Stark level crossing and optical–rf double resonance in NaK $D^1\Pi$

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ABSTRACT

We report here Λ-doubling splitting and permanent electric dipole moment d_p measurements for a number of vibrotational levels of NaK D $^1\Pi$ state. Two different methods, which are not Doppler limited, were used. Stark effect induced level crossing was registered as fluorescence polarization changes with external electric field, which allowed to obtain, from one fit, the values of electric dipole moment and Λ-doubling splitting Δ_{ef} between e, f substates of an individual rotational state. Another method consisted in obtaining the ratio Δ_{ef}/d_p from electric field dependence of the intensity of forbidden line appeared in fluorescence as a result of e-f Stark mixing, along with direct Δ_{ef} measurements by optical-rf double resonance. Signal simulations and data fitting were accomplished using direct Hamiltonian diagonalization accounting for Stark interaction within rotational states $J \pm \Delta J$, $\Delta J = 0, 1, 2$ in initial, excited and final state. Dipole moment values obtained confirm theoretical predictions.

1. INTRODUCTION

There is interest in determination of permanent electric dipole moment d_p of a molecule since this quantity reflects very sensitively the details of electronic structure. At the same time there is still a lack of information about electric dipole moments for short-living excited states of diatomic molecules including alkali dimers. We present first d_p measurements for $^{23}Na^{39}K$ $D\ ^1\Pi$ state rovibronic levels by two different methods[1]. (i) Measurements of external electric field ε-dependence of the relative intensity of a forbidden line, which appears in fluorescence as a result of e–f Stark mixing[2]. Indeed, due to the combination of $\Delta J = 0, \pm 1$ and $+ \leftrightarrow -$ selection rules, only the (P, R)-doublet emission is allowed at P- or R-type excitation, whereas only Q-singlet emission is allowed at Q-type excitation, see Fig. 1. If, however, external electric field is applied, the $+ \leftrightarrow -$, or e/f Stark effect mixing in a $^1\Pi$ state with fixed J gives rise to the appearance of a "forbidden" line. The intensity ratio $I_Q/I_{P,R}$ or *vice versa* of a "forbidden" line to the "parent" one is mainly governed by the $|(d_p\varepsilon)/\Delta_{ef}|$ parameter, allowing to obtain the absolute value $|d_p/q|$, where Λ–doubling splitting $\Delta^J_{ef} = q[J(J+1)-1]$. The q value was measured by us independently by optical–radio frequency (RF) double resonance method. (ii) Stark analogue of Hanle effect, or Stark effect induced level crossing, has been registered via changes of fluorescence linear polarization degree $P(\varepsilon)$ with external electric field ε and allowed to obtain, from one fit, both d_p value as well as Λ-doubling splitting between e,f substates of an individual rotational state J, see Fig. 1.

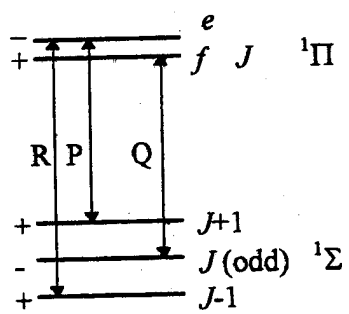

Fig.1. Selection rules for $^1\Sigma - ^1\Pi$ transition

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2. THEORETICAL APPROACH

The general theoretical approach is based on density matrix formalism, allowing to calculate the $^1\Pi$–$^1\Sigma$ fluorescence intensity in the presence of external electric field for any geometry and polarization type, using both analytical expressions in different order perturbation theory, as well as the direct numerical diagonalization of the Hamiltonian matrix, accounting for the interaction within the set $J \pm \Delta J$ of rotational states, both in the excited $^1\Pi$ state and in the ground $^1\Sigma$ state.

3. EXPERIMENTAL

$^{23}Na^{39}K$ molecules were formed thermally in a glass cell joined to the vacuum system by means of a dry valve. The cylindrical head of the cell was made from a special alkali-resistant glass tube. Electric field was produced by applying a static voltage across a pair of round polished stainless steel parallel Stark plates located inside the cell. Altogether three cells were used, differing in diameter (d) and spacing (l) of the electrodes, namely: (1) d=25 mm, l=2.9 ± 0.1mm; (2) d=7 mm, l=1.8 ± 0.1 mm; (3) d=7 mm, l=1.2 ± 0.1 mm. The cells have been filled with metallic potassium and sodium in a weight ratio of approximately 7:3, respectively. The metal-containing reservoir was kept at stabilized temperatures between 270° C and 320° C.

