Zeeman effect in CaF\(^{2\Sigma_{3/2}}\)

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The Zeeman effect in the excited \(A^{2\Pi_{3/2}}\) state of CaF is measured and analyzed over a wide range of magnetic fields. It is found that the splitting of the Zeeman levels is largely determined by the coupling between different rotational states and there are no low-field seeking states in the \(J = 3/2\) manifold of Zeeman levels at high magnetic fields. A model of the Zeeman spectrum based on the ligand-field theory of CaF is shown to be accurate in the interval of magnetic fields 0–5 Tesla. This demonstrates that the magnetic moment of the CaF(A\(^{2\Pi_{3/2}}\)) molecule is effectively determined by the spin angular momentum of a single electron and the orbital motion of the valence electron around the Ca\(^{2+}\) core. An analysis of the Zeeman spectrum as a function of the molecular rotational constant indicates that \(^{2\Pi_{3/2}}\) molecules should have significant rotational constants (at least as large as twice the rotational constant of CaF) to be amenable to magnetic trapping in high fields. © 2004 American Institute of Physics. [DOI: 10.1063/1.1814097]

INTRODUCTION

High-resolution Zeeman spectroscopy provides important information about the structure of open-shell molecules. Unlike intrinsic perturbations of molecular energy levels due to nonadiabatic, Coriolis, spin–orbit or hyperfine interactions, perturbations due to interactions with an external magnetic field can be controlled; measurements of the Zeeman effect may reveal otherwise unobservable perturbations and establish the symmetry of previously unknown perturbing interactions. 1 Zeeman spectroscopy may also be used to test theoretical models of molecular structure. For example, it was shown by Rice, Martin, and Field 2 that calcium monohalide molecules may be approximately described as a polarizable negative charge perturbing one-electron valence structure of the Ca\(^{+}\) ion. This ligand-field model implies that the magnetic moment of the calcium halide molecules is determined by the orbital motion of the valence electron around the Ca\(^{2+}\) core. While the ligand-field model has been shown to describe very well molecular properties such as electronic energies, transition moments, permanent dipole moments and spin–orbit interactions, 2, 3 it is not clear that it remains accurate for molecules in strong magnetic fields. A comparison of the measured Zeeman spectrum with a calculation based on the ligand-field theory would assess the applicability of the ligand-field model for the description of molecules in external fields.

Precise knowledge of the Zeeman spectrum of molecules is essential for the development of magnetic trapping experiments. 4–6 Magnetic traps confine rotationally ground-state molecules in low-field seeking states (the Zeeman levels with a positive derivative of energy with respect to the magnetic field) and the efficiency of the magnetic trapping depends on the gradient of the molecular Zeeman energy with respect to the trapping field. One of the most general methods for loading molecules in a magnetic trap relies on buffer-gas cooling. 5, 7, 8 The magnetic fields of the buffer-gas loading experiments vary from 0 to 4.5 Tesla and in order to predict the possibility of buffer-gas loading of specific molecules in a magnetic trap, it is necessary to analyze their Zeeman spectrum in the interval of magnetic fields between 0 and 5 Tesla. While \(\Sigma\)-state molecules were trapped in our experiments, 5 trapping of \(\Pi\)-state molecules has not yet been demonstrated. Work on magnetic trapping of \(\Pi\)-state OH molecules is underway. 9 The Zeeman effect of the rotationally ground-state molecules in the \(^{2\Pi_{1/2}}\) electronic state is very weak so the molecules in the \(^{2\Pi_{1/2}} J = 1/2\) state cannot be magnetically trapped. The Zeeman spectrum of rotationally ground-states \(^{2\Pi_{3/2}}\) molecules is, therefore, of particular importance for understanding the prospects of magnetic trapping of \(^{2\Pi}\) molecules.

In this work we measure the frequency shift for transitions between the Zeeman levels of the ground \(X^{2\Sigma^{+}}\) and excited \(A^{2\Pi_{3/2}}\) states of the CaF molecule over a wide range of magnetic fields. The analysis of the measurement based on the direction cosine transformation of the magnetic moment operator to the molecule-fixed frame yields the Zeeman spectrum of the CaF molecule in the \(X^{2\Sigma^{+}}\) and \(^{2\Pi_{3/2}}\) states. We show that the magnetic spectrum of the \(^{2\Pi_{3/2}}\) state is not affected by the coupling to the \(^{2\Pi_{1/2}}\) or \(B^{2\Sigma^{+}}\) states. We develop a theory of the Zeeman effect based on the ligand-field model and demonstrate that it is accurate for magnetic fields between 0 and 5 Tesla.

