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Authors
Weiss, P.S.
Covinsky, M.H.
Schmidt, H.

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Lawrence Berkeley Laboratory
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P.S. Weiss, M.H. Covinsky, H. Schmidt,
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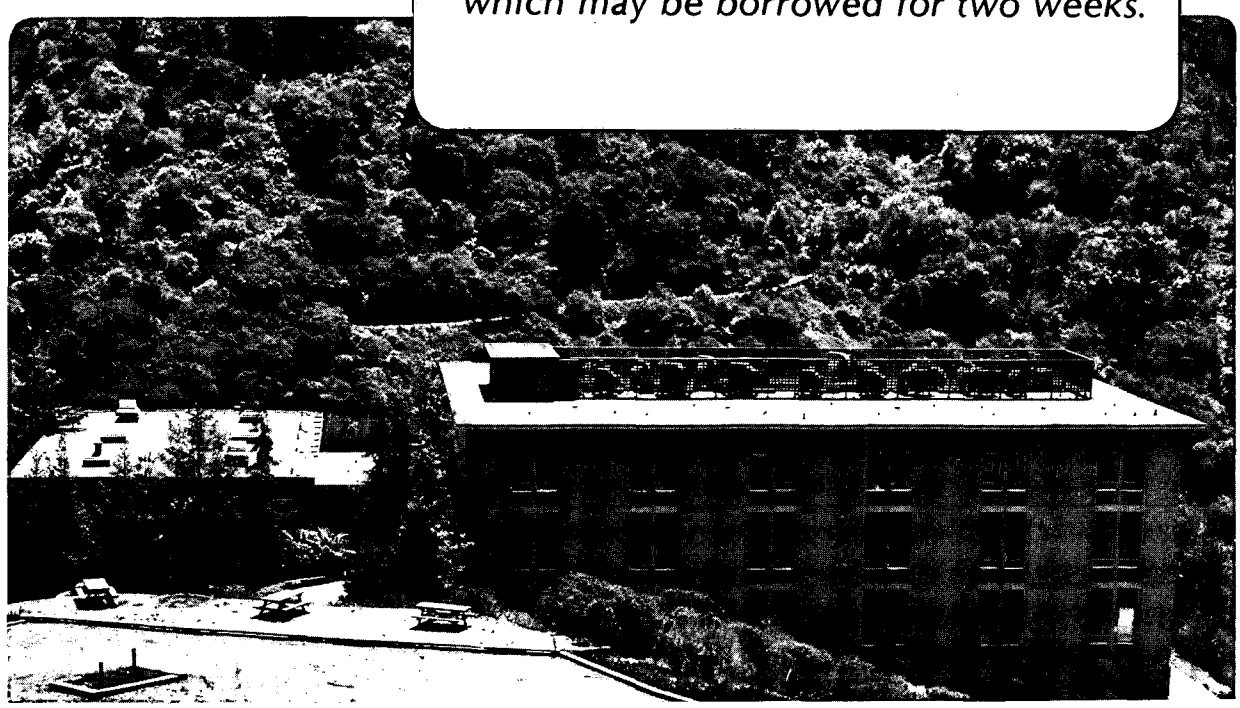

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POLARIZATION EFFECTS IN REACTIVE SCATTERING OF Na ATOMS IN THE 4D LEVEL

P.S. Weiss,[1] M. H. Covinsky, H. Schmidt,[2]
B.A. Balko and Y.T. Lee

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
and Department of Chemistry, University of California
Berkeley, CA 94720 USA

and

J.M. Mestdagh

Service de Physique des Atomes et des Surfaces,
CEN Saclay - 91191 Gif sur Yvette CEDEX - France

1. Present address: IBM Almaden Research Center, K31/802, 650 Harry Road, San Jose, CA 95120-6099 USA

2. Permanent address: Braun A.G. Forschung - Frankfurter Str. 145, D6242 - Kronberg - FGR

ABSTRACT

Experiments performed using a crossed beam apparatus have shown that the reactivity of Na(4D) with HCl and O_2 changes substantially as the 4d orbital alignment is varied. This change is found different for the two reactions. The favorable alignment for the reaction with HCl has the d orbital aligned along the relative velocity vector of the reactants. This result is consistent with a long range electron transfer initiating the reaction and suggests that the Na-Cl axis dominates over the H-Cl axis in determining the favorable atomic orbital alignment. For the reaction with O_2, the NaO formation has a high translational energy threshold, and the favored orbital alignment varies as a function of the NaO laboratory scattering angle. Very restricted conditions are found to be necessary for the reaction: near collinear geometry and the d orbital perpendicular to the molecular axis.