The linearly polarized light from cw Ar^+-laser was used to excite $X\,^1\Sigma^+ \rightarrow D\,^1\Pi$ transitions in ^{23}Na ^{39}K molecules. Laser induced fluorescence (LIF) at right angles, both to the laser beam and to the electric field ε, see Fig. 2, originating from the ca. 0.5 - 1.2 mm diameter laser beam excitation region, has been imaged onto the entrance slit of a double monochromator providing an overall spectral resolution up to 0.3 Å. We restricted the observation zone to the size of ca. 1.5 mm in height, thus diminishing the possible influence of electric field inhomogenity.

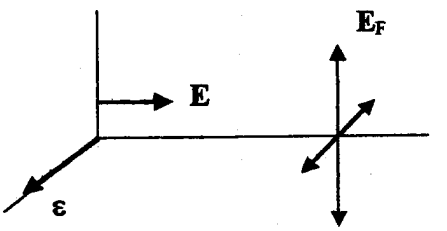

Fig.2. Geometry of the experiment

The particular $D\,^1\Pi \rightarrow X\,^1\Sigma^+$ LIF progressions, originating from the definite $D\,^1\Pi$ v', J' states, were identified from the recorded LIF spectrum by comparison of line positions and relative intensities with the ones calculated by means of spectroscopic constants set[3], for the transitions mentioned[3] at excitation with Ar^+-laser lines. The degree of linear polarization was measured by dividing the entrance slit of the monochromator in height in two parts, placing two orthogonal polarizers in front of them. Light guides conducted fluorescence light from the two respective parts of the exit slit to the two photomultipliers, with subsequent counting of one-photon pulses from the two channels. The unpolarized LIF, at absence of external electric field, excited by the laser light with $\hat{\mathbf{E}}$-vector set parallel to the observation direction, was used to calibrate the channels before each experiment.

In the case of optical – electric RF double resonance experiments, we used 1 ÷ 300 MHz (0.2 W, 50 Ω) Wavetek RF oscillator supply, which was connected to the same Stark plates instead of static electric field source. Fast oscilloscope, which was placed closely across the plates, served as 50 Ω load and as RF output drift monitor. The resonance was measured by sweeping the frequency of the RF generator.

4. MEASUREMENTS AND RESULTS

Intensity ratios. Fig.3 demonstrates the effect of static electric field on the spectrally resolved LIF from v'=7, J'=23 and v'=12, J'=7 levels leading to the appearance of forbidden Q line due to e–f mixing. Fitting procedure by means of three Gaussians was used to obtain "forbidden"/"parent" line ratio $I_Q/I_{P,R}$. The intensity ratios $I_Q/I_{P,R}$ obtained in different cells and experiment geometry, are shown as settings-in in Figs. 4 and 5. Least-square data processing allowed to get q/d_p ratios. The averaged values are $(2.40\pm0.25)\times10^{-6}$ cm^{-1}/D for v' = 7, J'=23 and $(2.10\pm0.20)\times10^{-6}$ cm^{-1}/D for v'=12, J'=7 state.

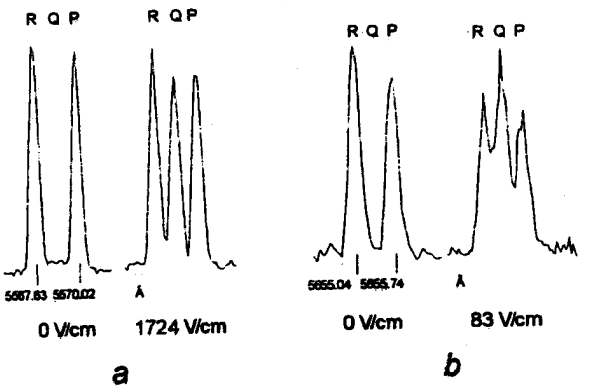

Fig. 3. Effect of electric field on spectrally resolved LIF for NaK $D\,^1\Pi \rightarrow X\,^1\Sigma^+$ system. (a) - transition from v'=7, J'=23; (b) - from v'=12, J'=7