EXPERIMENT

A detailed description of the apparatus used is given in Ref. 10. CaF molecules are produced via laser ablation of calcium fluoride in cryogenic helium gas. A cylindrical cell containing a hot-pressed powder pellet of CaF\(_{2}\) is maintained at 0.5 K by a \(^{3}\)He refrigerator. The cell is filled with helium gas at a typical density of \(10^{16} \text{cm}^{-3}\). An ablation beam from a pulsed frequency-doubled Nd:YAG laser with a typical pulse energy of 9 mJ is focused onto the CaF\(_{2}\) sample. Fol-
allowing the ablation pulse, CaF molecules enter the helium gas, rapidly thermalize with it translationally and rotationally, and then are lost due to diffusion to the cell walls on a typical timescale of 30 ms. The cell is placed coaxially inside a bore of a superconducting solenoid magnet which produces magnetic fields up to 4 Tesla. The molecules are detected using laser absorption on the $X^2\Sigma^+(v''=0,J'=1/2) - A^2\Pi_{3/2}(v'=0,J'=3/2)$ transition at 15 666.10 cm$^{-1}$. A detection beam from a cavity-stabilized ring dye laser propagates along the centerline of the cell. The linewidth of the laser is sub-MHz, much smaller than the typical width of observed spectral lines. The beam is linearly polarized along an axis perpendicular to the direction of the magnetic field. Laser absorption is determined by dividing signals from photomultiplier tubes which monitor laser intensity before and after the beam passes through the cell. The tubes are fitted to multi-channel matrix elements of the operator that give the components of the photodetector on the magnetic field axis.

THEORY

The theory of the Zeeman spectrum of II-state molecules was developed by Veseth and co-workers and described in detail for specific cases by several authors. We use the method outlined by Friedrich and co-workers. The total Hamiltonian of the CaF molecule in a magnetic field can be written as

$$\hat{H} = \hat{H}_0(n,J) + \hat{V}_B,$$

where $\hat{H}_0(n,J)$ is the field-free Hamiltonian describing the energy levels of the molecule with given values of the total angular momentum $J$ and other quantum numbers denoted collectively by $n$ and $\hat{V}_B$ is the Zeeman Hamiltonian describing the interaction of the molecule with an external magnetic field. It can be written in the form

$$\hat{V}_B = -\mu_Z B,$$

where $\mu_Z$ is the component of the molecular magnetic dipole moment operator along the magnetic field axis and $B$ is the magnitude of the magnetic field. The magnetic moment operator can be defined in the molecule-fixed coordinate frame in terms of the components of the electronic orbital angular momentum ($L$) and the electronic spin angular momentum ($S$) of the molecule as follows:

$$\mu_z^\pm = (L_z^\pm + g_s S_z^\pm)\mu_B,$$

where $L_z^\pm$ and $S_z^\pm$ are the raising and lowering operators of $L$ and $S$, $L_z$ and $S_z$ are the operators that give the components of $L$ and $S$ along the interatomic axis, $\mu_B$ is the Bohr magneton and $g_s = 2.0023$. The space-fixed $Z$-component of the magnetic dipole moment operator is related to the molecule-fixed components (3) and (4) by the direction cosine transformation which yields

$$\mu_z^m = \frac{1}{2} (\Phi_z^m \mu_z^+ + \Phi_z^m \mu_z^-) + \Phi_z^m \mu_\xi.$$

An effective form for the zero-field Hamiltonian $\hat{H}_0$ in Hund’s case (a) basis was derived by Kaledin and co-workers and the matrix elements of the operator (5) in Hund’s case (a) basis were explicitly given in the work of Friedrich and co-workers. Diagonalization of the Hamiltonian (1) yields the energy levels of the diatomic molecule parameterized by the projection $M$ of the total angular momentum $J$ on the magnetic field axis.

