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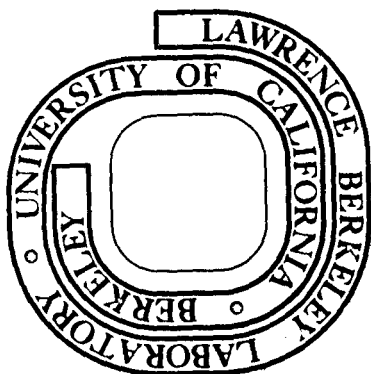
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THE MAGNETIC MOMENT OF Se_2

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ABSTRACT

Atoms of the oxygen group form diatomic molecules with a multiplet

ground state. Of these, O_2 and S_2 conform to Hund's (b) coupling and

have an appreciable magnetic moment, whereas Te_2 is better described as

having case (c) coupling with a very small effective magnetic moment.

Although the Se_2 molecule is intermediate between these two cases, it is

closer to case (c) than to case (b). A method of calculating the magnetic

moment and Zeeman effect of a molecule of this series with Hund's case (c)

coupling is described and applied to Se_2. The calculations result in a

value of 5.97×10^{-2} Bohr magnetons for the mean effective moment of the

Se_2 molecule at 1000 K. in a field of 14 kilogauss. This value was found

to be consistent with the results obtained experimentally by the use of

a molecular beam deflection technique similar to that of Stern and Gerlach.

INTRODUCTION

Elements of the oxygen family are among the relatively few whose atoms have an even number of electrons and yet form diatomic molecules with a multiplet ground state. Lighter members of this series of diatomic molecules, such as O_2 and S_2, appear to conform to Hund's case (b) coupling, but as the molecular weight increases the coupling shifts toward Hund's case (c).[1] For O_2 and S_2 the ground state can be described as a $^3\Sigma_g^-$ state, using the notation appropriate to Hund's case (b). For progressively heavier members of the series two of the components of the triplet move up in energy relative to the third until for Te_2 they are some 2800 cm^{-1} higher.[2] The ground state is then the low lying singlet denoted the 0_g^+ state, and the two higher components constitute the doubly degenerate 1_g state. One effect of the change in the type of coupling is the reduction in the effective magnetic moment of the molecule which results from the stronger coupling of the spin with the internuclear axis.

As might be expected, Se_2 is intermediate between O_2 and S_2 on the one hand and Te_2 on the other. The splitting between the 0_g^+ and the 1_g states, as determined by Barrow and coworkers from spectroscopic measurements,[3] is 366.6 cm^{-1}. The 1_g state will therefore have an appreciable population above 500 K.

A previous attempt in this laboratory to measure the magnetic moment of the Se_2 molecule by means of the technique of Stern and Gerlach failed to detect a measurable moment.[4] This low moment was erroneously attributed to a large energy gap between the 0_g^+ and the 1_g states. Since then we have carried out a calculation which indicates that the effective magnetic moment of Se_2 is of the order of several hundredths of a Bohr magneton,

and an attempt has been made to verify this value experimentally with an

improved apparatus. What follows is a description of the calculations and

the experimental results.

CALCULATION OF THE ZEEMAN EFFECT AND THE MAGNETIC MOMENT

If a molecule in a particular quantum state with a magnetic moment $\vec{\mu}$ is subjected to a magnetic field $\vec{H}$, the change in energy of that state, ΔE, is given by the relation, $\Delta E = -\mu_{eff} H$, where μ_{eff} is the component of $\vec{\mu}$ in the direction of the field. ΔE is then the energy associated with the Zeeman effect. Calculations of ΔE and μ_{eff} for the ground electronic states of Se_2 were carried out using the technique outlined by Hougen.[5]

