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Symmetry Breaking of Angular Momentum Distribution of Diatomic Molecules in an External Field

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Abstract

If an ensemble of atoms or molecules is excited by linearly polarized light, then usually one expects linearly polarized fluorescence form the ensemble. This reflects a symmetry of the excitation process, namely the fact that the electric field in a light wave and consequently the angular momentum distribution of atoms or molecules in an excited state can be characterized by a double headed arrow $\Longleftrightarrow$. An ensemble of particles in an excited state possesses a net alignment. In this paper some processes that for molecules in an external field can break this symmetry are reviewed. As a result of symmetry breaking the ensemble of molecules acquires a net orientation of angular momentum, that can be characterized by a single headed arrow $\Longrightarrow$, and one can expect a circularly polarized fluorescence from this ensemble.

1. Introduction

Usually when molecules or atoms are excited by linearly polarized light, linearly polarized fluorescence from an ensemble of such particles is expected. For linearly polarized excitation the fluorescence circularity rate is most often zero. This reflects a symmetry of the excitation process. Linearly polarized light produces *alignment* of angular momentum of atoms. In case of alignment the angular momentum spatial distribution can be characterized by a double headed arrow $\Longleftrightarrow$. If we want to interpret this in terms of population of magnetic sublevels of angular momentum J state, then one can see that in an aligned system magnetic sublevels of different $|M_J|$ are populated unequally, while magnetic sublevels $+M_J$ and $-M_J$ have the same population.

There exists a long history of studies, theoretical as well experimental, of processes that are able to break this symmetry and from an initially aligned ensemble of atoms produce angular momentum *orientation*, that can be characterized by a single headed arrow $\Longrightarrow$ or a different population of magnetic sublevels $+M_J$ and $-M_J$. As a result of this symmetry breaking a net helicity is introduced in an ensemble and one can expect circularly polarized fluorescence form such an ensemble of molecules or atoms.

For the first time alignment – orientation conversion was predicted and experimentally observed in anisotropic collisions of initially aligned atoms [1–4]. Anisotropic collisions directed at a specific angle with respect to the direction of initially created atomic alignment was the process able to cause symmetry breaking and alignment – orientation conversion.

2. Alignment – orientation conversion in an external electric field

It is easy to understand the main reasons for symmetry breaking and alignment – orientation conversion. A simple way to describe an ensemble of atoms or molecules is by means of quantum density matrix [5, 6] with elements $f_{MM'}$ which is obtained as a solution of the stationary density matrix equation of motion and which describes the coherence between sublevels with magnetic quantum numbers M and M' in a state with definite angular momentum J value. The explicit form of density matrix elements contain a factor $\Gamma_{MM'} + \mathrm{i}\omega_{MM'}$, namely

$$f_{MM'} \propto \frac{1}{\Gamma_{MM'} + \mathrm{i}\omega_{MM'}} \tag{1}$$

where

$$\omega_{MM'} = \frac{E_M - E_{M'}}{\hbar} \tag{2}$$

is the splitting between Zeeman sublevels M, M' with energies E_M, $E_{M'}$, while

$$\Gamma_{MM'} = \frac{\Gamma_M + \Gamma_{M'}}{2} \tag{3}$$

is the rate of relaxation of coherence between M, M' sublevels; Γ_M and $\Gamma_{M'}$ being relaxation rate constants of respective magnetic sublevels. It can be seen from the analysis of the form of Eq. (1) that, generally speaking, at broad spectral line excitation there are two basic reasons for the appearance of alignment – orientation conversion in the excited state angular momenta distribution. Indeed, as it follows from the analysis presented in Ref. [6–8], to bring alignment – orientation conversion into existence one must have such a perturbation which leads to the asymmetry, with respect to the M, M', either in energy splitting in the form

$$\omega_{MM\pm1} \neq \omega_{-M\mp1-M} \tag{4}$$

or in M-dependent coherence relaxation rate constants in the form

$$\Gamma_{MM\pm1} \neq \Gamma_{-M\mp1-M}. \tag{5}$$

Historically from external fields an electric field was the first studied as a factor producing orientation in the initially aligned ensemble of particles. Lombardi [9] studied atoms in an electric field and discovered that it can mix atomic states together in such a way, that in a particular transition lefthanded and righthanded circularly polarized light in

atoms in an external electric field will be absorbed and emitted with different efficiency. As a result alignment can be converted into orientation and consequently linearly polarized excitation of atoms in an electric field can produce a circularly polarized fluorescence. In this case orientation will be created along the direction of an external field. This type of orientation is called *longitudinal* orientation.

