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MAGNETIC PROPERTIES OF METALLIC CLUSTERS

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The molecular beam deflection profile for sodium trimers Na_3 shows the familiar one Bohr magneton peaks astride a central peak of comparable intensity on the beam axis. The magnetism is attributed to the odd electron spin. Spin rotation and hyperfine interactions produce avoided crossings in the Zeeman diagram. Diabatic transitions occur at the avoided crossings if the beam traverses a region of rapidly changing transverse magnetic field. Results are given for Li_3, Na_3, and K_3, plus a number of mixed alkali trimers and larger sodium polymers.

1. INTRODUCTION

This report is an outgrowth of an attempt to study the properties of bare metallic clusters[1,2] in the range where the transition to crystalline solid behavior is expected to set in, e.g. for ~ 20 atoms per cluster. Initially, our intention was to investigate odd polymers, starting with the alkali trimers, in order to measure electron spin densities via hyperfine structure patterns in the electron spin resonance (ESR) spectra[3]. The ESR measurements on K_3 were unsuccessful because of the absence of the expected Stern Gerlach (SG) peaks in the deflection profile.

2. SPIN FLIPS

Following this we found that although SG peaks, corresponding to magnetic moments of 1 μ_B, do show up in the Na_3 profile, a central peak also appears, indicating the presence of a range of magnetic moments from zero to plus and minus one μ_B (see Fig. 1a). Further experiments on Na_3 in a deflecting magnet which contained a hole drilled vertically through the poles perpendicular to the beam, revealed an enhancement of the central peak (see Fig. 1b). This enhancement results from spin flips occurring in the drilled hole (where the magnetic field varies rapidly), which is located midway between the entrance and exit of the magnet. A spin flip at this point results in nearly compensating deflections in the two halves of the magnet. This shifts intensity in the deflection profile from the SG peaks to

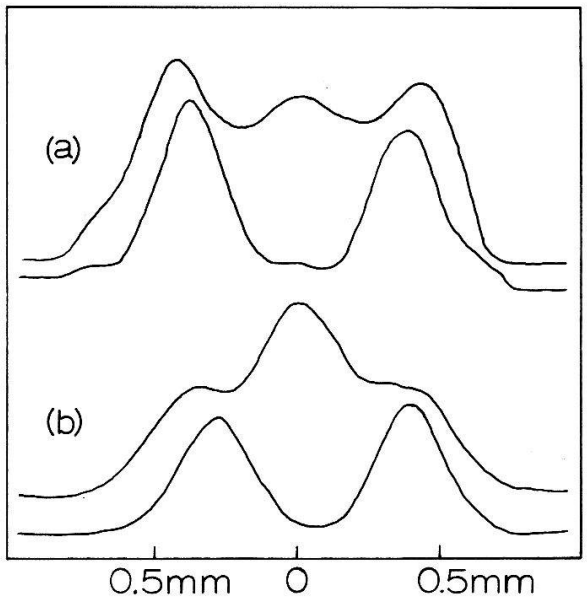

Fig. 1. Magnet "A" deflection profiles. (a) The Na_3 profile is superposed on an atom profile taken at 1/3 Na_3 deflecting field. Outer peaks represent 1 μ_B trimers. (b) Same as (a) but with drilled magnet, both at 2.5 kG. Large increase in central peak arises from spin reversals in the hole. In (a) relative intensity of low moment peak is approximately ½. For K_3 it is ~ 9/10; for Li_3 it is < 1/10.

