

# Electric field induced alignment-orientation conversion in diatomic molecules: analysis and observation for NaK

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## Abstract

This article reports the observation of the molecular fluorescence circularity under irradiation with linearly polarised light. This alignment-orientation conversion phenomenon arises as a result of partial transformation from alignment of the ensemble of  $^1\Pi$  state molecular angular momenta into their orientation under the effect of non-linear dc Stark effect. Circularity rate up to 0.12 was observed in  $D^1\Pi \rightarrow X^1\Sigma$  fluorescence of  $^{23}\text{Na}^{39}\text{K}$  molecules in agreement with the theoretically predicted value. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

As is well known, excitation by linearly polarised light  $\mathbf{E}$ , caused by symmetry considerations, is capable to create alignment of the angular momenta which results in linear polarisation of observed fluorescence, and is not capable to create orientation which would result in circular polarisation of fluorescence. For a considerable time there has been major interest in analysing the conditions under which these strict symmetry rules may be broken, thus leading to alignment-orientation conversion (AOC) see [1] and references therein. The required conditions may be caused by an external perturbation, in particular, external field, producing such magnetic sublevels splitting  ${}_J\omega_{MM'} = (W_M - W_{M'})/\hbar$  which satisfies  ${}_J\omega_{MM\pm 1} \neq {}_J\omega_{-M\mp 1-M}$  [1]. This condition is obeyed when non-linear dependence of the energy shift  $W_M$  on external magnetic or electric field strength takes place. The

appearance of magnetic field induced AOC in diatomic molecules was observed earlier [2], while Stark effect induced AOC was considered only theoretically [1,3].

In present article the electric field  $\mathbf{F}$  induced AOC has been observed in  $D^1\Pi$  state of NaK molecule, where the non-linear Stark energies lead to the condition for  $\omega_{MM'}$  mentioned above already in the first approximation. The AOC signals have been registered in  $D^1\Pi \rightarrow X^1\Sigma$  transition ( $R$ - and  $P$ -emission) from  $\nu'(J') = 7(23)$  and  $12(7)$  rovibronic levels as emergence of the degree of circularity

$$C = (I_r - I_l)/(I_r + I_l), \quad (1)$$

using the appropriate geometry of linearly polarised excitation, observation and electric field  $\mathbf{F}$  direction,  $I_{r,l}$  being right- and left-handed circularly polarised fluorescence intensities. The presented calculation of the expected AOC signals has been based on the  $^1\Pi$  state Stark effect studies performed earlier in Refs. [4,6].

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## 2. Theoretical description

The main peculiarity of  $^1\Pi$  state consists in the fact that each rotational energy level  $J$  is splitted in two different parity components usually denoted as  $e$  and  $f$ . This effect is called  $\Lambda$ -splitting leading to the energy splitting  $\Delta_{ef}^J = qJ(J+1)$ ,  $q$  being  $\Lambda$ -doubling constant. Let us consider the interaction of diatomic molecules with cw broad band (with respect to  $\Delta_{ef}^J$ ) laser light causing  $^1\Pi(v', J') \leftarrow ^1\Sigma(v'', J'')$  transition which creates the excited state density matrix  ${}^{kl}f_{MM'}$ , where  $k$  and  $l$  denote either  $e$  or  $f$ . In the density matrix formalism the intensity of the fluorescence light possessing polarisation vector  $\hat{\mathbf{E}}_f$  and originating from the  $^1\Pi$  state in the  $J' \rightarrow J''_1$  transition can be expressed as [3]:

$$I(\hat{\mathbf{E}}_f) = I_0 \sum_{MM'\mu} \sum_{kl} \langle M^1 \Pi k | \hat{\mathbf{E}}_f^* \hat{\mathbf{D}} | \mu^1 \Sigma \rangle \times \langle M'^1 \Pi l | \hat{\mathbf{E}}_f^* \hat{\mathbf{D}} | \mu^1 \Sigma \rangle^* {}^{kl}f_{M'M}, \quad (2)$$

