

Electric-dipole moment of CaF by molecular-beam, laser-rf, double-resonance study of Stark splittings

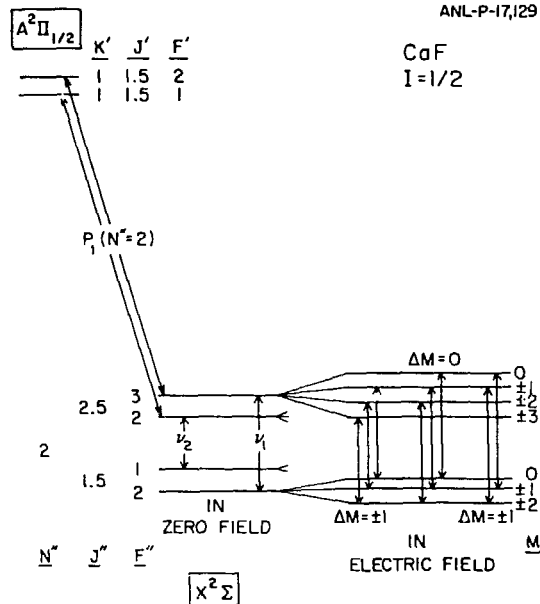
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The electronic structure of diatomic molecules is much more complex for open-shell systems (radicals) than for the normal closed-shell systems, and the development of an adequate theoretical understanding will require a substantial upgrading of experimental knowledge in both quality and quantity. The alkaline-earth monohalide family of radicals, with only a single electron outside closed-shell cores, would appear to be a logical starting point for such studies, and there has been a great increase in work in this area in the last few years in spite of the special difficulties of working with free radicals. As the work of measuring the vibrational and rotational structure of the electronic states has become more complete, attention has turned to study of the much weaker spin-rotation and hyperfine interactions. Within the last three years, these interactions have been studied systematically at high precision in the calcium monohalide family with the molecular-beam, laser-rf double-resonance technique. The same method has now been modified and extended to make possible measurement of the electric-dipole moments of these molecules through observation of the Stark splittings of radiofrequency transitions. It is hoped that when considered together, the several types of data will make it possible to understand the ground-state electronic wave functions of these molecules at least qualitatively.

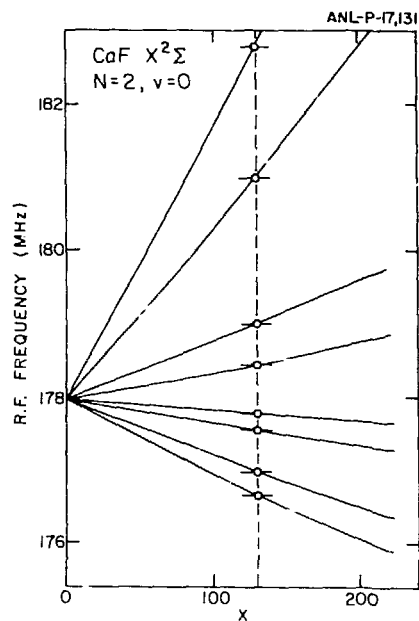
CaF was chosen for our first measurement of this kind. Figure 1 shows the energy levels and transitions relevant for the measurement. The four hyperfine levels of the  $v'' = 0, N'' = 2$  rovibrational state of the CaF  $X^2\Sigma^+$  ground electronic state are shown near the center of the figure. A cw dye laser tuned to the red (right-hand) hyperfine component of the  $P_1(N'' = 2)$  optical line depletes the population of the  $F = 3$  hyperfine level of the  $X$  state. The depleted level can be repopulated by applying the radiofrequency  $\nu_1$ , and the repopulation can be observed by noting a resonant increase in the fluorescence caused by a suitable probe laser beam. This "normal" double-resonance scheme is modified in the present arrangement by making the rf transition  $\nu_1$  occur in a homogeneous d.c. electric field. In the field, the Stark effect causes the levels to split apart (as indicated schematically at the right of the figure) by an amount dependent on both the field strength and the dipole moment. Measurement of the splittings thereby leads directly to a determination of the dipole moment.

Figure 2 shows the resonance frequency calculated for each of the eight components of  $\nu_1$  as a function of a parameter  $X = 2.464 \times 10^{-5} \mu^2 E^2$  which measures the field strength ( $\mu$  is the electric dipole moment and  $E$  the electric field strength). The measured resonance frequencies are consistent with the calculated ones only for the value  $X = 130.0$  MHz, and from this and the measured field strength we conclude that  $\mu = 3.07(7)$  Debye for the  $X^2\Sigma^+$  ( $v = 0$ ) ground state of CaF. This result, together with a new dipole moment result for  $\text{Ca}^{35}\text{Cl}$  obtained using a microwave-laser technique, constitute the only electric-dipole moment information currently available for the entire family of alkaline-earth monohalide radicals.

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**Fig. 1.** CaF molecular levels and transitions relevant to measurement of the electric-dipole moment. The moment is determined by measuring the Stark splitting of the 8 components of the rf transition  $\nu_1$ . An extension of the molecular-beam, laser-rf, double-resonance technique is used.



**Fig. 2.** Stark shifts in CaF. The solid curves show the resonance frequencies calculated for the 8 Stark components of  $\nu_1$  (see Fig. 1), calculated as a function of the parameter  $X \propto \mu^2 E^2$ . The measured frequencies, shown by open circles, determine the value of X and consequently of the dipole moment  $\mu$ .

### New Directions

Construction of a new apparatus to allow high-resolution laser- and radiofrequency spectroscopy of slow ions is in progress. Although the first experiments will very likely be with atomic ions, it is planned to extend the program to small molecular ions once the new techniques are well understood. Although molecular ions are not "new", high-precision spectroscopy in this area is totally new and can be expected to yield interesting surprises. The studies should be of interest both for basic molecular structure and for applied areas such as astrophysics and plasma studies.

The planned collinear geometry of the laser and ion beams will lead to several advantages: (1) very long interaction times, (2) narrow fluorescence lines due to a large reduction of the velocity spread, and (3) the convenience of Doppler tuning the ions into resonance with the laser photons. Although the apparatus will be used initially for laser-fluorescence studies, the possibility of modifying the system to make possible ion-beam, laser-rf double resonance for ultrahigh precision spectroscopic studies is of great interest.

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