In the absence of a magnetic field, the Hamiltonian for the Se_2 molecule consists of two parts, the rotational term and the spin-spin interaction:

$$\mathcal{H} = B \ [(J_x-S_x)^2 + (J_y-S_y)^2] + 2\lambda(\vec{n}\cdot\vec{S})^2,$$

$$= B \ [J^2-J_z^2 + S^2-S_z^2] - B(J_+S_- + J_-S_+) + 2\lambda S_z^2,$$

where B, J and S are the rotational constant, the total angular momentum operator and the spin operator, respectively. The subscripted quantities J_x, J_y, J_z, S_x, S_y and S_z are operators corresponding to the components of the angular momentum and spin in the coordinate directions, and the operators J_+, J_-, S_+ and S_- are defined by means of the relations,

$$J_\pm = J_x \pm i \ J_y; \ S_\pm + S_x \pm i \ S_y.$$

These refer to molecule-fixed axes with the z direction along the inter-nuclear axis. The unit vector along the internuclear axis is $\vec{n}$, and λ is a constant equal to half the separation in energy between the 0^+ and 1 states.

We use as basis functions the Hund's case (a) wave functions denoted by $|\Lambda S\Sigma;\Omega JM\rangle$, the notation being that of Hougen,[5] with the symbols having their usual significance relative to the various constituents of the angular momentum. For the states of Se_2 under consideration, $\Lambda = 0$, $S = 1$, and

$\Sigma = \Omega = 0$ or ± 1. Matrix elements of the operators for these basis functions are also given by Hougen.[5] The energy levels and first order wave functions are given in Table 1. State 1 of the table corresponds to the 0_g^+ state, and states 2 and 3 to the 1_g state. For homonuclear diatomic molecules, only level with odd N are allowed, where N is the total angular momentum exclusive of spin. Hence J will be even for the rotational levels of state 1 ($J = N - 1$) and state 3 ($J = N + 1$), and odd for those of state 2 ($J = N$).

We now introduce the magnetic field as a perturbation. Only states of the same parity and nuclear statistics will be mixed by the magnetic field. The appropriate selection rule is $\Delta J = 0, \pm 1$. For the 0_g^+ state $\Delta J = 0$ is sufficient since states of proper symmetry with J differing by ± 1 are some 367 cm^{-1} higher. For the 1_g state, however, states corresponding to $\Delta J = \pm 1$ with the proper symmetry are only a few wave numbers distant, so the second order Zeeman contributions must be considered as well. The perturbing Hamiltonian is,

$$\mathcal{H}' = 2\mu_B H S_Z,$$

where μ_B is the Bohr magneton and S_Z the projection of the spin in the direction of the field, given with reference to laboratory-fixed coordinates. A transformation to molecular coordinates is carried out by means of the direction cosine matrix α:

$$\mathcal{H}' = 2\mu_B H[\alpha_{Zz}S_z + 1/2(\alpha_{Z+}S_- + \alpha_{Z-}S_+)].$$

The α matrix elements are given by Townes and Schawlow[6] and by Hougen.[5]

Table 2 lists the matrix elements of S_Z in terms of the basis function set. From these and the wave functions of Table 1 the first order contributions to the magnetic moments of the three electronic states are found to be the expressions of equations (1). The first order Zeeman effect is the

product of these moments and the magnetic field.

$$\mu_1(J,M) = 4M\delta\mu_B,$$

$$\mu_2(J,M) = \frac{2M}{J(J+1)}\mu_B, \tag{1}$$

$$\mu_3(J,M) = 2M\left[\frac{1}{J(J+1)} - 2\delta\right]\mu_B.$$

In these expressions $\delta = B/\lambda = 4.90 \times 10^{-4}$.

Since the average value of M for a given value of J is zero, the mean moment is zero also. However an estimate of the mean absolute magnitude of the moment can be obtained by substituting for M its mean absolute value, $J(J + 1)/(2J + 1)$, summing or integrating over J, and dividing by the rotational partition function (approximately 3860 at 1000 K.). The values thus obtained are, in hundredths of a Bohr magneton, 7.63 for state 1, 2.01 for state 2 and 6.64 for state 3, at 1000 K. At this same temperature the mean overall value for the equilibrium mixture of the three states would be 5.83 $\times 10^{-2}$ Bohr magnetons.