If the initial alignment is directed at an angle which differs from 0 or 90 degrees with respect to an electric field, than the action of the electric field can cause conversion of alignment into orientation which will be directed perpendicularly to the direction of the electric field – *transversal* orientation. This effect in barium and cesium atoms was studied by Hylborn and coworkers [10]. They used in their experiment two external fields. The first one was a magnetic field which tilted initial alignment created by linearly polarized laser excitation. Then an electric field acted upon this tilted alignment and caused alignment – orientation conversion.

In great detail electric field action as an agent capable to convert alignment into orientation was examined in case of molecules. The interest was attracted mainly to the case when *transversal* orientation is created. Again initially one must have alignment of molecules. There are different ways to create this initial alignment. For example in a supersonic nozzle beam expansion of molecular gases very often due to collisions in the process of the beam formation, initial alignment can be created almost automatically. This type of molecular alignment in molecular beams is observed experimentally for different gases in different conditions. For a review of this type of alignment see for example [11]. By appropriately applied external electric field this alignment can be further transformed into orientation. In [12] calculations were performed to show that this orientation can be achieved at rather modest electric field strength dependent on the permanent dipole moment of molecules and rotational state angular momentum value. The created orientation can be very selective. One can orient selectively chosen definite rotation states of molecules. In Fig. 1 the molecular orientation in arbitrary units in case of NaK ground electronic state $^1\Sigma$ is shown for different angular momentum J levels. Even molecules composed from different atomic isotopes can be oriented selectively. By changing the electric field strength slightly the sign of angular momentum orientation can be easily changed. It means that by changing the electric field one can switch direction of the molecular orientation. Of course, one must keep in mind that this type of orientation can be used only for molecules with permanent electric dipole moment – for heteronuclear diatomic molecules. In calculations performed in [12] constants and parameters of the NaK molecule, which is known to possess rather large electric dipole moments in its ground as well as in electronically excited states, were used.

Further studies of optically excited molecules in an external electric field was performed in [13]. It was shown that in time resolved spectroscopy the behavior of the angular momentum distribution in an external electric field of optically aligned molecules can provide a useful tool to separate linear and quadratic contributions to the Stark effect (energy level splitting in an external electric field). For example, a molecular $^1\Pi$ state which possesses quadratic Stark effect due to rotational state mixing in an external

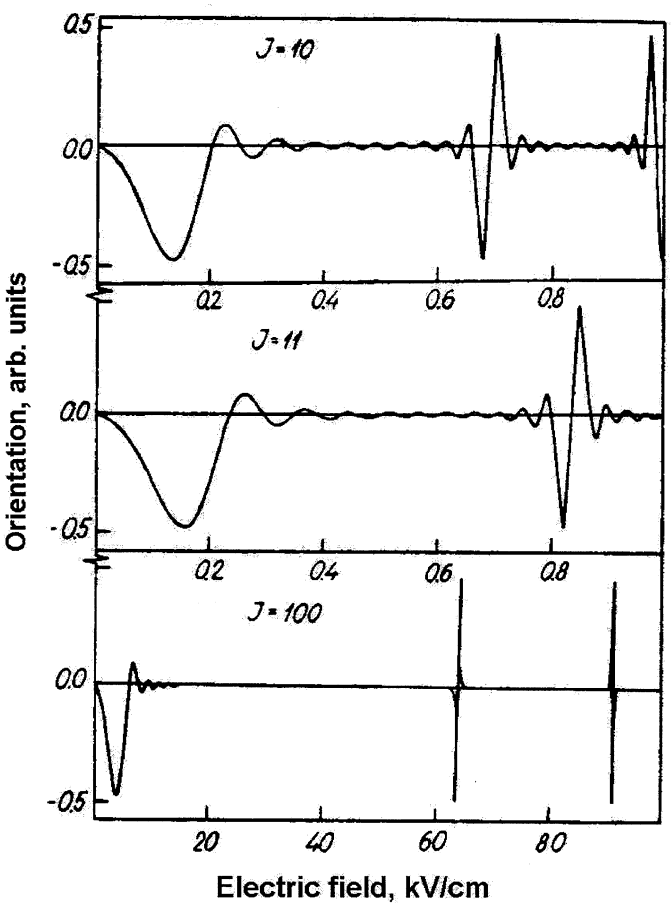

Fig. 1. Alignment – orientation conversion dependence on electric field strength, calculated for NaK molecule in its ground electronic state for three different values of angular momentum: $J = 10$, $J = 11$, and $J = 100$.

electric field and at the same time due to opposite parity Λ doublet component mixing in a field possesses quasi linear Stark effect [14] can be studied. It is an interesting object to examine this type of molecular behavior in an electric field.