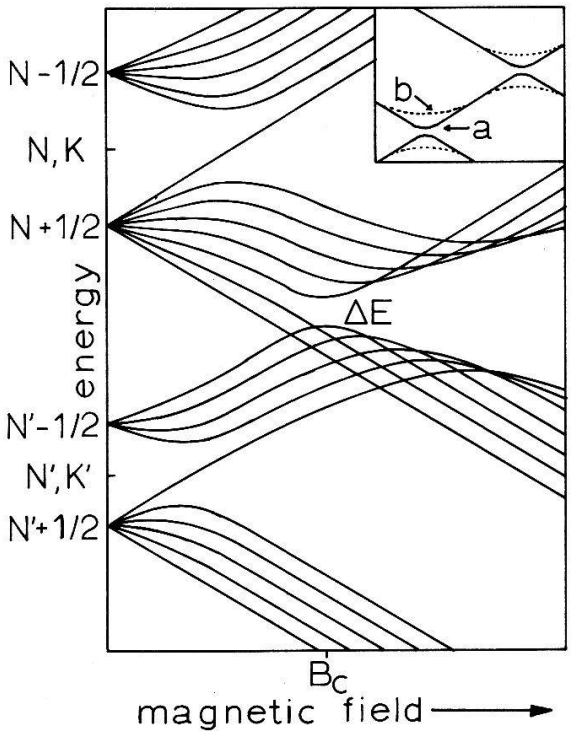

Fig. 2. Zeeman diagram. Simplified schematic patterns not to scale. Spin rotation interaction splits N levels. Avoided crossing shown at magnetic field B_c. Hyperfine splitting (not shown) produces multiple avoided crossings. Inserts a and b suggest origin of μ_B and low moment peaks, respectively. Principal state changing transitions occur at crossings like ΔE. Low moment fraction depends on number and widths of crossings.

the central peak. It is shown later that spin flips can also occur in the entrance or exit of a magnet[4]. These spin flips of course will constitute a background against which it is difficult to detect refocussed molecules in the projected molecular beam magnetic resonance (MBMR)[5] experiments.

3. AVOIDED CROSSINGS

The spin rotation coupling in the molecule results in avoided crossings[4,6] in the Zeeman diagram (see Fig. 2). In these regions transitions can occur if the rate of change of transverse deflecting field has the appropriate magnitude[7], estimated below. The avoidance of crossing is produced by certain level repulsions[8], notably those between levels of different rotational quantum numbers K or N, with $\Delta M_J = 0$. The location of the first crossing depends on the energy difference between the neighboring K or N levels at zero field.

In the following we make order of magnitude estimates, according to a possible model, which must suffice until the larger task of calculating the energy level structure of the molecule has been completed. Assuming for the moment that Na_3 is a symmetric top, the moment of inertia is readily determined. A study of the level structure indicates that in the range N = 0 - 80 the average spacing is approximately equal to a rotation constant $R \sim 0.1\ cm^{-1}$. Thus we expect to find the first avoided crossings at applied magnetic fields of the order of 1 kG, which is in our experimental range. This figure will vary somewhat with N and K, so molecules in different levels will encounter crossings at different magnetic fields. From time of flight profile measurements we estimate that translational temperatures are around 80 K, and that the main molecular populations are in the range around N = 20.

4. MAGNETIC MOMENT DISTRIBUTION

The observed deflection profiles are directly related to a distribution of magnetic moments, which at any applied field depends on the level populations and the slopes of the level diagram at the chosen field. The observed magnetic moments will be small in the vicinity of an avoided crossing, and approach 1 μ_B in regions remote from any crossing (see insert in Fig. 2). In addition to the avoided crossing referred to above, associated with the spin rotation coupling, there is another set of crossings associated with the hyperfine structure (not shown in Fig. 2). Together they determine

the level slopes to be probed by the applied field. The important transitions are determined mainly by the first crossing in the 1 kG field range, which serves to convey a molecule from a level in one N,K manifold of levels to a different N',K' manifold with a different distribution of hyperfine related crossings, causing the observed distribution of moments, even at the same field, to be changed. The spin flips in the magnet hole was the first evidence for such transitions. Other examples follow below.

We may estimate the energy gap at the avoided crossing which provides the above first transitions by an argument which is a modification of the Landau-Zener theory[7]. Let a molecule with velocity v traverse a crossing of energy gap ΔE, whose equivalent width in field units is $\Delta B \sim \Delta E/\mu_B$. The traversal will be adiabatic if $\Delta t > \hbar/\Delta E$, and combining the above we have for the adiabatic traversal $(\Delta E)^2 > \hbar\mu_B (\partial B_z/\partial x)v$. Typical experimental values for the quantities are velocity in the x direction $v = 1.5 \times 10^5$ cm/s, gradient of the transverse field along the beam $\partial B_z/\partial x = 5 \times 10^3$ G/cm. This establishes ΔE in the range around 30 MHz. Since the flipping in the hole involves a double pass back and forth through the same crossing, we see that a net transition occurs only if the crossing is mixed, i.e. neither strictly diabatic nor strictly adiabatic. Thus a net spin flip will occur if the transition is diabatic on one pass and adiabatic on return, or vice versa.