An alternative theory of the Zeeman effect in the CaF molecule may be derived based on the ligand-field model. Rice, Martin, and Field showed that the molecular function of CaF in the $^3\Pi$ state can be expanded in terms of $\text{Ca}^{2+}$-centered one-electron functions as follows:

$$|A^2\Pi\rangle = 0.831|4p(\text{Ca}^+)\rangle - 0.490|3d(\text{Ca}^+)\rangle.$$

The relation between Hund’s case (a) molecular functions $|JM\Lambda S\Sigma\rangle$ and the atomic functions at infinite interatomic separation is given by the angular momentum transformation

$$|JM\Lambda S\Sigma\rangle = \sum_j \sum_{j_A} \sum_{j_B} |JMj_Aj_B\rangle (-1)^{j-j\omega} (j\omega 10)[(S)(j_A)(j_B)]^{1/2} (L)^{1/2} \sum \sum L_A \Lambda_A L_B \Lambda_B |L\Lambda\rangle \times \langle L\Lambda S\Sigma|j\Omega\rangle \left\{ \begin{array}{ccc} L_A & S_A & j_A \\ L_B & S_B & j_B \end{array} \right\} \langle \Lambda_A \Lambda_B |c\Lambda\rangle,$$

where $A$ and $S$ are the projections of $L$ and $S$ on the intermolecular axis, $L_A$ and $L_B$ are quantum numbers of the electronic orbital angular momentum operators of atoms $A$ and $B$, $S_A$ and $S_B$ are quantum numbers of the electronic spin angular momentum operators of atoms $A$ and $B$, $j_A$ is the vector sum of $L_A$ and $S_A$, $j_B$ is the vector sum of $L_B$ and $S_B$, $j$ is the vector sum of $j_A$ and $j_B$, $l$ denotes quantum numbers of the angular momentum for the orbital motion of the nuclei about each other, $L$ is the vector sum of $L_A$ and $L_B$, $J$ is the vector sum of $l$ and $j$, $c$ is a quantum number distinguishing the molecular states with the same values of $\Lambda$, $S$ and $\Sigma$; $\Lambda_A$ and $\Lambda_B$ are the projections of $L_A$ and $L_B$ on the intermolecu-
lar axis, $\Omega = \Lambda + \Sigma$, the symbols $\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle$ are Clebsch–Gordan coefficients, the symbol in big curly braces is a 9-j-symbol and $(j_i)$ is a short-hand notation for $(2j_i + 1)$.

The ligand-field model shows that the CaF molecule is composed of an open-shell Ca$^+$ ion and a closed-shell F$^-$ atom so we assume for the present case $L_B = S_B = J_B = 0$, $j = j_A$, $S_A = 1/2$ and $L_A = L_{Ca^+}$, where $L_{Ca^+}$ is the orbital angular momentum of the valence electron around the Ca$^{2+}$ core. The transformation $\langle A_A A_B | c \Lambda \rangle$ is reduced to

$$\langle \Lambda_0 | c \Lambda \rangle = \delta_{\Lambda_0 \Lambda}. \quad (8)$$

The coupled atomic functions $|JM_{j,\Lambda}|$ are defined in terms of space-fixed functions of the Ca$^+$ atom

$$\langle A^2 \Pi_{\Omega} | \hat{V}_B | A^2 \Pi_{\Omega'} J' M \rangle = (0.831)^2 (-1)^{J+J'} + 2\Omega \sum_{j_A} \sum_{j_A} \sum_{j_M} \langle j_A - \Omega | J \Omega | 0 \rangle \langle j_A - \Omega | J' \Omega | 0 \rangle$$

$$\times \langle L_A = 1, \Lambda S_A | j_A \Omega \rangle \langle L_A = 1, \Lambda S_A | j' \Omega \rangle$$

$$\times \sum_{m_{L_A}} \sum_{m_{S_A}} \sum_{m_{m_{L_A}}} \sum_{-1} \langle j_A m_{L_A} | m_{L_A} | J M \rangle \langle j_A m_{L_A} | m_{L_A} | J' M \rangle$$

$$\times \langle L_A = 1, m_{L_A} | S_A | j_A m_{J_A} \rangle \langle L_A = 1, m_{L_A} | S_A | j_A m_{J_A} \rangle$$

$$\times \mu_B B (m_{L_A} + g_S m_{S_A})$$

$$+ (0.490)^2 (-1)^{J+J'} + 2\Omega \sum_{j_A} \sum_{j_A} \sum_{j_M} \langle j_A - \Omega | J \Omega | 0 \rangle \langle j_A - \Omega | J' \Omega | 0 \rangle$$

$$\times \langle L_A = 2, \Lambda S_A | j_A \Omega \rangle \langle L_A = 2, \Lambda S_A | j' \Omega \rangle$$

$$\times \sum_{m_{L_A}} \sum_{m_{S_A}} \sum_{m_{m_{L_A}}} \sum_{-2} \langle j_A m_{L_A} | m_{L_A} | J M \rangle \langle j_A m_{L_A} | m_{L_A} | J' M \rangle$$

$$\times \langle L_A = 2, m_{L_A} | S_A | j_A m_{J_A} \rangle \langle L_A = 2, m_{L_A} | S_A | j_A m_{J_A} \rangle$$

$$\times \mu_B B (m_{L_A} + g_S m_{S_A}). \quad (11)$$

The ligand-field theory provides atomic expansions for the other molecular states of CaF which can be used to evaluate the matrix elements of the magnetic dipole moment operator between different adiabatic states. As will be shown in the next section, however, the Zeeman spectrum of CaF$^+(2\Pi_{1/2})$ can be accurately described with only one electronic state in the basis. In the following, we will denote the calculations based on the direction cosine transformation of the magnetic moment as the accurate calculations, while the results obtained with the ligand-field model will be referred to as the ligand-field calculations.

