Precise Stark-Effect Measurements in the $^2\Sigma$ Ground State of CaCl

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By use of the molecular-beam microwave-optical double-resonance technique the first high-precision Stark-effect measurement of an alkaline-earth monohalide has been performed. Low-field Stark shifts of rotational transitions in the $v = 0$, $X^2\Sigma$ state of CaCl exhibited an unexpectedly complicated field dependence which, however, has been shown to be in complete agreement with an exact theoretical calculation.

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Alkaline-earth monohalides have attracted the interest of many research groups during recent years. Most of these molecules exhibit optical transitions in the visible region which make them good candidates for high-resolution laser spectroscopic work. On the other hand, they are very attractive for semiempirical calculations[1,2] because of their highly ionic chemical bond with a single unpaired metal-atom–centered valence electron. Despite this relatively simple electronic structure the electric dipole moment of these molecules is still a matter of discussion. Theoretical estimates by Klynning and Martin[2] based on the Rittner model[3,4] predicted $\mu \simeq 0.36$ D for the CaCl molecule. However, this seems to be unplausibly small and there is some experimental evidence that the dipole moment might be approximately one order of magnitude larger. In the investigation of the microwave (mw) rotational spectrum of CaCl by Möller *et al.*[5] the saturation-effect modulation technique[6] has been used. The relatively low saturation intensities experienced in these experiments indicate that the dipole moment should be larger than about 3 D. A somewhat more exact experimental estimate was given by Dagdigian,[7] who measured the deflection of a molecular beam by an electric quadrupole. The measurements were carried out in the strong-field region where all effects of spin-rotation doubling and hyperfine structure may be neglected and simple second-order perturbation theory can be applied. The reported value for the dipole moment is $\mu = 3.6(6)$ D.

The particular goal of the present experiment was to provide a precise and reliable value for the dipole moment by studying the Stark shift of particular hyperfine-structure components. This requires an experimental technique which combines good sensitivity with the very high resolution necessary for resolving the small hyperfine-structure splittings arising from the chlorine

nucleus. These conditions can be fulfilled only by rf-optical or mw-optical double-resonance experiments. Ground-state rotational transitions with resolved hyperfine structure have recently been reported by Ernst and Törring[8] using mw-optical polarization spectroscopy (MOPS).[9] In this cell experiment the linewidth is limited mainly by pressure broadening to about 1 MHz. A largely improved resolution is obtained if molecular-beam techniques can be applied. Using the molecular-beam laser-rf double-resonance method, Childs and Goodman have performed the first highly precise measurements of spin-rotation and hyperfine-structure splittings in alkaline-earth monohalides.[10] Recently Ernst and Kindt have demonstrated that this technique can also be used to measure rotational transitions of these molecules in the mw region.[11] Since the technique has been described several times in the literature (see Refs. 10 and 11 and references therein) only a brief description will be given here. A collimated molecular beam traverses a strong single-frequency laser beam. When in resonance with an appropriate optical transition this laser will deplete a particular ground-state level by an optical pumping process. The molecular beam then passes through a second region where it interacts with mw or rf radiation which can be swept in frequency while the laser frequency is kept fixed. If the depleted level is refilled by induced mw or rf transitions within the ground-state manifold this can be observed in a third region by an increase of fluorescence intensity induced by the same laser which is used for the optical pumping. One of the main advantages of this technique is that the field strength in the transition region can be kept so low that possible influences on the linewidth and on line positions can be completely neglected. In our experiments allowed electric dipole transitions were stimulated with a mw intensity of only about 5×10^{-6}

W/cm^2. With careful shielding of the Earth's magnetic field the linewidth is then determined by the time of flight through the transition region, i.e., 25 kHz. mw transition frequencies can thus easily be determined with an accuracy of a few kilohertz. The same is true when a homogeneous electric field is added to the mw field for Stark-effect measurements. Both fields are parallel in our experiment so that the selection rule for induced transitions is $\Delta M_F = 0$. The electric dipole moment is determined by measuring the influence of the static electric field on the mw transition frequencies.

Stark shifts have been measured for three hyperfine components of the $N = 2 \leftarrow 1$ rotational transition in the vibrational ground state of the CaCl molecule. The energy-level diagram of these two rotational states in the absence of an external field is shown in Fig. 1 with the measured transitions indicated by arrows. It should be noted that all three transitions (a, b, and c) start from a level with $F = 0$. The observed lines are therefore only shifted but not split when the electric field is applied. The experimentally determined line shifts are plotted in Fig. 2 as a function of the electric field strength. For all three transitions the Stark shift is quite unusual and shows an unexpectedly complicated pattern.