After pulsed excitation of molecules, in time resolved fluorescence in the exponential decay signal one can expect to have relatively slow harmonic modulation for which linear Stark effect will be responsible. In the same signal sharp narrow peaks will appear. Separation in the time scale of these peaks will be fully determined by a quadratic component of the Stark effect. Qualitatively such type of signal is show in Fig. 2. The distance between these sharp peaks will increase with increasing the angular momentum of the excited state. At the same time the sharpness of the peaks will increase as well.

Finally, in [15] it was demonstrated how an alignment – orientation conversion can help to determine permanent electric dipole moments as well as Λ doubling constants in $^1\Pi$ states of diatomic molecules. In this case Λ - doublet component mixing in an external field is a factor which provides a required asymmetry in magnetic sublevel splitting and causes alignment – orientation conversion. This process is mainly governed by two molecular parameters. These are the permanent electric dipole moment d of the molecular state and the Λ doubling constant q. Usually when one measures traditional signals for this type of spectroscopy, such as appearance of forbidden spectral lines as a result of Λ doublet mixing [16], only the ratio of d/q can be

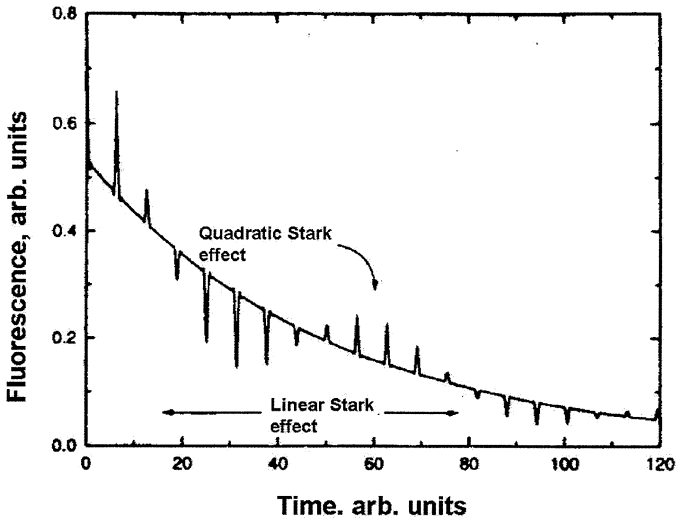

Fig. 2. Separation of linear and quadratic Stark effect in time dependent fluorescence of molecules after pulsed excitation. Slow harmonic modulation of the signal reflects linear Stark effect and sharp peaks reflect quadratic Stark effect.

determined with sufficient accuracy. Sophisticated techniques such as optical – radio frequency double resonance method are required to separate these signals [17]. At the same time alignment – orientation conversion provides a simple and accurate enough method to measure these quantities [15].

Although the quantum mechanical description of all effects described above is straightforward, it is helpful to have a more intuitive picture of how a net orientation arises from an initially aligned system. The crucial physical ingredient in this picture is the precession of the atomic or molecular angular momentum due to atomic or molecular interaction with an external electric field.

It can be shown that in case of quadratic Stark effect the angular velocity ω_E of this precession depends upon the angle θ that the angular momentum forms with the external electric field **E**. Namely, [18]

$$\omega_E \propto \frac{E^2 d \cos\theta}{J}. \tag{6}$$

This formula tells us that angular momenta with opposite signs of the projections on the external field directions precess in opposite directions. This, as it is shown in [19], allows us in a simple vector model to explain the alignment – orientation conversion phenomenon. Let us imagine that the initial alignment is at the angle 45 degrees with respect to the electric field **E** which defines z axis. If this distribution evolves in an external electric field then the part of angular momentum distribution that has positive projection on the field direction precesses in the opposite direction than the part of this distribution with negative projection on the field direction. This means that at some point both parts of the angular momenta distributions as a result of precession will have the same projection on the xy plane and a net transversal orientation will be created.

