

Rotational Zeeman Effect in ArHF

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The first observation of the rotational Zeeman effect in a van der Waals molecule is presented. The spectrometer used in this study is a Fourier-transform microwave spectrometer employing an evacuated Fabry-Perot cavity and a pulsed gas nozzle, both of which are placed inside the bore of a superconducting solenoid. The rotational Zeeman parameters for ArHF are $g_{\perp} = -0.005\,03(12)$ and $(\chi_{\parallel} - \chi_{\perp}) = -1.7(11) \times 10^{-30} \text{ cm}^3$. The molecular quadrupole moment is $Q_{\parallel} = 2.79(77) \times 10^{-26} \text{ statcoulomb cm}^2$.

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The rotational Zeeman effect is the observation of the effects of high magnetic fields on the rotational transitions of a molecule.¹ This effect results from an interaction of a molecular magnetic dipole moment with the external field. For a molecule in the $^1\Sigma$ electronic state, the molecular magnetic moment arises from the rotating charges that comprise the molecule, this characterized by the molecular g tensor, and from an electronic response of the molecule proportional to the applied field, this characterized by the molecular magnetic-susceptibility tensor. In general, when these tensors are averaged over the rotational motion of the molecule, the three independent diagonal elements of the g tensor and the two independent magnetic-susceptibility anisotropies are measured. For a linear molecule we measure the perpendicular g value, g_{\perp} , and the single independent magnetic-susceptibility anisotropy, $\chi_{\parallel} - \chi_{\perp}$. When the molecular Zeeman data are combined with structural data, dipole moments and quadrupole moments of molecules can be calculated,² which in turn can be used to obtain experimental values of the one-electron properties $\langle r \rangle$ and $\langle r^2 \rangle$. From a large body of data which has been collected, semiempirical theories have been used successfully to predict dipole moments,³ quadrupole moments,³ and the diagonal elements of the magnetic-susceptibility tensor.⁴ These theories have provided a quantitative measure of electron delocalization and aromaticity.⁴

Recently the properties of very weakly bound molecular complexes (van der Waals molecules) have come under intense experimental and theoretical study. One experimental method, the microwave spectroscopy of molecular beams, has provided a large body of structural and electronic data on van der Waals molecules of the type $X\text{-HY}$ (where $X = \text{Ne, Ar, Kr, Xe, and Y} = \text{F, Cl, Br}$).⁵⁻⁷ These studies have provided some

insight into the nature of the very weak binding present in these systems but detailed understanding of the weak forces will benefit from new kinds of systematic studies of the electronic properties of weakly bound complexes. The study of the rotational Zeeman effect in van der Waals molecules represents a major step forward in obtaining this information. Accordingly we report the first observation of the molecular Zeeman effect in a van der Waals molecule: ArHF.

The spectrometer used in this study is a Fourier-transform microwave spectrometer employing a pulsed gas nozzle and an evacuated Fabry-Perot cavity. The nozzle and cavity are placed in the bore of a superconducting solenoid which generates the external magnetic field. This spectrometer, except for the molecular resonance region, is similar to a zero-field spectrometer designed and developed by Flygare and Balle three years ago.^{8,9} The major modification to the molecular resonance region was the construction of a vacuum chamber with a Fabry-Perot cavity to fit inside the 12-in. bore of the magnet and Dewar assembly (see Fig. 1). The mirrors are 8 in. in diameter with a spherical concave surface. The design specifications of the mirrors are given elsewhere.⁸ All the materials used in the Fabry-Perot cavity assembly are nonmagnetic to insure good field homogeneity between the mirrors. The magnet was designed to provide less than 2% inhomogeneity in field strength over 8 in. along the bore. The microwave connections allow either $\Delta M = 0$ or $\Delta M = \pm 1$ selection rules to be observed. Another major change was in the use of a modified Veeco model PV-10 piezoelectric valve¹⁰ instead of a solenoid valve as our pulsed gas nozzle. Additional valve modifications not mentioned in Ref. 10 included replacing all magnetic parts with their nonmagnetic equivalents. The ArHF complexes were made by expanding a gas mixture of 4% HF in Ar