1. INTRODUCTION

Reactive scattering of alkali atoms with various molecules has been studied extensively over the past two decades [1]. A wide variety of experimental techniques have been used to elucidate the dynamics of these reactions, as well as the effect of reactant translational, vibrational and rotational excitation on chemical reactivity [2]. What happens when electronically excited alkali atoms are used, however, has been investigated only recently in a series of experiments which combine crossed beams and laser excitation techniques [3-6].

In experimental studies of the scattering of electronically excited atoms, one of the more interesting aspects is using the laser excitation step to control the alignment and the orientation of the excited atomic orbital before the collision. This atomic orbital polarization was observed to have a pronounced effect in several inelastic processes [7-9]. Analogous studies on reactive scattering have recently started to receive some attention [10].

This paper reports on the results of a crossed molecular beams investigation of such polarization effects in reactions of sodium atoms excited to the 4D level with HCl and O_2 molecules.

$$Na(4D) + HCl \rightarrow NaCl + H \quad \Delta H^\circ_0 = -94.1 \text{ kcal/mol} \qquad (1)$$

$$Na(4D) + O_2 \rightarrow NaO + O \quad \Delta H^\circ_0 = -40.8 \text{ kcal/mol} \qquad (2)$$

Previous studies on the identification of the reaction products, as well as the product angular and velocity distributions of these

reactions, are summarized in ref [3,11-12]. Although both processes (1) and (2) proceed through a direct mechanism, some important differences in reaction dynamics seem to exist. From all evidence, reaction (1) takes place via an early dissociative electron transfer of the Na valence electron to HCl [11]. In contrast, the high translational energy threshold for product formation in reaction (2) suggests that, although important in the scattering process, an early, long range electron transfer does not seem to play a significant role in the reaction between Na(4D) and O_2. The electron transfer that leads to product formation most likely occurs at very short distances and seems to involve excited states of the negative molecular ion O_2^- [12-13]. It was hoped that these differences in reaction dynamics could be further clarified with the investigation of polarization effects of the excited atomic orbitals.

2. EXPERIMENT

2.1 APPARATUS

The experimental arrangement, shown schematically in Fig. 1, has been described elsewhere [4]. Briefly, two supersonic beams of reactants are crossed orthogonally under single collision conditions. Reaction products are detected with a triply differentially pumped mass spectrometer which is rotatable about the collision region in the plane defined by the two reactant beams. Two single frequency dye lasers are used to prepare the Na(4D) via a stepwise excitation scheme shown in ref [3]. The laser beams cross the scattering region orthogonally to the reactant beams along the rotation axis of the detector. Both laser beams are linearly polarized by passing them through the same polarizer. The direction of polarization can be rotated in the scattering plane thus allowing one to study how the Na reactivity depends on the alignment of the 4d orbital with respect to the relative velocity vector.

In the experiments reported here, the reaction products are detected at several fixed laboratory scattering angles θ as a function of the laser polarization angle β. The angles θ and β are defined respectively with respect to the Na velocity, and the relative velocity of the collision partners, as shown in the Newton diagram of Fig. 2.

2.2 ALIGNMENT RESULTING IN THE LASER EXCITATION

In experiments conducted using linear polarization, the maximum alignment of a 4D level is 4D m=0 which corresponds to a pure dz^2 orbital aligned along the direction of laser polarization (the z-axis). Of course, since Na has both a fine and hyperfine structure, such a complete alignment cannot be achieved. One might think it is possible, however, to theoretically calculate the actual alignment of the 4D level under experimental conditions by including all these energy levels in the optical pumping equations. Unfortunately, the only tractable calculations make use of optical pumping rate equations which are just valid for low laser power [14]. The power needed for our experiments is simply too high to make a realistic estimate with this type of calculation.