**RESULTS**

Figure 1 shows the frequency shift for the $(X^2 \Sigma^+, N = 0, M = 1/2)$ and $(X^2 \Sigma^+, N = 0, M = -1/2)$ transitions as a function of the magnetic field in the interval 0–4 Tesla. $N$ denotes the quantum number for the rotational angular momentum of the electronic ground-state molecules. The measured data (represented by symbols) are in excellent agreement with the direction cosine calculations (curves). For these calculations, we have neglected the coupling to the $A^2 \Pi_{1/2}$ and $B^2 \Sigma^+$ states of CaF and assumed that the Zeeman energy of the magnetic levels in the $X^2 \Sigma^+$ state is given by $g_s \mu_B B$ as follows from our previous analysis.

The comparison with the measurement, therefore, shows that the Zeeman effect in the excited state of CaF is determined by the pure $A^2 \Pi_{3/2}$ state and the shift of the ground-state Zeeman levels is linear in the entire interval of magnetic fields considered. The frequency shift for the transitions from the low-field seeking state $(M = +1/2)$ of CaF($X^2 \Sigma^+, N = 0$) increases with the magnetic field at low fields, passes

$$|JM_{j,\Lambda}| = \sum_{m_{L_A}} \sum_{m_{S_A}} \sum_{m_{m_{L_A}}} |L_A m_{L_A}| |S_A m_{S_A}| |m_{L_A}|$$

$$\times |J_m_{L_A} | J M_{m_{L_A}} \rangle \langle L_A m_{L_A} | S_A m_{S_A} | J m_{J_A} \rangle.$$  \quad (9)
through a maximum and becomes negative at high fields reflecting a peculiar Zeeman energy variation in the excited state molecule. The frequency shifts for the transitions from the low-field seeking state and the high-field seeking state \((M = -1/2)\) of \(\text{CaF}(X^2 \Sigma^+, N = 0)\) cross at the magnetic field \(B = 3.55\) Tesla so both Zeeman energy levels of the ground-state molecule may be detected by the same frequency laser.

Figure 2 presents the Zeeman spectrum of the \(\text{CaF}\) molecules in the \((^3 \Pi_{3/2}, J = 3/2)\) state. The energy of the \(M = +3/2\) Zeeman level increases with the magnetic field in the interval 0–2.5 Tesla and decreases at higher magnetic fields. All Zeeman levels of the \(\text{CaF}(^3 \Pi_{3/2}, J = 3/2)\) molecule are high-field seeking states at \(B > 2.5\) Tesla. This indicates that \(^3\Pi\)-state molecules with rotational structure similar to that of \(\text{CaF}\) cannot be captured in high-field magnetic traps.

The results of the ligand-field model are in good agreement with the accurate calculations. The largest deviation of the ligand-field model results from the accurate calculations does not exceed 8% in absolute magnitude. This demonstrates that the magnetic moment of the \(^3 \Pi_{3/2}\) state of \(\text{CaF}\) is effectively determined by the spin angular momentum of a single valence electron and the orbital motion of the valence electron around the \(\text{Ca}^{2+}\) core.

The Zeeman effect in \(\Pi\)-state molecules is often estimated by the diagonal matrix elements of the Zeeman interaction Hamiltonian. The Zeeman energy is then given by

\[
E_M = \frac{\mu_B B}{J(J+1)} (\Lambda + g_S \Sigma).
\]

While this approximation is expected to be accurate at low magnetic fields, it neglects the coupling between different \(J\)-states of the molecule and fails at high magnetic fields. To elucidate the effect of the coupling between different rotational states on the Zeeman effect in \(\text{CaF}(^3 \Pi_{3/2}, J = 3/2)\), we present in Fig. 3 a comparison of the result (12) with the accurate calculations of the Zeeman energy. The approximation (12) is not valid at magnetic fields larger than 0.7 Tesla and the coupling between the rotational states of \(\text{CaF}\) not only reverses the magnetic field dependence of the Zeeman levels with \(M = +3/2\) and \(M = +1/2\), but also suppresses the Zeeman effect at high magnetic field.