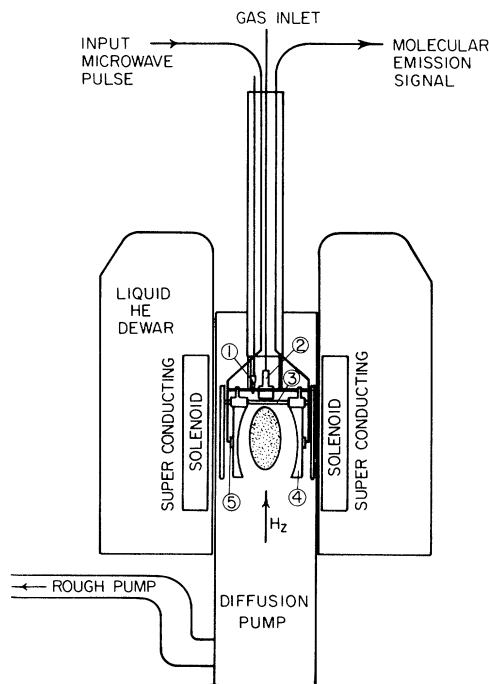


FIG. 1. Molecular resonance region of pulsed Fourier-transform Fabry-Perot microwave spectrometer. (1) Mirror tuning gear box; (2) pulsed piezoelectric valve with nozzle; (3) mirror support structure; (4) mirror; (5) microwave feedthrough. Note: Size of vacuum chamber is greatly exaggerated in this figure to show detail.

initially at room temperature and 10 psi through a 0.16-cm hole. As a result of the gas expansion only the ground vibrational state is sufficiently populated to allow the observation of microwave transitions. To get sufficient throughput with the piezo valve, a 400-V, 8-msec pulse was applied to the bimorph crystal. The spectrometer resolution is about 25 kHz.

ArHF was chosen for our first study because of the ease in interpreting its spectrum, since it will not be complicated by nuclear quadrupole interactions. The $J=1 \rightarrow 2$ zero-field spectrum of ArHF was measured. The nuclear spin-nuclear spin hyperfine splittings of HF were not resolved. The $J=1 \rightarrow 2$, $\Delta M = \pm 1$ transitions for ArHF were measured at three different field strengths: 16 993, 19 909, and 23 041 G. The field strength was determined by measuring the $J=0 \rightarrow 1$, $M=0 \rightarrow -1$, and $M=0 \rightarrow +1$ lines of OCS and fitting the field to the splitting of these lines with use of previously measured parameters.¹¹ The observed spectrum contained two peaks which result from the molecular magnetic moment in ArHF. These peaks are broadened by unresolved

splittings due to the magnetic-susceptibility anisotropy and nuclear spin-nuclear spin interactions. In the analysis of the data, the effects of nuclear spins were ignored. With use of an analytical expression given elsewhere,¹ the splitting between the two peaks can be expressed as

$$\Delta\nu(\text{ArHF}) = \pm 2H\mu_0 g_{\perp}/h, \quad (1)$$

where H is the magnetic field, μ_0 is the nuclear magneton, h is Planck's constant, and g_{\perp} is the perpendicular component of the molecular g value. The indeterminacy of the sign in Eq. (1) arises because the sign of a $\Delta M = |1|$ transition cannot be determined by means of plane-polarized radiation. Dividing both sides of Eq. (1) by $2H\mu_0/h$ and averaging our three splittings at three different fields yields $g_{\perp} = 0.005\,03(12)$. The magnetic-susceptibility anisotropy causes a shift in the average position of the two measured peaks from the zero-field line center. The analytical equations for the $J=1 \rightarrow 2$, $\Delta M = 1$ transitions were averaged over the susceptibility anisotropy splittings, where each line was weighted by its intensity factor to give

$$\nu_{\text{av}} = \nu_0 + (2.8/105)H^2(\chi_{\parallel} - \chi_{\perp}), \quad (2)$$

where ν_{av} is the average position of the two measured peaks, ν_0 is the zero-field line position, and $\chi_{\parallel} - \chi_{\perp}$ is the magnetic-susceptibility anisotropy. Equation (2) is linear in H^2 where the magnetic-susceptibility anisotropy is the slope, giving $\chi_{\parallel} - \chi_{\perp} = (-2.57 \pm 1.69) \times 10^{-10}$ MHz/G². To test the quality of the molecular Zeeman values, these parameters were used in a computer simulation of the spectrum which included the nuclear spin-nuclear spin interaction of HF, and were found to be satisfactory. The results of this comparison are shown in Table I. The translational Stark effect