5. DOUBLE MAGNET EXPERIMENTS

Further evidence for the nature of transitions is provided by double magnet experiments (neither magnet contains a drilled hole), in which the beam is spread out into its typical profile (Fig. 1a) by the first "A" magnet. A collimator slit then selects a narrow portion of the profile to pass through the "B" magnet, which analyzes the moment distribution of the selected portion. We refer to the areas in a profile as follows: low moment (LM) as in the central peak of Fig. 1a; and mu Bohr (MB) as in the outer peaks of the same figure. In the single magnet profile of Fig. 1a the measured area for the MB is approximately one half of the whole. If the selector collimator is set on the + MB peak (excluding the low moments), the output is divided approximately as follows: 1/2 +MB, 1/4 -MB, and 1/4 LM. In a related experiment the selector collimator is set on beam center (completely rejecting all 1 MB molecules emerging from the "A" magnet), and

the output of the analyzing "B" magnet is approximately as follows: 3/4 LM, 1/8 +MB, 1/8 -MB. It is clear that any narrow element of the moment distribution of a single magnet profile is capable of transforming so as to reproduce all moments in the profile, in varying proportions. The above figures are for deflecting fields in the range 1 - 3 kG, and the quoted fractions vary somewhat with field. An analysis of the transition probabilities is consistent with these results.

The foregoing is not surprising in view of the nature of the Zeeman diagram containing many with avoided crossings, whose spacings depend on the particular N,K manifold which is populated, and including many populated levels the slopes of which are to be probed by an analyzing magnet. In still further experiments the two magnets were set up as before to select the MB out of "A" (see Fig. 3). The +MB peak and the -MB (refocussed) peaks are easily seen, with a LM population between. The result is that some 1/4 of the +MB intensity shifts to -MB when the homogeneous "C" field is turned on at 8 kG. Transitions involved here occur at the exit of the "A" magnet, at the entrance to the "B" magnet, and at both the entrance and exit of the "C" magnet. The interposition of the third "C" magnet forces the molecules to traverse the mixed avoided crossings twice more, thus increasing the chance of a net spin flip with four passes instead of two.

We may inquire into differences among the alkali trimers implied by the above model. In particular, in view of the foregoing, why is it that the potassium trimer K_3 behaves so differently from Na_3? In order to determine the fraction of LM component, comparing Na_3 and K_3, we estimate roughly the fraction of space along a Zeeman level which is occupied by crossings. Assuming applied fields larger than the relevant couplings, this fraction will vary as $a(s)\lambda/R$, where $a(s)$ is the hyperfine coupling constant, λ is the atomic spin orbit coupling constant (assumed to be proportional to the spin rotation coupling constant) and R is the average rotation constant referred to earlier. In this way the fraction of the LM component for K_3 is approximately double that for Na_3, in agreement with the experiments. The preliminary results show that the LM fraction is probably less than 1/10 for Li_3, which is also consistent with this scaling model.

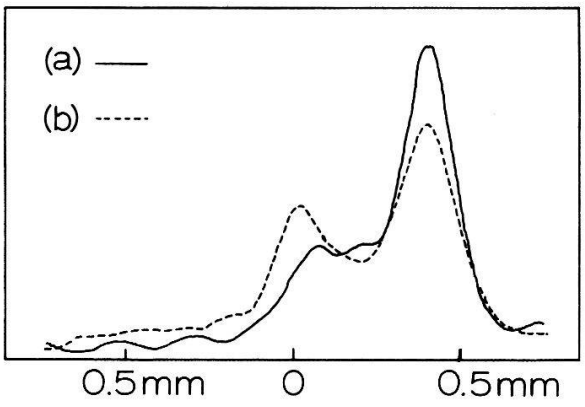

Fig. 3. Double magnet profiles. The +1 μ_B trimers are selected after deflection in the "A" magnet. (a) The 1 μ_B peak near +0.5 mm is from a second deflection in the "B" magnet. The refocussed peak near zero (beam center) arises from 1 μ_B spin reversals at exit of "A" and entrance of "B". (b) Homogeneous "C" magnet turned on to 8 kG. Note the significant increase in refocussed intensity and corresponding decrease in double deflected intensity.