The one reliable procedure for estimating the percentage of alignment in the 4d orbital is to measure the anisotropy of the fluorescence from the Na(4D). A fluorescence monitor, shown in figure 1, allows measurement of the Na(4D→3P) fluorescence intensity emitted in the direction of the monitor as a function of the polarization angle of the lasers. A typical result, showing a sine wave oscillation of the signal as a function of the laser polarization angle β, is shown in figure 3. The amplitude of the sine wave reflects the completeness of alignment. Using the very extensive set of equations expressing the theory of light emission by polarized atoms given in ref [14], the fluorescence signal corresponding to the present measurements is given by:

$$I(\gamma) = \frac{C}{3^{1/2}} \left[\begin{Bmatrix} 2 & 2 & 0 \\ 1 & 1 & 1 \end{Bmatrix} \cdot \rho^0_0 + \frac{1}{2} \begin{Bmatrix} 2 & 2 & 2 \\ 1 & 1 & 1 \end{Bmatrix} \cdot (3\cos^2\gamma - 1) \cdot \rho^2_0 \right] \qquad (3)$$

In expression (3), γ is the angle defined by the fluorescence monitor and the lasers polarization direction, $\{:::\}$ are 6-j coefficients, ρ^0_0 is the isotropic part of the 4D level density matrix, and ρ^2_0 describes the alignment of this level. The ratio ρ^2_0/ρ^0_0 reflects the percentage of alignment of the 4d orbital. Using this equation and the fluorescence data obtained in our experiments, then, the 4D level is aligned approximately 45% in the $4dz^2$ orbital.

3. RESULTS

3.1 $Na(4D) + HCl \rightarrow NaCl + H$

Polarization dependence of product formation has been investigated at five laboratory scattering angles θ: 35, 40, 44, 50 and 56 degrees, for a collision energy of 5.6 kcal/mol. Typical results are shown in figure 4. The experimental results are fit with the expression:

$$I_r(\beta) = A \sin(2\beta + \phi) + B \qquad (4)$$

where I_r is the reactive signal at angle θ, β is the polarization angle with respect to the relative velocity vector (see in Fig. 2), and ϕ is a phase factor defining the position of the reactive signal peak. The ratio 2A/B, then, gives the amplitude of the polarization effect. Results are shown in table 1 for the five scattering angles that have been investigated. This compilation points out that reaction is most favored when the 4d orbital is approximately parallel to the relative velocity vector and depends only slightly on the laboratory scattering angle of the reaction products.

3.2 $Na(4D) + O_2 \rightarrow NaO + O$

The polarization dependence of the NaO product signal from reaction (2) has been measured at a collision energy of 18 kcal/mol for four laboratory scattering angles: 30, 36, 40 and 50 degrees. A sample of the results is shown in figure 5. As with the HCl experiment, expression (4) is used to fit the data. The important quantities from the fits are given in table 2. The results are substantially different from those of reaction (1) since the favored polarization angle for the oxygen reaction changes dramatically as the scattering angle is varied.

4. DISCUSSION

4.1 REACTIONS OF Na(4D) WITH HCl MOLECULES.

Let us first consider the results shown in table 1 obtained with the detector sitting at 50 and 56 degrees in the laboratory frame. With this experimental configuration, backward scattered products with center-of-mass scattering angles between 150 and 180 degrees are detected. The collisions associated with this backward scattered NaCl product must be the type in which Na hits Cl along the Cl-H molecular axis at very small impact parameters. From table 1, it is clear that the reaction is enhanced by having the 4d orbital aligned within 10 degrees of the relative velocity vector. The favorable geometry for this scattering is thus given by scheme 1. The orbitals in scheme 1 are not to scale.

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Scheme 1

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This scheme corresponds to the configuration of an asymptotically prepared 4d(dz^2) orbital that is aligned along the symmetry axis of the C∞v point group. Since this arrangement has the largest Σ character, it would be expected that a Σ intermediate, such as $Na^+(^1S)$-$HCl^-(^2\Sigma)$, would be formed easily in the long range electron transfer mechanism proposed in reference [5].

Let us now look at those products detected at laboratory

scattering angles between 35 and 40 degrees. For these angles, the reaction products observed are still substantially backward scattered. For example, laboratory scattering at 40 degrees is roughly associated with center-of-mass scattering at about 120 degrees. It is expected, then, that the impact parameter of Na with respect to the Cl atom of HCl will still be small. Because the reaction products are a little less backward scattered, however, it is likely that the HCl axis will make a small angle with the direction of the relative velocity vector. Recalling the polarization effect presented in table 1, it appears that the favored asymptotic alignment preparation for reaction is again with the 4d(dz^2) orbital pointing nearly along the relative velocity vector. The geometry which would account for the less backward scattered product can thus be represented as in scheme 2.

