were formed thermally in a glass cell joined to the vacuum system by means of a dry valve. The cylindrical head (Fig. 3(b)) of the cell was

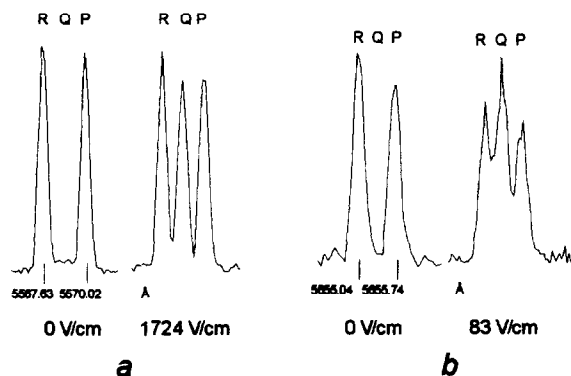


Fig. 2. Effect of static electric field on spectrally resolved LIF for the NaK  $D^1\Pi \rightarrow X^1\Sigma^+$  system: (a) transition from  $v' = 7$ ,  $J' = 23$ ; (b) transition from  $v' = 12$ ,  $J' = 7$ .

made from special alkali-resistant glass tube. The electric field was produced by applying rf or static voltage across a pair of round polished stainless steel Stark plates. A separation of  $0.85 \pm 0.05$  mm between the Stark plates was used for the resonance measurements. For dc Stark mixing altogether three cells were used, differing in diameter and spacing of the electrodes. The metal-containing reservoir was kept at a stabilized temperature between  $270^\circ\text{C}$  and  $320^\circ\text{C}$ .

Linearly polarized light from a cw Ar<sup>+</sup> laser was used to excite  $X^1\Sigma^+ \rightarrow D^1\Pi$  transitions in  ${}^{23}\text{Na}{}^{39}\text{K}$  molecules. Fluorescence at right angles, both to the laser beam and to the electric field  $\epsilon$ , was imaged onto the entrance slit of a double monochromator (M) and registered in a photon counting regime. The particular  $D^1\Pi \rightarrow X^1\Sigma^+$  LIF progressions were identified from the recorded LIF spectrum by comparison of line positions and relative intensities with the ones calculated by means of a spectroscopic constant set as given in [1], for the transitions mentioned there at excitation by Ar<sup>+</sup> laser lines.

In the optical–electric rf double resonance experiments we used a 1–300 MHz (0.2 W, 50  $\Omega$ ) Wavetek rf oscillator (RF) supply, which was connected to the Stark plates (E). The rf field voltage enabled us to produce  $\epsilon_{rf}^0 \leq 20$  V cm<sup>-1</sup>. A fast oscilloscope (OSC), placed closely across the plates, served as 50  $\Omega$  load and as rf output drift monitor. An auxiliary generator output producing a dc voltage proportional to the generated frequency was used to measure the voltage by means of a digital voltmeter. A computer (PC) together with the CAMAC system controlled the driving and data collection of the experiment. In the dc Stark mixing experiments a dc voltage source was connected to the same Stark plates instead of the rf source. Polarizers (P) and the polarization plane rotator (R) fixed the polarization conditions for excitation–registration.

### 4. Signals and results

#### 4.1. Optical–rf double resonance signals

These were obtained by measuring the intensity of 'forbidden' lines as a function of the electric field frequency. Multiple frequency sweeping in a chosen

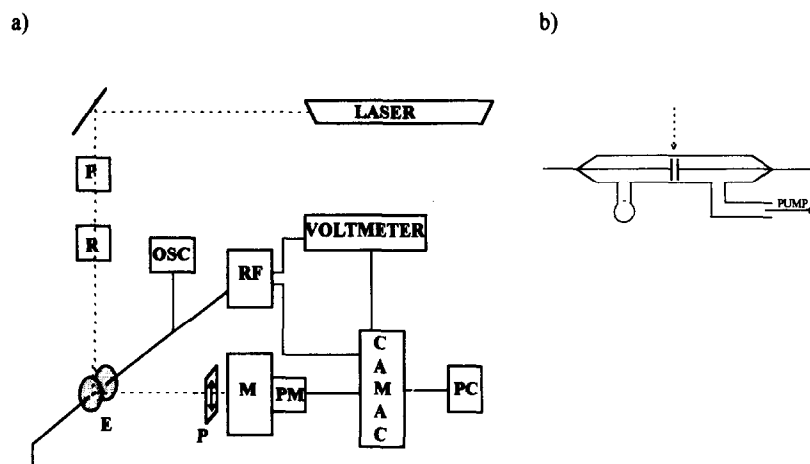


Fig. 3. (a) Experimental set-up: P = polarizers, R = polarization plane rotator, E = Stark plates, OSC = oscilloscope, RF = radiofrequency generator, M = spectrometer, PM = photomultiplier, PC = computer; (b) thermal cell.

range and signal accumulation were used. The accumulation time varied from 10 min to 1 h. In order to diminish the influence of LIF intensity drift during signal accumulation the normalized difference  $(I_F - I_{F_0})/I_{F_0}$  was considered to be a result of a single measurement, that is the difference between intensity at current frequency  $F$  and at some reference frequency  $F_0$ .