where  $I_0$  is proportionality coefficient and  $\hat{\mathbf{D}}$  is the transition dipole moment unit vector. The excited state density matrix elements  ${}^{kl}f_{MM'}$  may be written as [3]

$${}^{kl}f_{MM'} = \frac{\tilde{\Gamma}_p}{\Gamma + i^{kl}\omega_{MM'}} \sum_{\mu} \langle M^1 \Pi k | \hat{\mathbf{E}}_f^* \hat{\mathbf{D}} | \mu^1 \Sigma \rangle \times \langle M'^1 \Pi l | \hat{\mathbf{E}}_f^* \hat{\mathbf{D}} | \mu^1 \Sigma \rangle^*. \quad (3)$$

Here  $\mu$  are magnetic sublevels of the ground  $^1\Sigma$  state with rotational quantum number  $J''$  while  $M, M'$  are magnetic sublevels of the excited state with rotational quantum number  $J'$  belonging to the  $\Lambda$ -doublet components  $k, l$ . The unit vector  $\hat{\mathbf{E}}$  describes exciting light polarisation,  $\tilde{\Gamma}_p$  is the reduced absorption rate,  $\Gamma$  is the excited state effective relaxation rate,  ${}^{kl}\omega_{MM'}$  is the energy splitting between,  $M, M'$  sublevels belonging either to the same ( $l = k$ ) or to the different ( $l \neq k$ )  $\Lambda$ -doublet components, thus accounting both for  $\Lambda$ -doubling and Stark effect level shifts. In such formalism density matrix diagonal elements reflect population of the respective magnetic sublevels, while the nondiagonal matrix elements reflect coherences between the respective substate

wavefunctions (WF). The structure of Eq. (2) allows one to notice that the terms entering the sums are formed as the excited state density matrix elements  ${}^{kl}f_{MM'}$  multiplied by the observation density matrix elements.

Note, that the WF's in Eqs. (2) and (3) are not the usual  $|JM\rangle$  WF's owing to the fact that, though electric field destroys the spherical symmetry, it does not change the axial symmetry, therefore  $\mathbf{J}$  is not a good quantum number any more, while  $M$  is still conserved. The WF's included in Eqs. (2) and (3) are obtained in a coupled-basis set as an expansion over the non-perturbed states with different  $J'_i (i = e, f)$  values, as well as different  $J''$  values, which are mixed by the static external electric field  $\mathbf{F}$ . For  $^1\Pi$  excited state we have

$$|M^1 \Pi k\rangle = \sum_{J'=1}^{\infty} \sum_{i=e,f} C_{\Pi i}^k(J', M) |J' M\rangle, \quad (4)$$

thus obtaining, as it is usually done, a new WF for each  $k = 1$  and 2 constructed as the linear combination of  $e$  and  $f$  substates with the mixing coefficients  $C_{\Pi e, f}^k(J', M)$ . Similarly, for the ground  $^1\Sigma$  state the  $J''$  mixing can be taken into account using

$$|\mu^1 \Sigma\rangle = \sum_{J''=0}^{\infty} C_{\Sigma}(J'', \mu) |J'' \mu\rangle. \quad (5)$$

Coefficients  $C_{\Pi i}$  and  $C_{\Sigma}$  have to be calculated from the diagonalisation of the Hamiltonian accounting both for molecular rotation and Stark effect.

The explicit form of the dipole transition matrix elements with  $|JM\rangle$  WF's can be found [1,3] by applying the definition of scalar multiplication in cyclic coordinates along with the Wigner–Eckart theorem and expressing cyclic components of vector  $\hat{\mathbf{E}}$  via spherical angles  $\theta$  and  $\varphi$  ( $z$  axis coincide with the direction of external field). After performing these transformations one must use Eqs. (4) and (5) to pass to the WF's entering Eqs. (2) and (3). As a result, one arrives at the expressions for the intensities  $I_r, I_l$  and for the difference  $I_r - I_l$  which is responsible for appearance of circularity:

$$I_r - I_l = \frac{\sin 2\theta}{2} K(J', J'', J''_1, \varphi, {}^{kl}\omega_{MM'}). \quad (6)$$