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Scheme 2

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Note that the 4d orbital is aligned roughly along the Na...Cl axis, so makes a small angle with the H-Cl axis. This, in effect, shows the importance of the Na-Cl axis over the H-Cl axis in the alignment of the 4d orbital. Since these reactive collisions are associated with small impact parameters, the effect of "orbital following", which is related to the locking radius idea discussed in reference [7], is not expected to affect the present discussion.

Scheme 2 corresponds to the Cs point group. In this symmetry group, Na^+-HCl^- , as well as the dz^2 orbital, has A' character. As

proposed in Ref [11], the reaction of Na(4D) with HCl thus proceeds through a long range electron transfer to form $Na^+(^1S)$-$HCl^-(^2\Sigma)$, which is symmetry allowed in this geometry.

In the case of Cs geometry, however, electron transfer to HCl from a 4d(dz^2) orbital aligned perpendicular to the relative velocity vector is also symmetry allowed. We might wonder why this configuration leads to less reactive signal than scheme 2. A likely answer is that a dz^2 orbital is prolate with respect to its z axis. With scheme 2, the 4d orbital is able to feel the Cl atom at longer distances, and can thus transfer its electron at larger Na...Cl-H distances than when the dz^2 orbital is perpendicular to the Na...Cl axis.

4.2 REACTION OF Na(4D) WITH O_2 MOLECULES.

The favorable alignment for reaction with O_2 looks very different from that for reaction with HCl as is apparent from tables 1 and 2. Unlike the HCl experiment, the best alignment angle for reaction with O_2 changes significantly as the laboratory scattering angle is varied.

As described in Ref. [3,12], the NaO product is strongly backward scattered and has a narrow velocity distribution that peaks at low velocity. This means that an almost one-to-one correspondence between laboratory and center-of-mass scattering angles exists: 40-50 degrees in the laboratory corresponds to about 160-180 degrees in the center-of-mass coordinate system and 30 degrees corresponds to about 40 degrees.

Let us consider backward scattered products in the center-of-mass reference frame, which would be those products that appear in the laboratory at 40-50 degrees. We see from table 2 that, within 20 degrees, the preferred alignment for reaction is with the 4d orbital perpendicular to the relative velocity vector. Because the products are backward scattered, the approach geometry is expected to be collinear or near collinear Na...O-O. The reactive collision geometry, then, should resemble scheme 3.

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Scheme 3

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A molecular state of mixed character Σ and Δ emerges from the 4d orbital in reactive scheme 3, while a state of pure Σ character results from the 4d orbital when the alignment is along the Na...O-O molecular axis. Since the latter configuration is less reactive, it can be concluded that, in scheme 3, the molecular state Δ leads to reaction rather than Σ.

This conclusion seems to contradict an earlier work where the reaction of Na(4D) with O_2 was proposed to result from the transfer at very short Na-O_2 distances (about 0.2 nm) of the Na valence electron to form the excited state $A^2\Pi u$ of O_2^-, i.e. the state responsible for the dissociative electron attachment in electron/O_2 scattering [13]. The formation of an Na^+-$O_2^-(^2\Pi u)$ intermediate is indeed forbidden along reactive scheme 3 since it requires a $\Delta \rightarrow \Pi$ symmetry change. Reference [13], in fact, may still be correct because at short Na-O_2 distance, the presence of the Na^+ core is likely to alter the pure Π character of the $O_2^-(A^2\Pi u)$ by mixing it with neighboring states of Δ character, thus making this electron transfer possible under reactive scheme 3. This point will be further discussed in Ref [12].

Let us turn now to the small laboratory scattering angles 30 and 36 degrees which correspond respectively to scattering at 40 and 130 degrees in the center-of-mass frame. These products are most likely to result from scattering with finite impact parameters. The important result apparent in table 2 is that the alignment angle of the 4d orbital for maximum reaction rotates as the scattering angle is

changed. For backward scattering, it is perpendicular to the relative velocity vector and it tends to tilt slightly toward parallel when the product center-of-mass mass scattering angle is decreased. These features suggest that in order for reaction to take place the following conditions have to be satisfied:

i) A collinear Na...O-O geometry must be reached at the classical turning point

ii) When this configuration is achieved, the dz^2 orbital has to be perpendicular to the Na...O-O molecular axis.