The strong deviation from a simple quadratic effect can be explained by considering the mutual coupling of the three angular momenta of molecular rotation N, electron spin S, and nuclear spin I, respectively. In Fig. 1, a Hund's case-b β_J coupling scheme is assumed; e.g., the total angular momentum F is formed by a coupling of I with the intermediate angular momentum J resulting from the coupling of N and S. However, especially for low values of N, a Hund's case-b β_s basis may be more appropriate in which I and S are coupled to an intermediate angular momentum F_1 which in turn couples with N to F. The actual coupling is intermediate between these two limiting cases depending on N and the mutual coupling parameters. When a static electric field E_Z is applied the vector of molecular rotation and the magnetic field associated with this rotation will start to precess around the Z direction. Coupling of S or F_1, respectively, with N will
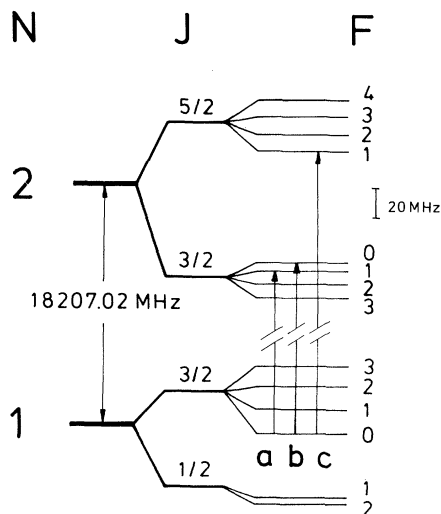

FIG. 1. Level diagram showing the hyperfine components of the $N = 2 \leftarrow 1$ transition in the $X^2\Sigma$ ($v = 0$) state of $Ca^{35}Cl$. Three microwave transitions (a, b, and c) which were used for the Stark-effect measurements are indicated by arrows.
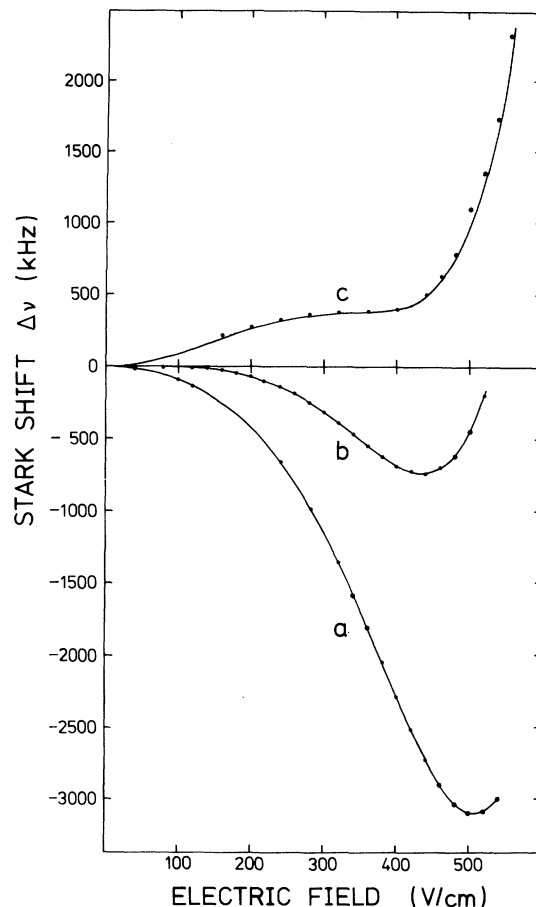

FIG. 2. Stark shift $\Delta\nu$ vs electric field for the three microwave transitions a, b, and c. Measurement errors are contained in the size of the data points. The solid lines represent the calculated line shifts for $\mu = 4.265$ D.

thus be changed more and more to a coupling with N_z. This resembles the well-known Paschen-Back effect observed with strong magnetic fields in atomic spectra.

No simple analytic expression for the molecular energies can be given in the transition region when the Stark energy is comparable to the spin-rotation and hyperfine coupling energies. Therefore a computer program was written for numerical diagonalization of the total energy matrix. Details of the theory will be given in a forthcoming paper.[12] The program allows a simultaneous fit of all the experimental data given in Fig. 2. The electric dipole moment was the only adjustable parameter in this fit. Dunham coefficients and spin-rotation and hyperfine-structure parameters were taken from Refs. 5 and 13, respectively, and were kept fixed in the fit. The result is

$$\mu = 4.265(3) \pm 0.02 \text{ D}.$$

The two errors given represent the statistical standard deviation and the uncertainty in the calibration of the Stark field. The latter contribution to the absolute error can be easily reduced by an improved construction of the Stark electrodes. This will also reduce line broadening due to the field inhomogeneities so that measurements can be extended to higher field strengths. The fitted dipole moment has been used to calculate the theoretical Stark shifts. These are given by the solid curves in Fig. 2. The agreement between theory and experiment is striking. This reflects not only the accuracy of the present measurements but also the high quality of the constants which have been kept fixed in the fit. Small systematic deviations slightly outside the experimental uncertainties are found only for the $J = \frac{5}{2}$ $- \frac{3}{2}$ transition. These may be attributed to a residual Zeeman shift due to an incomplete shielding of the Earth's magnetic field. This shows up also in slightly asymmetric line shapes for this transition.

It has been demonstrated that molecular-beam mw-optical double resonance is an excellent tool for a precise and reliable determination of electric dipole moments in radicals. It should be noted that the extremely high resolution of a beam experiment is essential for the observation of the details in the Stark shifts shown in Fig. 2. In a cell experiment the linewidth would be of the order of the maximum observed shift so that all finer details would be obscured. With the present accuracy vibrational effects on the dipole moment will be easily observable. Measurements in excited vibrational states are in progress.[12]

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