Here the function  $K(J', J'', J''_1, \varphi, {}^{kl}\omega_{MM'})$ , which is

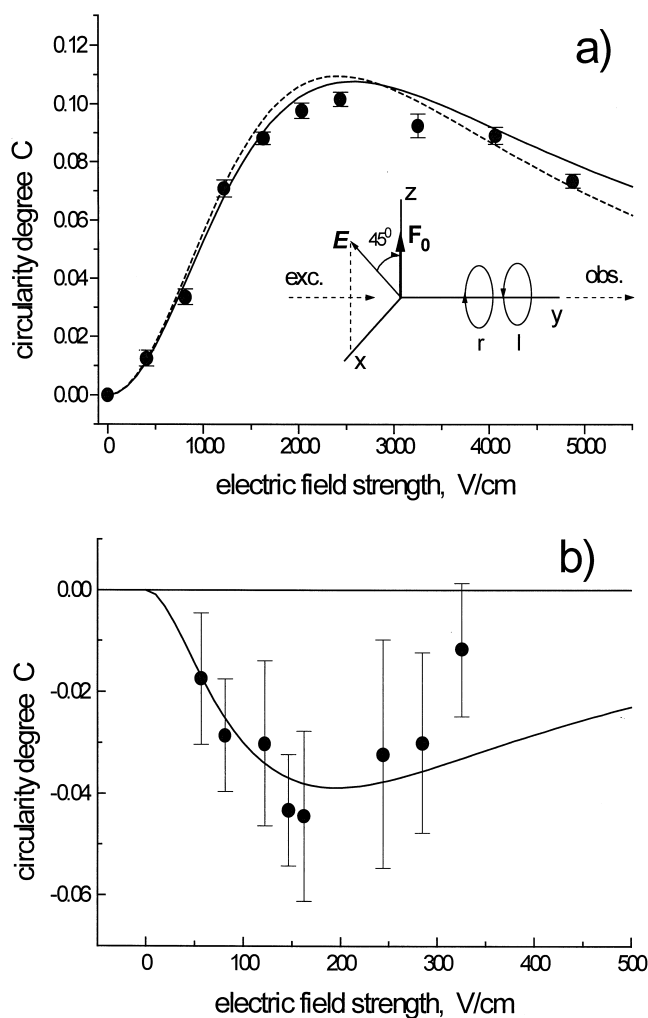


Fig. 1. Experimentally obtained (full circles) and calculated fluorescence circularity degree  $C$  as dependent on electric field strength  $F$ . (a) — for  $\nu'(J') = 7(23)$ , (b) — for  $\nu'(J') = 12(7)$ . Dashed line represents the first order  $^{(1)}W_M^{el}$  approximation.

independent of  $\theta$ , appears as a result of summation over all indices in Eqs. (2)–(5) and represents a rather cumbersome expression. As it immediately follows from Eq. (6), the maximal circularity degree appears at  $\theta = 45^\circ$ , while for  $\theta = 0^\circ$  and  $\theta = 90^\circ$  the circularity degree is zero. The expression for  $I_r + I_l$  necessary to calculate  $C$  can also be found from Eqs. (2)–(5). Note that  $K(J', J'', J''_1, \varphi, \omega_{MM'})$  is determined for a particular transition  $J'' \rightarrow J' \rightarrow J''_1$  and definite spherical angle  $\varphi$  of linear polarised excitation if the Stark energy pattern  $W_M^{el}$  is known. In the first approximation  $^{(1)}W_M^{el}$  may be obtained in a simple

analytical form:

$$^{(1)}W_M^{el} = \frac{1}{2} \Delta_{ef}^J \pm \sqrt{(\Delta_{ef}^J)^2 / 4 + d_p^2 F^2 M^2 / [J'(J' + 1)]^2}, \quad (7)$$

where the energy of  $^1\Pi \nu'(J')$  state  $f$  sublevel is considered to be zero at  $F = 0$ .