For the 1_g states (states 2 and 3) the second order contributions must also be considered for the reasons mentioned previously. The Hamiltonian is unchanged and the second order terms for the magnetic moment are given by relations of the form,

$$\mu_2'(J,M) = 4\mu_B^2 H \left[\frac{<2;J,M|S_z|3;J-1,M>^2}{E_2(J) - E_3(J-1)} + \frac{<2;J,M|S_z|3;J+1,M>^2}{E_2(J) - E_3(J+1)}\right].$$

A similar expression gives $\mu_3'(J,M)$, except that the number labels are interchanged on the energies and on the spin matrix elements. In these expressions the electronic part of each state is labelled by the number of the state only. The energies are those of Table 1. The matrix elements can be evaluated from Tables 1 and 2 with the following results:

$$\mu_2'(J,M) = \left[\frac{T(J+1,M)}{E_2(J) - E_3(J+1)} \left(\frac{1}{J+1} - \delta \right)^2 \right.$$

$$\left. + \frac{T(J,M)}{E_2(J) - E_3(J-1)} \left(\frac{1}{J} + \delta \right)^2 \right] 4\mu_B^2 \, H,$$

$$\mu_3'(J,M) = \left[\frac{T(J+1,M)}{E_3(J) - E_2(J+1)} \left(\frac{1}{J+1} + \delta \right)^2 \right.$$

$$\left. + \frac{T(J,M)}{E_3(J) - E_2(J-1)} \left(\frac{1}{J} - \delta \right)^2 \right] 4\mu_B^2 \, H,$$

where

$$T(J,M) = \frac{(J+1)(J-1)(J+M)(J-M)}{(2J+1)(2J-1)}$$

$$= \frac{(J^2-1)(J^2-M^2)}{4J^2-1} \, .$$

Even for a field of 10 kilogauss these second order moments are considerably smaller than the first order moments. Since they are functions of M^2 rather than M they are independent of the sign of M and so will not be symmetric about zero as are the first order moments.

From the above it is evident that the magnetic moment and the Zeeman splitting of the Se_2 molecule are determined primarily by the first order perturbation terms. Although a few molecules will have a moment of the order of one Bohr magneton, e.g. those with J = 1, M = 1, in the second electronic state, most will have a moment considerably smaller.

The distribution of total moments among the molecules at 1000 K. and a field of 14 kilogauss was calculated by means of a computer and the results are shown in the graph of Fig. 1. This shows the predominance of very low values as well as the slight skewness caused by the second order contributions. For each of the electronic states the mean absolute value of the moment was also calculated as was the mean absolute moment of the equilibrium mixture of states. The values are only slightly different from the first order moments

calculated previously. Given in hundredths of a Bohr magneton, the mean

absolute value for state 1 is 7.67, for state 2, 2.29, for state 3, 6.75,

and for the equilibrium mixture, 5.97.

EXPERIMENTAL

The apparatus used in these investigations, shown in Fig. 2, is essentially that described previously,[4] except that a chopper and lock-in amplifier have been added and the collimating channel has been replaced by an adjustable slit. In the same manner as before, measurements of the beam profile obtained with the magnet on were compared with measurements obtained with the magnet off. The slit width of 0.016 in. (0.041 cm) was approximately two thirds the width used previously. Cadmium selenide heated to 1125 (±5) K. provided the beam of Se_2 molecules. The magnet field strength and gradient were 14 kilogauss and 55 kilogauss/cm respectively. Ten scans were made of the beam profile with the magnet off and an equal number with the magnet on, each scan consisting of 22 individual measurements.