3. Alignment – orientation conversion in an external magnetic field

Usually, contrary to an electric field, it is assumed that a magnetic field alone is not able to break the symmetry of angular momentum spatial distribution and cause alignment – orientation conversion. In general, the main reason why an electric field is able to convert alignment into orientation but a magnetic field is not, is because the electric field is characterized by a polar vector, but the magnetic field – by an axial vector, and this means that these fields possess a different symmetry under reflection in a plane.

However in case of a magnetic field this obstruction can be circumvented if in addition to the linear Zeeman effect there exist any perturbing factor changing the symmetry of the overall perturbation and causing at least slight non-linearity in a primarily linear Zeeman effect. The cause of this non-linear dependence of the magnetic sublevel energy upon the field intensity and magnetic quantum number M_J can be of different origin. For example, it can be magnetic predissociation as studied in a number of works [8, 20–22].

In case of magnetic field it is easy to test that the linear Zeeman effect when the magnetic energy is

$$E_M = g\mu_B MB, \tag{7}$$

where g is the Lande factor, μ_B is the Bohr magneton and B is the magnetic field strength, leads to symmetric energy level splitting in a sense that $\omega_{MM\pm1} = \omega_{-M\mp1-M}$ and is not able to lead to alignment – orientation conversion, see Eq. (4). It means that in case of linear Zeeman effect at linearly polarized excitation one can not expect circularly polarized fluorescence if there are no additional perturbing factors.

In case of Te_2 molecule in an external magnetic field, possessing in its excited B state magnetic as well as rotational predissociation, sufficiently pronounced alignment – orientation conversion signal was registered [8] in the $B1_u^-$ component of the $B\,^3\Sigma_u^-$ state complex as an appearance of a degree of fluorescence circularity $C(B)$ up to 0.05, under linearly polarized $X1_g^- \rightarrow B1_u^-$ excitation in the presence of a static magnetic field up to $B = 0.4$ T. In Fig. 3 the circular polarization rate of the fluorescence detected from Te_2

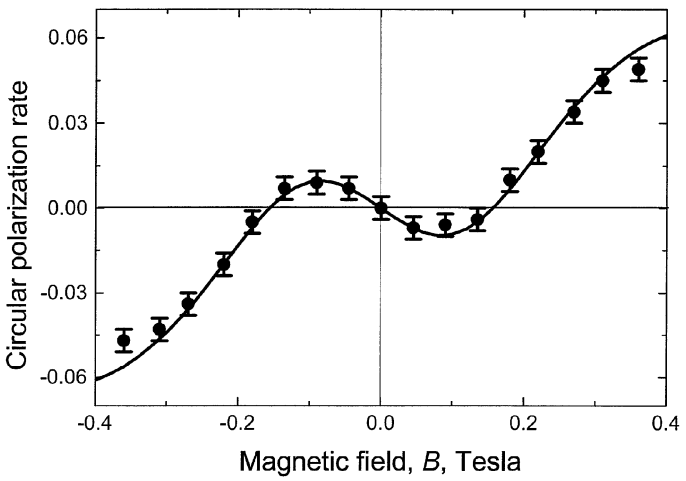

Fig. 3. Alignment – orientation conversion in excited state of Te_2 molecule in an external magnetic field. Joint action of the level mixing in the magnetic field and rotation and magnetic predissociation causes appearance of circularly polarized light.

molecule depending on magnetic field is depicted. The effect has been described as a result of the asymmetric splitting of Zeeman sublevels, see Eq. (4) due to the presence of a small quadratic component in the Zeeman effect energy shift term. We found it to be a nice example of the magnetic field assisted $\Delta J = \pm 1$ mixing of states with different electronic parities, or $e \sim f$ mixing, not only between Ω-doubling components $B1_u^- \sim B1_u^+$ of the electronic $B\ ^3\Sigma_u^-$ state, but rather that of the $B1_u^- \sim B0_u^+$ close together situated components interaction. It is important to stress that both interactions are forbidden in the absence of external magnetic field. Besides, an important role of alignment – orientation conversion in Te_2 molecule plays magnetic as well as natural predissociation.

Another situation when an external magnetic field can cause alignment – orientation conversion is atoms or molecules with strong hyperfine structures in a magnetic field. In this case alignment – orientation conversion effect can take place in two different ways. First, magnetic sublevels of the different hyperfine levels are mixing in a magnetic field. Due to this reason magnetic sublevels with the same magnetic quantum number, but belonging to different hyperfine levels are mixed together. As a result, for example, from a particular magnetic sublevel $M = 0$, contrary to the usual symmetric situation circularly polarized photons with righthanded circularity and lefthanded circularity are not emitted with the same efficiency. This means that from an initially aligned ensemble, a net orientation of the atoms or molecules can arise.