It is easy to see that, as  $F$  increases leading to  $d_p F M / [J'(J' + 1)] \gg \Delta_{ef}^J / 2$ , the Stark energy shifts exhibit linear asymptotic behaviour with respect to  $F$ . To account for the interaction between  $J'$  and

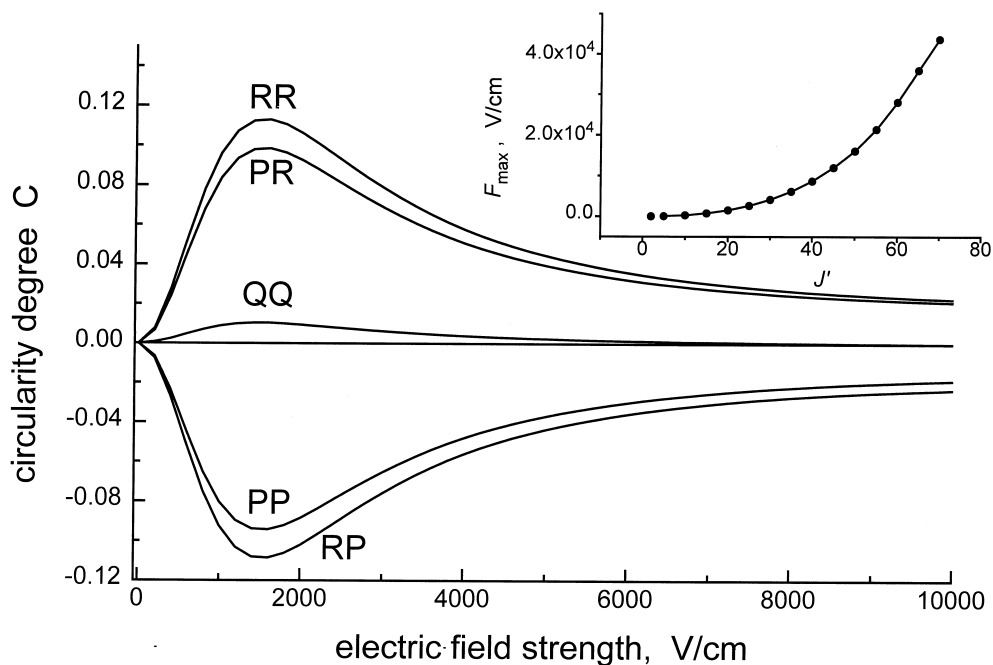


Fig. 2. Circularity degree dependence on electric field strength for all allowed fluorescence transitions,  $J' = 20$ ,  $d = 6.4 \text{ D}$ ,  $q = 1.51 \times 10^{-5} \text{ cm}^{-1}$ ,  $\Gamma = 6 \times 10^7 \text{ s}^{-1}$ . Inset of the picture shows  $J'$ -dependence of electric field strength in maximum.

$J' \pm 1$  excited state levels it is necessary to pass to the second order approximation  ${}^{(2)}W_M^{el}$ . when analytical expression is still possible [5]. However, strictly speaking, for large enough  $F$  values the second-order perturbation treatment becomes incorrect as well, and one has to solve the secular equation system for the relevant Hamiltonian matrix. The manifestation of second and higher order corrections in Stark effect induced fluorescence intensity changes was studied previously [6].

As a result of the above mentioned routine, it becomes possible to calculate  ${}^1\Pi$  state fluorescence circularity degree under linearly polarised excitation caused by external dc electric field. The simulation of expected  $C(F)$  dependencies will be presented in Section 4.