Because of a small variation in beam position and intensity with time in the course of a run, and also because not all the scans were made at the same time, it was necessary to center and normalize the data for each scan. By means of a computer a curve was fitted to the measurements of the undeflected beam (i.e., those made with the magnet off) using the method outlined by Deming.[7] The curve used was a truncated Fourier series of the form,

$$I(x) = a_0 + a_1 \cos[\omega(x - x_0)] ,$$

where x is the coordinate along the width of the beam. This curve provided a reasonable fit to the theoretical beam profile. Once the values of a_0, a_1, ω and x_0 which gave the best fit were found, these were used to adjust the data. The centering consisted simply of subtracting x_0 from each of the position readings so that the beam profile was effectively centered at x = 0. The normalization involved two steps: First, the quantity $(a_0 - a_1)$ was subtracted from the intensity measurements so that these profile intensities

were referred to a zero base line. Next the intensities were multiplied

by the factor $50/a_1$ to give the undeflected beam profile a nominal maximum

of 100. The width of the profile was also adjusted by means of the parameter

ω which is equal to the quantity π/w where w is the width of the profile

at half the maximum intensity. Multiplying the position values by the factor

$48\omega/\pi$ resulted in a profile with w nominally equal to 48 thousandths of an

inch (0.122 cm). Although the parameters used in these adjustments were

obtained from measurements of the undeflected beam profiles only, the correc-

tions were applied to data obtained with the magnet on as well.

The ten pairs of scans resulting from the adjustment procedure were then

averaged by means of a graphic method. First, the adjusted data for each

scan were plotted and the points connected by straight lines to give a line

plot like that of Fig. 3. Readings were then taken from the plot at intervals

of 0.004 in. (0.01 cm) and the ten readings for each position were averaged.

This was done separately for the undeflected beam and for the deflected beam.

The result of this is shown in Fig. 4. The standard deviation of either

curve is 3 to 4 units for the center portion, increasing to 5 to 6 units

for the extremities.

In the undeflected profile a bump or shoulder is present at a distance

of about 40 thousandths of an inch (0.1 cm) to the left of beam center.

Since this is the position of one of the magnet polepieces it seems likely

that interference or scattering from this polepiece is responsible. We

have no explanation for the lack of this feature on the other profile. The

slight asymmetry in the deflected beam profile is caused by the non-uniform

field gradient.

The simplest method of comparing the experimental results with the theo-

retical ones is to calculate the decrease in signal intensity at the center of the beam which would result from the deflection of Se_2 molecules by the magnetic field.[8] For a distribution of moments such that of Fig. 1 the problem can be managed by a computer. Under the experimental conditions given above the signal should decrease by about 11% at beam center when the magnet is on. The experimentally obtained decrease shown in Fig. 4 is 7.5 (±4.5)%, which is within experimental error. Although the distribution of Fig. 1 is for a temperature of 1000 K. and the measurements were taken at 1125 K, the effect of the temperature difference should be well within experimental error. In any case a correction for this difference would tend to improve the agreement.

DISCUSSION

From the results reported here it appears that the magnetic moment of a diatomic molecule which conforms fairly closely to Hund's case (c) in its coupling, such as Se_2, can be calculated with reasonable accuracy by the method outlined. It is clear from the theoretical results that the small effective moment of the Se_2 molecule as compared with S_2 or O_2 is due primarily to a change in the type of coupling rather than to a shift in the relative populations of the electronic states caused by the large differences in the energies of those states.

The extent to which the change in the type of coupling affects the magnetic moment can be seen clearly by contrasting the results obtained with Se_2, shown in Fig. 4, with some results obtained in this laboratory with S_2, shown in Fig. 5. Although the experimental conditions for the S_2 measurements were somewhat different (H = 5 kgauss, ∇H = 27 kgauss/cm, T = 965 K, slit width = 0.010 in. = 0.025cm), the difference between the two sets of results is due primarily to the difference in magnetic moments. The data of Fig. 5 show a difference of 60% in the intensities at the beam center, which indicates a mean absolute magnetic moment of at least 0.3 Bohr magnetons, a value five times that of Se_2.

The calculational method outlined here and the formulae can be applied directly to other diatomic molecules consisting of atoms from the oxygen family, provided that the value of $\delta = B/\lambda$ is reasonably small and that the rules concerning hetero- and homo-nuclear molecules are observed.