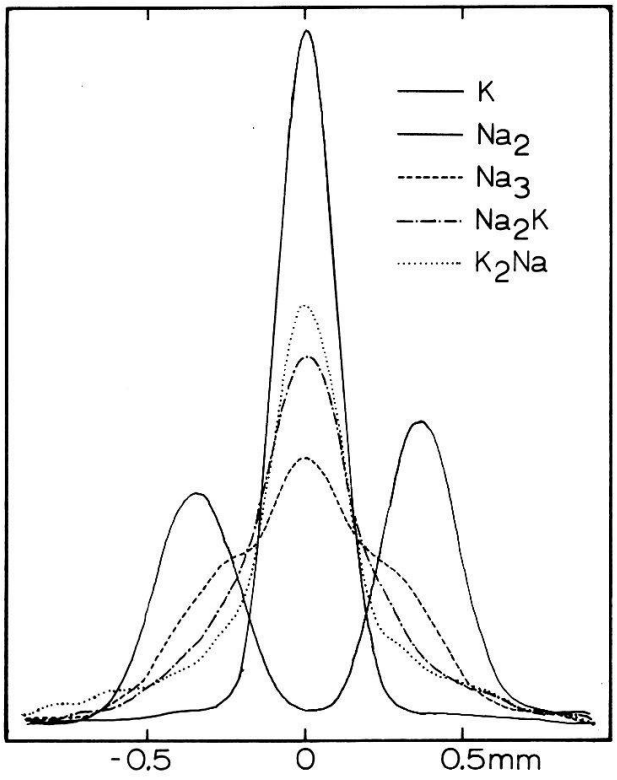

Fig. 4. Mixed molecules. Several trimer profiles scaled so the 1 μ_B peaks lie at deflections around 0.3 mm. Resolution is indicated by the Na_2 central peak. Stern Gerlach peaks are for K atoms. The low moment component increases in the series Na_3, Na_2K, K_2Na, (K_3, not shown). Other molecules show further reduced magnetism with increasing mass.

6. POLYMERS AND MIXED MOLECULES

Results were also obtained for a number of mixed alkali molecules and for Na polymers up to Na_7. Some of the results are indicated in the profiles of Fig. 4. The trend is consistent with the above scaling, with a general upward trend in LM fraction as the molecular mass increases, for example in the trimer series: Na_3, Na_2K, NaK_2, K_3. Preliminary results on Li_3 and Li_2Na are generally consistent with the proposed pattern. Several other polymers were investigated, either by recording profiles, as in Fig. 4, or by observing the decrease in the magnitude of the central peak when a deflecting magnet is turned on. The strength of the magnetism observed in the following generally decreases with molecular weight, because the throwout power decreases with mass, and also because the LM fraction increases with mass: Na_5, Na_7, Na_2K, Na_4K, Na_6K. We observe no magnetism, to the accuracy of the experiments, in the following even molecules: Na_2, K_2, K_4, Na_3K, and Na_5K.

7. CONCLUSIONS

The adoption of the molecular beam method for these investigations was motivated by a desire to eliminate substrate interactions[9,10] which affect molecules supported in a matrix. Although the molecular beam experiments have their own difficulties, it is already clear that they reveal molecular properties which might otherwise be suppressed in the matrix. As for the original aim, to investigate the larger clusters containing twenty or more atoms, there is considerable promise, particularly for the light species of lithium, at least insofar as deflection sensitivity is concerned. There remain some conditions under which hyperfine measurements may be made with the conventional MBMR method. Direct experiments on transitions at the avoided crossings are more promising[6]. We are setting up experiments to perform resonance experiments in the radio frequency range, with the RF excitation taking place in the "C" magnet.

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