$$\vec{E} = \vec{V} \times \vec{B}/c \quad (3)$$

has been ignored, where \vec{V} is the velocity of the gas, \vec{B} is the magnetic field strength, c is the speed of light, and \vec{E} is the electric field experienced at the molecule. We approximated the magnitude of the electric field under the worst possible conditions, that is the case where the velocity vector of the gas is perpendicular to the external field vector, which gave $E = 0.04$ statvolt/cm. This value was included in a full matrix program to calculate the spectrum, which leads to maximum errors of 3% for $\chi_{\parallel} - \chi_{\perp}$ and 0.1% for g_{\perp} . Since our reported errors for $\chi_{\parallel} - \chi_{\perp}$ and g_{\perp} greatly exceed the errors introduced due to

TABLE I. Molecular Zeeman splittings for the $J = 1 \rightarrow J = 2$ transition in ArHF^a.

Transition M	Magnetic M'	Magnetic field (G)	Observed (MHz)	Calculated ^b (MHz)	Difference ^c (kHz)
0	1	16 993(91)	12 260.633(2)	12 260.635	-2
0	-1		12 260.499(5)	12 260.505	-6
0	1	19 909(85)	12 260.646(7)	12 260.645	1
0	-1		12 260.495(4)	12 260.492	3
0	1	23 041(23)	12 260.655(5)	12 260.656	-1
0	-1		12 260.481(6)	12 260.479	2

^aZero-field transition measured at 12 260.571(3) MHz.^bWeighted average over the calculated unresolved hyperfine components including the HF spin-spin interaction.^cObserved-calculated.

neglecting the effects of Eq. (3), the translational Stark effect can be ignored.

Theoretical expressions for the molecular g value have been given elsewhere.¹² If we assume that the properties of Ar and HF are unchanged upon complexation, we can derive an expression for g_{\perp} which depends on the g_{\perp}^{HF} (Ref. 13) of free HF and a correction due to a shift in the center-of-mass position when HF complexes with Ar. The zero-order equation for g_{\perp}^{ArHF} is

$$g_{\perp}^{\text{ArHF}} = \frac{g_{\perp}^{\text{HF}} I^{\text{HF}} \langle 1 + \cos^2 \xi \rangle}{2I^{\text{ArHF}}} - \frac{2m_p R D_z^{\text{HF}} \langle \cos \xi \rangle}{|e| I^{\text{ArHF}}}, \quad (4)$$

where ξ is the instantaneous angle between the line that connects Ar to the center of mass of HF and the HF bond, and the brackets indicate that the enclosed function of ξ is averaged over the ground vibrational wave functions. Here I^{HF} and I^{ArHF} are the moments of inertia of HF (Ref. 14) and ArHF,⁵⁻⁷ R is the center-of-mass shift from HF to ArHF, and m_p , e , D_z^{HF} are mass of a proton, the electronic charge, and the electric dipole moment of HF.¹⁵ If we assume $\xi = \theta$ where θ is the angle between the HF bond and the a inertial axis (the difference between θ and ξ is a few tenths of a degree⁷), everything in Eq. (4) is known and we can calculate g_{\perp}^{ArHF} . If we take a structure for ArHF with the proton between Ar

and F, then D_z in Eq. (4) is positive and $g_{\perp} = -0.00435$. If we place the F between Ar and H, resulting in a negative sign for D_z^{HF} , $g_{\perp} = +0.01013$ is obtained. If we can expect that the zero-order equation for g will account for most of the observed value, the negative value for g is in far better agreement with experiment and theory than the positive value. Also the negative value of g is consistent with the isotopically determined structure of ArHF where the H is between the Ar and F.^{6,7} This strongly suggests that the sign of the dipole moment in ArHF is +ArHF-. Equation (4) predicts a value of g which is 14% below the observed value. The effect of including an induced dipole on Ar [calculated using E from a multipole expansion of HF (Ref. 7)] was included and was found to be small and aggravated the discrepancy, giving $g_{\perp} = -0.0040$. The molecular quadrupole moment for a linear molecule is given by