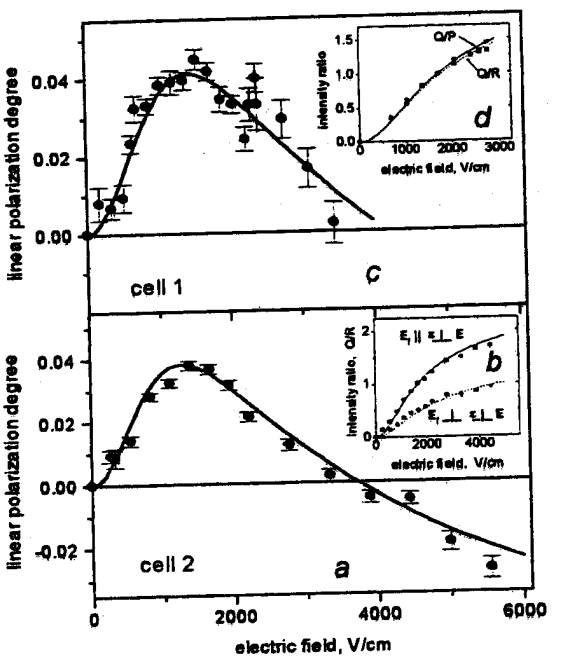

Fig. 4. Linear polarization degree and intensity ratios measured in LIF from $D\,^1\Pi$ state with v' = 7, J'=23. (a),(c)–electric field dependence of the polarization degree obtained on $R(22)$ component; (b), (d)–electric field dependence of intensity ratios I_Q/I_P or I_Q/I_R.

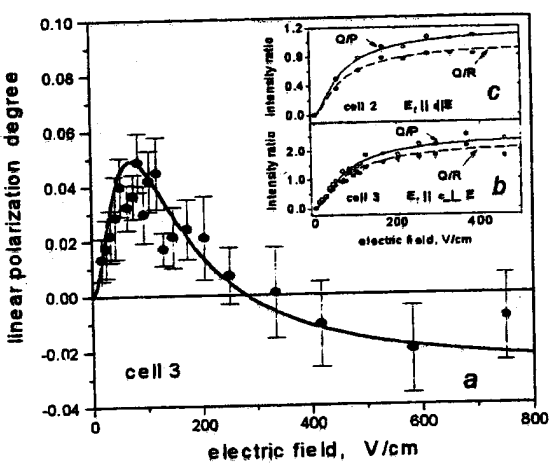

Fig.5. Linear polarization degree and intensity ratios measured in LIF from $D^1\Pi$ state with v'=12, J'=7. (a) - electric field dependence of the polarization degree obtained on $P(8)$ component; (b), (c) - electric field dependence on intensity ratios I_Q/I_P or I_Q/I_R.

Optical-electric RF double resonance. Fig. 6 (dots) presents experimental data obtained by registering the intensity of a "forbidden" Q-line as dependent on the RF electric field frequency, demonstrating resonance intensity increase for $v'=7$, $J'=23$ and $v'=12$, $J'=7$ levels. The signal accumulation time varied from 10 minutes to 1 hour. Optical-RF double resonance signals were obtained for a number of v', J' levels, see Table 1. Although the resonance signal width exceeded the one expected from the natural broadening, probably with a tendency to exhibit some structure, we assumed that the signals are reliable enough to determine the e/f separation Δ^J_{ef}, yielding q. This makes it possible to determine the permanent electric dipole moment d_p in question, using q/d_p values obtained from intensities ratios, see Table 1.

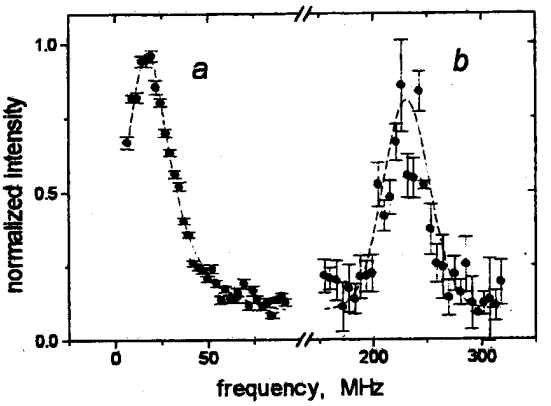

Fig.6. Optical-rf double resonance signals.
(a) - $v'=12$, $J'=7$, (b) - $v'=7$, $J'=23$.