For the first time this type of alignment – orientation conversion as a result of hyperfine interaction in a magnetic field in context of nuclear spin $I = 1/2$ was studied by Lehmann in cadmium [23, 24]. He examined optical pumping of cadmium atoms in a magnetic field. Baylis described this effect in sodium [25]. The first experiment to directly detect a net circular polarization of the fluorescence from an initially aligned excited state in an external magnetic field was reported by Krainska-Miszczak [26]. In this work the optical pumping of ^{85}Rb with a π polarized D_2 line was studied. In great detail this effect was examined by Han and Schinn in sodium atoms [27]. Quantum mechanically this alignment to the orientation conversion process may be viewed as resulting from hyperfine F level mixing in an external magnetic field and the interference of different excitation – decay pathways in such mixed levels.

In all above cases the joint action of the magnetic field and hyperfine interaction creates different populations of the magnetic sublevels $+M_F$ and $-M_F$ of the hyperfine levels F. This means that a *longitudinal* orientation of atoms along the direction of an external magnetic field is created.

A different situation takes place, when we consider excitation of molecules with hyperfine structure by linearly polarized light with its electric field vector directed at 45 degrees with respect to the external magnetic field. In this case due to joint action of the magnetic field an hyperfine interaction coherence created by a linearly polarized excitation between magnetic sublevels with $\Delta M = 1$ will be destroyed in such a way, that total orientation of molecules in the direction perpendicular to the external field **B** – *transverse* orientation, will be created [7]. In paper [28], as an example, parameters of the NaK molecule were used for numerical simulations of orientation and circularity signals for this type of alignment – orientation conversion. It was found that only levels with small rotational angular momentum J, comparable with a nuclear spin I, can be used to study experimentally appearance of transversal orientation as a result of action of a magnetic field in presence of hyperfine interaction. For levels with larger angular momentum quantum numbers the magnitude of created orientation decreases dramatically. This allows to conclude that atoms, that usually possess not very large angular momenta, are most appropriate candidates for experimental studies of alignment – orientation conversion and appearance of transversal orientation and, as a consequence, nonzero circularity rate of the fluorescence in the direction perpendicular to the direction of the external magnetic field.

Recently [29] such alignment orientation conversion signal in ^{85}Rb atoms was detected. Atoms were excited from the $5S_{1/2}$ ground state hyperfine levels $F_i = 2$ or $F_i = 3$ to the spectrally unresolved excited state $5P_{3/2}$ (resonant D_2 line) hyperfine level manifold. ^{85}Rb atoms possess large nuclear spin $I = 5/2$. When an external magnetic field was applied in a way that the angle between the polarization vector of the excitation light and the field was 45 degrees, a substantial alignment – orientation conversion was detected as an appearance of circularly polarized fluorescence in a direction perpendicular to the plane containing the magnetic field and light polarization vector, see Fig. 4. It means that a transversal orientation in the ensemble of ^{85}Rb atoms was created.