The Zeeman splitting of the \((^3 \Pi_{3/2}, J = 5/2)\) state is illustrated in Fig. 4. The \(M = 3/2\) state is determined by three components arising from the coupling of the \(J = 3/2, J = 5/2\) and \(J = 7/2\) states, while the maximally stretched \(M = 5/2\) state is determined by the interaction of only two rotational states \(J = 5/2\) and \(J = 7/2\). The Zeeman energy variation of the \(M = 3/2\) and \(M = 5/2\) states is, therefore, dramatically different. The energy of the \(M = 3/2\) state rises monotonically with the magnetic field, while the energy of the \(M = 5/2\) states increases at low fields, passes through a maximum and decreases at high fields, similarly to the energy variation of the maximally stretched state in the \(J = 3/2\) manifold of levels. The energy of the \(M = 5/2\) state is larger at low fields, while the \(M = 3/2\) state is the highest energy Zeeman level at high fields. This indicates that for the rotational states with \(J > \Omega\) in \(\Pi\)-state molecules, there will
always be at least one low-field seeking state at high fields. The ligand-field model results are again in good agreement with the accurate calculation.

The dashed lines of Fig. 3 represent the Zeeman spectrum of a $^2\Pi_{3/2}, J=3/2$ molecule with an infinitely large rotational constant. Because the coupling between rotational levels appears to have a dramatic influence on the Zeeman effect in CaF, the Zeeman effect in $^2\Pi_{3/2}$ molecules is expected to be sensitive to the magnitude of the molecular rotational constant. Figure 5 presents the Zeeman spectrum of a $^2\Pi_{3/2}, J=3/2$ molecule as a function of the rotational constant. A decrease in the rotational constant by a factor of 2 shifts the maximum in the energy variation of the $M = 3/2$ level to lower magnetic fields, while an increase by a factor of 2 produces the same energy levels as in the infinite rotational constant limit at magnetic fields less than 2 Tesla. The Zeeman spectrum of a molecule with a rotational constant similar to that of the OH molecule ($\sim 55$ times larger than the rotational constant of CaF) is determined almost entirely by the diagonal matrix elements (cf., Fig. 4) of the magnetic moment operator at $B=0–5$ Tesla. The Zeeman energy varies linearly with the field strength and the OH molecule is a good candidate for magnetic trapping experiments. We conclude that $^2\Pi_{3/2}$ molecules in the $J = 3/2$ state will not have any low-field seeking states in the limit of small rotational constant so only molecules with rotational constants larger than twice the rotational constant of CaF may be readily amenable for magnetic trapping.

**SUMMARY**

We have presented a measurement of the frequency shift for the $(X^2\Sigma^+, N=0, M=1/2)\rightarrow(A^2\Pi_{3/2}, J=3/2, M=3/2)$ and $(X^2\Sigma^+, N=0, M=-1/2)\rightarrow(A^2\Pi_{3/2}, J=3/2, M=-3/2)$ transitions in CaF molecules over a wide interval of external magnetic fields. A rigorous analysis of the measurement yields the Zeeman spectrum of the CaF molecule in the ground $X^2\Sigma^+$ and excited $A^2\Pi_{3/2}$ states. We have developed a model of the Zeeman effect based on the ligand-field theory of molecular structure and shown that it is accurate for CaF in the interval of magnetic fields 0–5 Tesla. This demonstrates that the magnetic moment of the CaF($^2\Pi_{3/2}$) molecule is determined by the spin angular momentum of a single electron and the orbital motion of the valence electron around the Ca$^{2+}$ core. The ligand-field theory is an important method for the analysis of molecular structure; it can be especially useful for understanding the physics of molecules in Rydberg states. We have shown that the Zeeman effect in CaF($^2\Pi_{3/2}$) is largely determined by the coupling between the rotational levels of the molecule and that all Zeeman levels of CaF($^2\Pi_{3/2}$) are high-field seeking states at magnetic fields greater than 2.5 Tesla. An analysis of the Zeeman spectrum as a function of the molecular rotational constant indicates that all Zeeman levels of $^2\Pi_{3/2}$ molecules in the $J = 3/2$ state will be high-field seeking states in the limit of small rotational constant. Therefore, only $^2\Pi_{3/2}$ molecules with significant rotational constants (at least as large as twice the rotational constant of CaF) may be amenable to magnetic trapping.

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