Fig. 4 presents experimental resonance signals for levels  $\nu' = 12, J' = 7$  and  $\nu' = 7, J' = 23$ . Although the

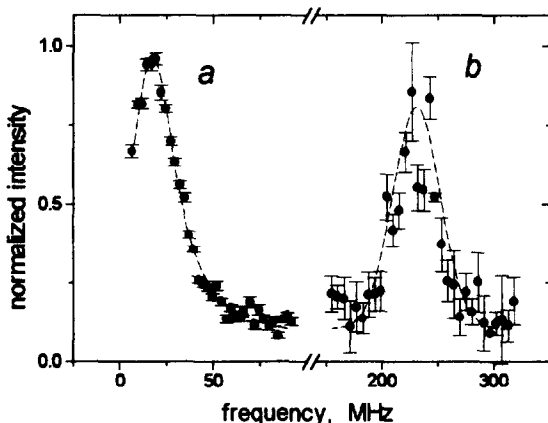


Fig. 4. Optical-rf double resonance signals: (a) –  $\nu' = 12, J' = 7$ ; (b) –  $\nu' = 7, J' = 23$ .

resonance signal width exceeded the one expected from the natural broadening, probably with a tendency to exhibit some structure, we assumed that the signal was reliable enough to determine the  $elf$  separation, yielding  $q$ . Resonance signals were registered for five  $\nu', J'$  levels; corresponding  $q$  values are given in Table 1.

#### 4.2. Intensity ratios

Fig. 2 demonstrates the effect of a static electric field on the spectrally resolved LIF from  $\nu' = 7, J' = 23$  and  $\nu' = 12, J' = 7$ , leading to the appearance of the forbidden  $Q$  line due to  $elf$  mixing. A fitting procedure using three Gaussians was used to obtain the 'forbidden'/'parent' line ratio  $I_Q/I_{P,R}$  dependences on electric field intensity.

Ratio signal simulation and data fitting were accomplished using direct Hamiltonian diagonalization, accounting for Stark interaction within rotational states  $J \pm \Delta J, \Delta J = 0, 1$  and 2 in initial, excited and final states [7]. Least-square data processing of the intensity ratios, obtained in different cells and geometries, allowed us to get  $q/d_p$  ratios. The averaged values are  $(2.4 \pm 0.25) \times 10^{-6} \text{ cm}^{-1} \text{ D}^{-1}$  for  $\nu' = 7, J' = 23$  and  $(2.1 \pm 0.2) \times 10^{-6} \text{ cm}^{-1} \text{ D}^{-1}$  for  $\nu' = 12, J' = 7$ . Taken together with  $q$  values obtained from

Table 1

Experimental values of NaK ( $D^1\Pi, v', J'$ )  $\Lambda$ -doubling constant  $q$  determined from RF-optical double resonance

$v'$	3	4	7	12	14
$J'$	23	19	23	7	19
$q$ ( $10^{-5} \text{ cm}^{-1}$ )	$1.39 \pm 0.06$	$1.32 \pm 0.06$	$1.42 \pm 0.07$	$1.03 \pm 0.08$	$1.33 \pm 0.05$

double resonance signals, the dipole moment values have been determined:  $d_p(v' = 7, J' = 23) = 5.9 \pm 0.9 \text{ D}$ ;  $d_p(v' = 12, J' = 7) = 4.8 \pm 0.9 \text{ D}$ .

## 5. Discussion

The  $q$  values presented in Table 1 lie between those obtained from conventional spectroscopic analysis [1],  $q_v = q_0 - q_1(v + 1/2) = 1.16 \times 10^{-5} - 1.5 \times 10^{-7}(v + 1/2) \text{ cm}^{-1}$ , and from the rf-optical double resonance signal [6] for NaK ( $D^1\Pi v' = 7, J' = 5$ ), yielding  $q = 1.5 \times 10^{-5} \text{ cm}^{-1}$ . Thus the  $q$ -factor values obtained do not disagree much with the previous data. Regarding the smaller  $q$  value for the  $v' = 12, J' = 7$  level, it corresponds to what can be expected due to the  $D^1\Pi-d^3\Pi$  perturbation. Although the singlet-triplet interaction does not change  $\Delta_{ef}^J$  directly since the  $e$  and  $f$  components of the  $D^1\Pi$  state are perturbed by the two  $\Lambda$ -doublet substates of the  $d^3\Pi$  state to about the same amount, this interaction diminishes the singlet character of the perturbed state to  $C_{1n}^2$ . The  $D^1\Pi-d^3\Pi$  mixing coefficient  $C_{1n}^2 = 1 - C_{3n}^2$  can be estimated using the calculated difference between the deperturbed  $D^1\Pi$  ( $v' = 12$ ) and  $d^3\Pi$  ( $v' = 13$ ) terms [3], with  $J' = 7$  being  $E_{1n} - E_{3n} = -3.87 \text{ cm}^{-1}$  and the level  $v' = 12, J' = 7$  shift  $\Delta E = 0.468 \text{ cm}^{-1}$  with respect to the deperturbed position. The estimated value of  $C_{1n}^2$  equals 0.87, thus giving a reduction of the  $q$  value since  $\Lambda$ -doubling in the  $D^1\Pi$  state has to be  $C_{1n} \langle D^1\Pi | L^\pm | 1\Sigma \rangle$ . As for the absolute dipole moment  $d_p$  values obtained here, they can be considered as very large when compared to typical

dipole moment values which have been measured for diatomic molecules, but they are consistent with theoretical predictions [8].

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