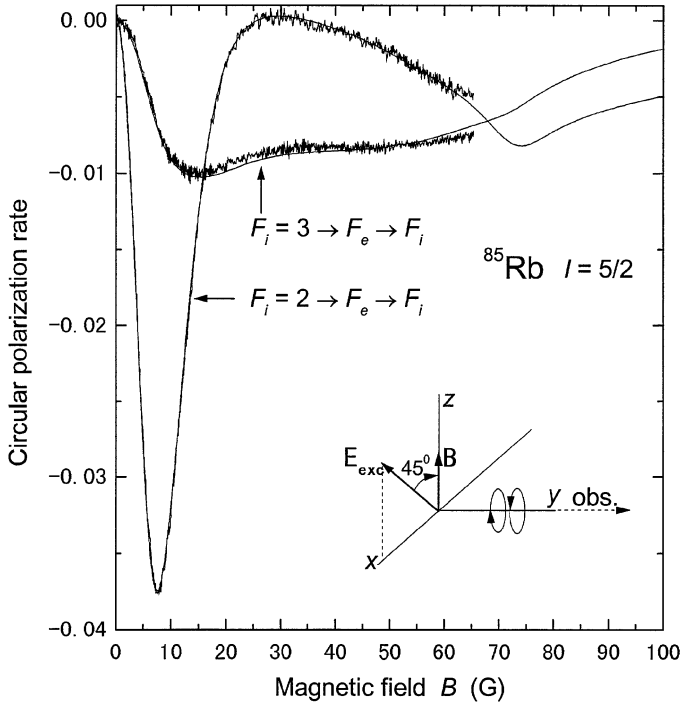

Fig. 4. Alignment – orientation conversion in ^{85}Rb atom caused by joint action of an external magnetic field and hyperfine interaction in atoms. Measured and calculated signal for excitation spectrally unresolved manifold of hyperfine level of $5P_{3/2}$ atomic state from two different spectrally resolved ground $5S_{1/2}$ state hyperfine levels.

4. Final remarks

All mentioned experiments demonstrate that alignment – orientation conversion which means symmetry breaking in angular momenta distribution can occur due to different physical reasons. Nevertheless always in case of longitudinal orientation there must be present an asymmetry between absorption and emission of light of opposite circular polarization along the magnetic field direction. This asymmetry is usually caused by a state mixing by a perturbation of definite symmetry.

In case of transverse orientation an asymmetry in coherence relaxation rates (5) or splitting of coherently excited magnetic sublevels (4) must be present.

Changes in the atomic or molecular properties in an external field can be used not only to study new effects and atoms or molecules itself, but also in case of known atomic or molecular parameters to study external fields.

The importance of plasmas for material processing has inspired experimental studies of the complex flow of glow discharges. Of particular importance has been a host of techniques developed to measure the spatial dependence of the electric field in a plasma. Among the most successful of these are optical techniques that take advantage of changes in the spectra of atoms and molecules caused by electric fields (the Stark effect.) These optical techniques are reviewed by Lawler and Doughty [30]. One of the most successful schemes for field measurement, first demonstrated by Moore, Davis and Gottscho [31], takes advantage of the field-induced breakdown of parity selection rules in the laser-induced fluorescence between $^1\Sigma$ and $^1\Pi$ states of diatomic molecules. In the absence of an electric field, dipole selection rules require that the laser induced $^1\Sigma(v'', J'') \rightarrow {}^1\Pi(v'J')$ transition occurs only to the lambda-doublet component of the $^1\Pi(v'J')$ state that has opposite total parity to the ground $^1\Sigma(v'', J'')$ state. The field-free fluorescence signal must again change parity as the $^1\Pi(v'J')$ fluoresces to the $^1\Sigma(v, J)$ state. For this reason, the parity of the initial $^1\Sigma(v'', J'')$ state must match the parity of the final $X^1\Sigma(v, J)$ state. This fact implies that, in the absence of an electric field, if one induces the Q-branch transition $^1\Sigma(v'', J') \rightarrow {}^1\Pi(v'J')$, only Q-branch transitions $^1\Pi(v'J') \rightarrow {}^1\Sigma(v, J')$ contribute to the fluorescence. If instead an R- or P-branch transition $^1\Sigma(v'', J' \pm 1) \rightarrow {}^1\Pi(v'J')$ is induced, only R- and P-branch fluorescence $^1\Pi(v'J') \rightarrow {}^1\Sigma(v, J' \pm 1)$ is observed. In the presence of a field, however, parity is no longer a good quantum number and these selection rules break down. Thus the ratio of Q-branch fluorescence to R- and P-branch fluorescence is sensitive to the local electric field. This technique was first demonstrated by Moore and coworkers using BCl [31]. The field-measurement technique has since been adapted to NaK [32, 33]. A complete theory of the polarization-and-field-dependent fluorescence has been presented by Derouard and Alexander and, more recently, by our group [16, 34].

In the NaK studies, spectacular field-dependent polarization effects are observed [32, 33]. The fact that the polarization-dependent fluorescence intensity depends strongly on electric field suggests an improved field-imaging scheme [35]. In this scheme, it is no longer necessary to spectroscopically resolve the Q-branch fluorescence from the R- and P-branch fluorescence. Instead the fluorescence is filtered from scattered laser light and then measured at specific polarizations with a CCD camera. The elimination of the need to resolve the wavelength of the fluorescence may prove to be advantageous: instead of the time-consuming process of creating a rastered image, the technique presented here could use a single physical setup to create a photographic image (or video) of the electric field surrounding an object.

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