ACKNOWLEDGEMENT

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Table 1. Wave Functions and Energies of the 0_g^+ and 1_g States of Se_2

State	Wave Functions	Energies
1 (0_g^+)	$\lvert 1;JM \rangle = \lvert 010;0JM \rangle + \frac{\varepsilon(J)}{\sqrt{2}}(\lvert 011;1JM \rangle + \lvert 01-1;-1JM \rangle)$	$E_1(J) = B[J(J+1)+1] + \lambda - [(\lambda-B)^2 + 4B^2J(J+1)]^{1/2}$
2 (1_g)	$\lvert 2;JM \rangle = \sqrt{\frac{1}{2}}(\lvert 011;1JM \rangle - \lvert 01-1;-1JM \rangle)$	$E_2(J) = BJ(J+1) + 2\lambda$
3 (1_g)	$\lvert 3;JM \rangle = \sqrt{\frac{1}{2}}(\lvert 011;1JM \rangle + \lvert 01-1;-1JM \rangle) - \varepsilon(J)\lvert 010;0JM \rangle$	$E_3(J) = B[J(J+1)+1] + \lambda + [(\lambda-B)^2 + 4B^2J(J+1)]^{1/2}$

$\lambda = 183.3 \text{ cm}^{-1}$; $B(0_g^+) = 0.08977 \text{ cm}^{-1}$; $B(1_g) = 0.08997 \text{ cm}^{-1}$; from references 1 and 3.

$\varepsilon(J) = \frac{2B\sqrt{J(J+1)}}{\lambda - B}$

Table 2: Elements of the S_z Matrix: $\langle 01\Sigma';\Omega'J'M' | S_z | \Sigma;\Omega JM \rangle$

Σ'	$\Sigma = -1$	$\Sigma = 0$	$\Sigma = +1$
		$J' = J+1$	
-1	$-\dfrac{1}{J+1}\left[\dfrac{J(J+2)(J+M+1)(J-M+1)}{(2J+1)(2J+3)}\right]^{1/2}$	$\dfrac{1}{J+1}\left[\dfrac{(J+1)(J+2)(J+M+1)(J-M+1)}{2(2J+1)(2J+3)}\right]^{1/2}$	0
0	$-\dfrac{1}{J+1}\left[\dfrac{J(J+1)(J+M+1)(J-M+1)}{2(2J+1)(2J+3)}\right]^{1/2}$	0	$\dfrac{1}{J+1}\left[\dfrac{J(J+1)(J+M+1)(J-M+1)}{2(2J+1)(2J+3)}\right]^{1/2}$
$+1$	0	$-\dfrac{1}{J+1}\left[\dfrac{(J+1)(J+2)(J+M+1)(J-M+1)}{2(2J+1)(2J+3)}\right]^{1/2}$	$\dfrac{1}{J+1}\left[\dfrac{J(J+2)(J+M+1)(J-M+1)}{(2J+1)(2J+3)}\right]^{1/2}$
		$J' = J$	
-1	$\dfrac{M}{J(J+1)}$	$\dfrac{M}{[2J(J+1)]^{1/2}}$	0
0	$\dfrac{M}{[2J(J+1)]^{1/2}}$	0	$\dfrac{M}{[2J(J+1)]^{1/2}}$
$+1$	0	$\dfrac{M}{[2J(J+1)]^{1/2}}$	$\dfrac{M}{J(J+1)}$
		$J = J-1$	
-1	$-\dfrac{1}{J}\left[\dfrac{(J+1)(J-1)(J+M)(J-M)}{(2J+1)(2J-1)}\right]^{1/2}$	$-\dfrac{1}{J}\left[\dfrac{J(J-1)(J+M)(J-M)}{2(2J+1)(2J-1)}\right]^{1/2}$	0
0	$\dfrac{1}{J}\left[\dfrac{J(J+1)(J+M)(J-M)}{2(2J+1)(2J-1)}\right]^{1/2}$	0	$-\dfrac{1}{J}\left[\dfrac{J(J+1)(J+M)(J-M)}{2(2J+1)(2J-1)}\right]^{1/2}$
$+1$	0	$\dfrac{1}{J}\left[\dfrac{J(J-1)(J+M)(J-M)}{2(2J+1)(2J-1)}\right]^{1/2}$	$\dfrac{1}{J}\left[\dfrac{(J+1)(J-1)(J+M)(J-M)}{(2J+1)(2J-1)}\right]^{1/2}$

Note: $\Omega=\Sigma$, $\Omega'=\Sigma'$ in all cases.