$$Q_{\parallel} = \frac{|e|}{m_p} g_{\perp}^{\text{ArHF}} I^{\text{ArHF}} + \frac{4mc^2}{|e|} (\chi_{\perp} - \chi_{\parallel}) \quad (5)$$

which yields $-2.79(77) \times 10^{-26}$ statcoulomb cm². From the quadrupole moment and the structure of ArHF we can get the second moment of the charge distribution anisotropy $\langle z^2 \rangle - \langle x^2 \rangle = 78.8 \times 10^{-16}$ cm². It is possible to get an estimate of $\langle z^2 \rangle - \langle x^2 \rangle$ for Ar, if one assumes that no exchange of electrons occurs between Ar and HF, by using the first-order expression:

$$\langle z^2 \rangle - \langle x^2 \rangle = (\langle z_0^2 \rangle - \langle x_0^2 \rangle)^{\text{HF}} \langle \frac{3}{2} \cos^2 \xi - \frac{1}{2} \rangle + 2r \langle z \rangle^{\text{Ar}} - 2R \langle z_0 \rangle^{\text{HF}} \langle \cos \xi \rangle + r^2 Z_{\text{Ar}} + R^2 Z_{\text{HF}} + (\langle z^2 \rangle - \langle x^2 \rangle)^{\text{Ar}}, \quad (6)$$

where $(\langle z_0^2 \rangle - \langle x_0^2 \rangle)^{\text{HF}}$ is the second moment of the charge distribution anisotropy in HF, r is the distance between Ar and the center of mass of ArHF, and $\langle z \rangle^{\text{Ar}}$ and $\langle z_0 \rangle^{\text{HF}}$ are the first moments of the charge distribution for Ar, which is along the axis from Ar to the center of mass of the HF and is obtained from the induced dipole of Ar, and for HF, which is along the HF bond axis and is calculated

from the dipole moment of HF. The total numbers of electrons for Ar and HF are denoted by Z_{Ar} and Z_{HF} , respectively. Equation (6) yields a result of $3 \times 10^{-17} \text{ cm}^2$ for $(\langle z^2 \rangle - \langle x^2 \rangle)^{\text{Ar}}$ where the error is as large as the value itself. The error arises from the measured value of $\langle z^2 \rangle - \langle x^2 \rangle$ in Eq. (6). This indicates that the electron cloud distortion cannot be determined within experimental error.

In conclusion, we have presented the first observation of the molecular Zeeman effect of a van der Waals molecule: ArHF. The molecular g_{\perp} value is $-0.00503(12)$ and $\chi_{\parallel} - \chi_{\perp}$ is $(-1.7 \pm 1.1) \times 10^{-30} \text{ cm}^3$. The molecular g value is approximately consistent with the value predicted by use of the electronic and magnetic properties of free Ar and HF, if one assumes a structure $\text{Ar} \cdots \text{HF}$. The quadrupole moment $Q_{\parallel} = -2.79(77) \times 10^{-26} \text{ statcoulomb cm}^2$. The new technique used here should be applicable to study the molecular Zeeman effect in any weakly bound complex that can be studied by pulsed Fourier-transform microwave spectroscopy in a Fabry-Perot cavity. Further investigation of the rotational Zeeman effect of $X\text{-HY}$ complexes is underway.

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Laser Production of a Very Slow Monoenergetic Atomic Beam

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With use of a resonant, counterpropagating laser beam the velocity of atoms in a neutral, thermal-sodium beam has been reduced to 40 m/s, or 4% of their initial velocity. These atoms have a kinetic energy comparable to the well depth of proposed optical traps. The "temperature" characterizing the atoms' relative motion was reduced to 70 mK.

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A single, free atom at rest would be the ideal spectroscopic sample. While laser cooling¹ has produced dramatic progress toward this goal for ions,² there has been relatively little progress

for neutral atoms. In earlier work³ we reported the first resonant laser deceleration of an atomic beam of neutral Na atoms.⁴ In this Letter we describe experiments in which we have deceler-