### 3. Experimental

The experimental set-up has been described in more detail in Ref. [6], hence we will dwell on it only briefly.  ${}^{23}\text{Na}{}^{39}\text{K}$  molecules have been formed in

thermal cells made from alkali-resistant glass and attached to a vacuum system via a dry valve. Characteristic working temperatures of the metal containing reservoir (weight ratio Na : K  $\approx$  1:3) were  $T \approx 525 \div 575 \text{ K}$ . A number of visible blue-green Spectra-Physics 171  $\text{Ar}^+$ -laser lines have been used to excite  $D {}^1\Pi \nu(J) \leftarrow X {}^1\Sigma^+ \nu''(J'')$  transitions. Visible LIF lines originating from the ca. 1 mm diameter laser excitation region was imaged onto the entrance slit of a double-monochromator and resolved by two 1200 lines/mm gratings blazed in the first order, providing an overall spectral resolution of ca. 0.03 nm. The dc electric field was applied to the carefully polished stainless steel Stark plates, ca. 0.8 cm in diameter, separated by a 1.2 mm gap. The excitation-observation geometry is schematically depicted in Fig. 1. A polariser and polarisation plane rotator were used to realise the  $\theta = (\widehat{EF}) = \pm 45^\circ$  excitation geometry. The LIF was observed along the exciting laser beam. The  $I_r$  and  $I_l$  circularly polarised components were singled out by means of  $\lambda/4$  plate followed by a linear polariser with its axis either parallel or perpendicular to  $\mathbf{F}$ . The  $D {}^1\Pi \nu'(J')$

state selection has been maintained by finding in the overall LIF spectrum the particular LIF progressions mentioned in Ref. [7] and originating from the chosen  $\nu'(J')$  level under study. The signal from a photomultiplier was registered using the photon counting technique. The experimentally obtained circularity degree was multiplied by a factor 1.25 which takes into account depolarisation in registration system and was determined by careful calibration of the registration channels with two orthogonal polarisers using the source of light with well-known degree of circularity.

#### 4. Results and discussion

Fig. 2 presents the circularity degree for NaK  $D^1\Pi$   $J' = 20$  state calculated for all allowed  $J', J'', J''_1$  combinations in different transition types. The  $q$  and  $d$  values were taken from Ref. [8]. An inset in Fig. 2 demonstrates the  $J$ -dependence of the electric field strength  $F_{\max}$  corresponding to maximal circularity degree. To illustrate the non-negligible contribution of higher than the first order terms in Stark energy expansion, the circularity for  $J' = 23$  was calculated both in first order energy approximation (dashed line in Fig. 1a) and accounting up to third order terms in Stark energy expansion (solid line in Fig. 1a).

Examples of the experimentally observed  $F$ -dependence of the circularity degree are presented in Fig. 1a, b for  $D^1\Pi$  state 7(23) and 12(7) rovibrational levels, respectively. The fitting (see solid curves in Fig. 1) has been performed using an approach which involves diagonalisation of the Hamiltonian accounting for dc Stark mixing between all  $J \pm \Delta J$  levels with  $\Delta J \leq 3$  in the initial, excited and final rovibronic states of a LIF transition, see Ref. [6] for details. We used the values of excited state  $\Lambda$ -doubling constant  $q$  and permanent electric dipole moment  $d$  which were previously measured in Ref. [8], namely  $d = 6.4 \text{ D}$ ,  $q = 1.51 \times 10^{-5} \text{ cm}^{-1}$  for 7(23) and  $d = 5.1 \text{ D}$ ,  $q = 1.03 \times 10^{-5} \text{ cm}^{-1}$  for 12(7). The excited state relaxation rate  $\Gamma = \tau^{-1}$

value was taken as  $\Gamma = 8 \times 10^7 \text{ s}^{-1}$  for both states to perform the best fitting of experimental values. This value exceeds the  $\tau^{-1}$  measured in Ref. [9] by a factor which is over than the expected increase of excited state  $\Gamma$  values because of collisions between NaK molecules and atoms. Fig. 1a,b demonstrates satisfactory agreement between theory and experiment. The results for 12(7) state in Fig. 1b are not so accurate because of large relative errors because of ca. 10 times smaller fluorescence intensities.

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