FIGURE CAPTIONS

Fig. 1.   Distributions of magnetic moments of the Se_2 molecule in a field of 14 kgauss.

Fig. 2.   Diagram of the apparatus.

Fig. 3.   Normalized and centered beam profile for scan No. 7.

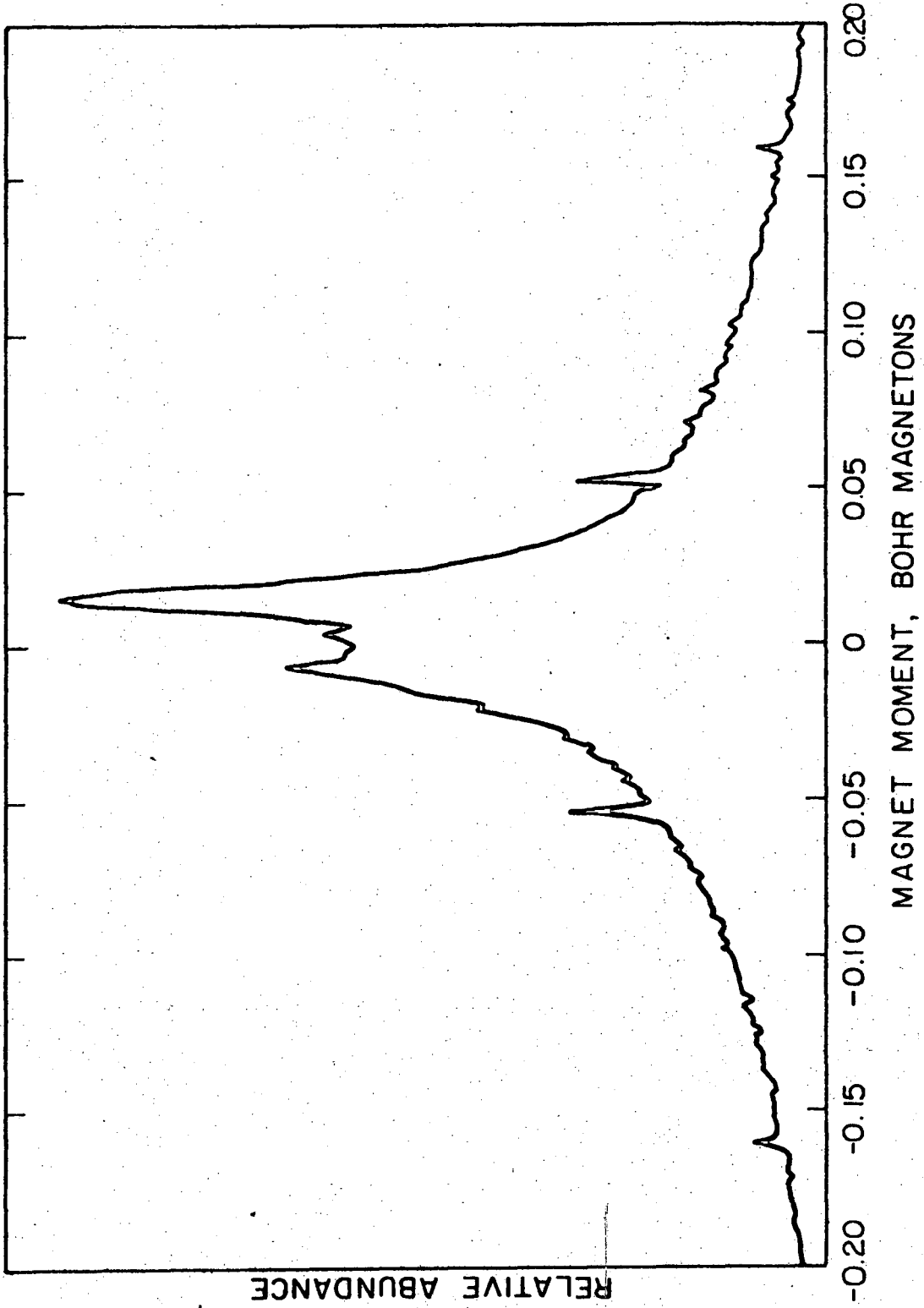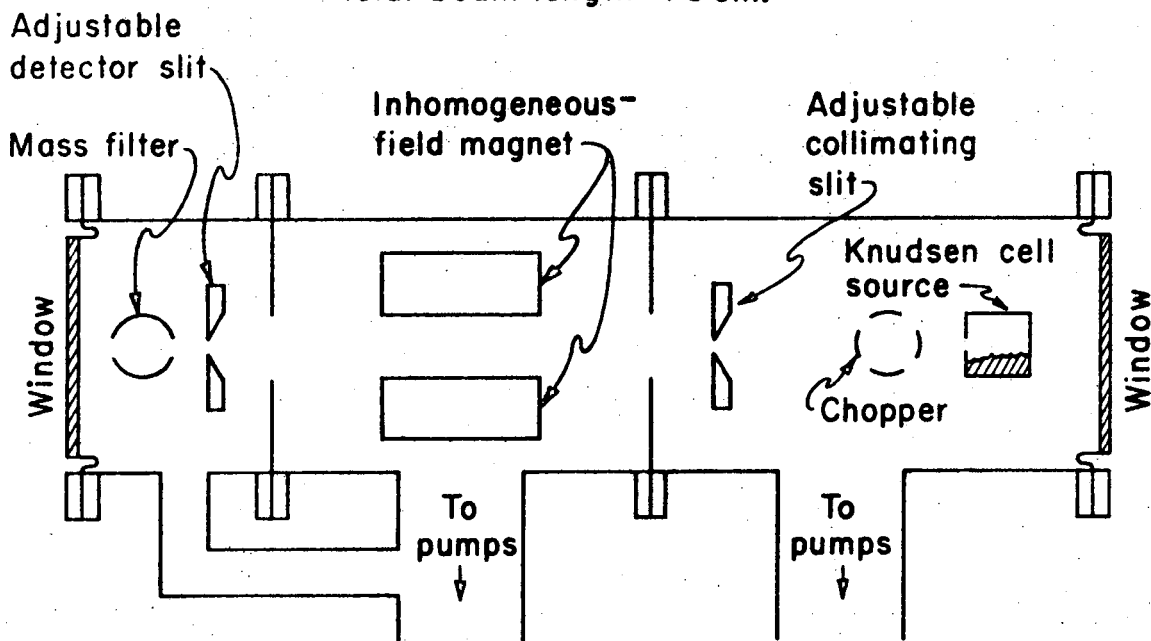Fig. 4. Se_2 beam profile.

Fig. 5. S_2 beam profile.

RELATIVE ABUNDANCE

MAGNET MOMENT, BOHR MAGNETONS

XBL 751-5625

Fig. 1.

Distances-
Knudsen cell to coll. slit-21 cm.
coll. slit to det. slit-41 cm.
total beam length-70 cm.

Adjustable
detector slit

Mass filter

Inhomogeneous-
field magnet

Adjustable
collimating
slit

Knudsen cell
source

Window

Window

Chopper

To
pumps

To
pumps

Inhomogeneous -magnetic - field molecular beam apparatus.

XBL702-2352

Fig. 2.

Fig. 3.

Fig. 4.

XBL753-6022

Fig. 5.