Table 1.

q-factors and dipole moments
(superscript P means, that values are obtained from polarization measurements)

v(J)	q, 10^{-5} cm^{-1}	d_p, Debye	d_p^{th}, Debye
3(23)	1.39±0.06	—	—
4(19)	1.32±0.06	—	—
7(23)	1.42±0.07 1.65±0.20^P	5.9±0.9 6.4±0.8^P	7.1
12(7)	1.03±0.08 1.10±0.20^P	4.8±0.9 4.5±0.8^P	6.5
14(19)	1.33±0.05	—	—

Polarization measurements. Experimentally measured for $v'=7$, $J'=23$ and $v'=12$, $J'=7$ levels electric field dependencies of the polarization degree are presented in Figs. 4 and 5. The results are obtained using the most favorable geometry when LIF is viewed from the "end" of exciting light vector $\hat{\mathbf{E}}$ ($\hat{\mathbf{E}} \perp \varepsilon$). The processing of experimental data was realized using theoretical dependencies $P(\varepsilon)$ calculated by accounting for Stark interaction among five rotational states J, $J \pm 1$, $J \pm 2$ by Hamiltonian matrices diagonalization for all J'', J' and J'', involved in the transition. The best fitting constants q and d_p, obtained from a two-parameter weighted least-square routine, yield the values in question, Table 1.

5. DISCUSSION

The dipole moments determined seem to be reliable, in particular since there is good agreement between the results gained from two independent methods. As for the absolute d_p values, they can be considered as very large when compared to typical dipole moment values which had been measured for diatomic molecules. Let us compare the measured d_p values with theoretical quantities[4]. In order to pass from *ab initio* $d_p^{th}(R)$ dependence[4] to the predicted d_p values for particular v', J' states, we have used the averaging routine yielding the following predicted $d_p^{th}(v', J')$ values for the states under study: $d_p^{th}(7, 23) = 7.1$ D and $d_p^{th}(12, 7) = 6.5$ D. see Table 1.

As follows from Table 1, the measured d_p value for the v'=12, J'=7 state is smaller than for the v'=7, J'=23, being also markedly smaller than the theoretically predicted value. As it is well known [3,5], levels belonging to the NaK $D\ ^1\Pi$ state are perturbed, at least to some extent, by the close lying $d\ ^3\Pi$ state. The level v'=7, J'=23 can be considered as almost unperturbed[3], whereas the level v'=12, J'=7 is shifted to ΔE = 0.468 cm^{-1} with respect to the deperturbed position. As a result, the experimentally measured d_p value for the level v'=12, J'=7 is expected to be ca. 15% smaller than could been suspected for unperturbed state. It is thus not excluded that the difference between d_p values obtained for the two states, see Table 1, reflects the role of perturbations. Hence, the experimentally measured d_p values do not disprove the *ab initio* calculation[4], accounting for the fact that the deperturbed quantities have been calculated.

The q values presented in Table I lies between ones obtained from conventional spectroscopic analysis[3] as q_0= 1.16×10^{-5} cm^{-1} and from the RF – optical double resonance signal[6] for NaK ($D\ ^1\Pi$ v'=7, J'=5), yielding q=1.5 $\times10^{-5}$ cm^{-1}. Thus, the q-factor values obtained do not disagree much with the previous data. Regarding Λ-doubling factor q, smaller value for v'=12, J'=7 level, it corresponds to what can be expected due to the perturbation, allowing to estimate ca. 13% diminution from the following considerations. Although the singlet-triplet $D\ ^1\Pi$ - $d\ ^3\Pi$ interaction does not change Λ-doubling splitting directly since e and f components of the $D\ ^1\Pi$ state are perturbed by the two Λ-doublet substates of the $d\ ^3\Pi$ state to about the same amount, this singlet-triplet interaction diminishes a singlet character of the perturbed state as $C^2_{^1\Pi}$. Hence, the matrix element of electronic–rotational interaction with the remote singlet Σ states has to be $C_{^1\Pi}\left\langle D\ ^1\Pi\middle|L^{\pm}\middle|^1\Sigma\right\rangle$, giving rise to diminution of Λ-doubling in $D\ ^1\Pi$ state.

In conclusion, the measurements constituted in the present work confirmed the existence of large permanent electric dipole moment in NaK $D\ ^1\Pi$ state.

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7. REFERENCES

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