This favored reaction configuration for non-backward scattered products is shown in scheme 4

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Scheme 4

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As far as molecular orbital symmetries are concerned, the configuration for highest reaction probability, shown in scheme 4, is equivalent to scheme 3. As was discussed for the scheme 3, the system should react best from the Δ molecular state of the $Na(4D)-O_2$ system.

The fact that a molecular state of Δ character seems to play an important role in the $Na(4D)+O_2$ reaction might be the reason why a very state specific feature was found in Ref. [3] in reactions of Na(4D and 5S) with O_2. The 5S level does not correlate to the molecular state of Δ character which favors the reaction. It is possible that when a Na(5S) atom approaches an O_2 molecule, the long range charge transfer

takes place efficiently and only quenching processes occur. On the other hand, when a Na(4D) orbital approaches O_2 with Δ character, long range charge transfer can be avoided and the trajectories will follow a covalent surface so that the Na and O_2 that have sufficient kinetic energy can approach close enough to allow the transfer of the electron from Na(4D) to an excited state of O_2^-.

5. CONCLUSION

The reactivity of Na(4D) with HCl and O_2 as a function of the alignment of the excited 4d orbital of Na has been measured using a crossed beam apparatus. The change in Na reactivity as the d orbital alignment is varied is found to be very different for the two reactions.

With HCl, the favorable alignment for reaction is with the 4d orbital along the relative velocity vector of the reacting pair regardless of the deviation of the HCl axis away from the direction of the relative velocity. This corresponds to the Na 4d orbital pointing to the Cl atom and is interpreted as the domination of the Na-Cl axis over the H-Cl axis in determining the alignment of the 4d orbital in the transfer of the Na valence electron to HCl.

With O_2, the best alignment for the reaction is found to be strongly dependent on the NaO product scattering direction. The reason for this seems to lie with the very restricted conditions necessary for the reaction to occur : near collinear geometry Na..O-O and the d orbital aligned perpendicular to the molecular axis. This indicates that an intermediate of Δ character should play an important role in the reactions of excited Na atoms with O_2. The experimental observation that reactions of excited Na with O_2 do not proceed when Na is in the 5S state but occur with Na(4D) may be explained by this. Avoiding a long range electron transfer and sufficient kinetic energy might be two of the necessary conditions for the formation of NaO.

ACKNOWLEDGMENTS

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TABLES

TABLE 1 Polarization effect measured in the Na(4D) + HCl reaction at a collision energy of 5.6 kcal/mol. The polarization angle β and the scattering angle θ are defined in figure 2.

Laboratory scattering angle θ (degrees)	Polarization angle β for maximum reaction (degrees)	Polarization angle β for minimum reaction (degrees)	Amplitude of of the polarization effect
35	-13 ± 7	-103 ± 7	8 %
40	-8 ± 7	-98 ± 7	6 %
44	-5 ± 7	-95 ± 7	9 %
50	-8 ± 7	-98 ± 7	8 %
56	4 ± 10	-86 ± 10	9 %

TABLE 2 Same caption as table 1 for the Na(4D) + O_2 reaction at a collision energy of 18 kcal/mol.

Laboratory scattering angle θ (degrees)	Polarization angle β for maximum reaction (degrees)	Polarization angle β for minimum reaction (degrees)	Amplitude of of the polarization effect
30	-9 ± 7	-99 ± 7	13 %
36	37 ± 7	-53 ± 7	8 %
40	61 ± 7	-29 ± 7	11 %
50	70 ± 7	-20 ± 7	7 %

FIGURE CAPTIONS

FIGURE 1 Schematic of the apparatus.

FIGURE 2 Scheme defining the laser polarization angle and the laboratory scattering angle. Note the positive direction for these angles are opposite one another.

FIGURE 3 Polarization dependence of the fluorescence signal. The 4d orbital rotates in the plane defined by the reagent beams. The polarization angle β is with respect to the relative velocity vector in a Na+HCl experiment.

FIGURE 4 Polarization dependence of the NaCl signal from the Na(4D) + HCl → NaCl + H reaction at a laboratory scattering angle of 44 degrees and a collision energy of 5.6 kcal/mol. The polarization angle β is with respect to the relative velocity vector as shown in figure 2.

FIGURE 5 Same caption as figure 4 for the Na(4D) + O_2 → NaO + O reaction at 40 degrees laboratory scattering angle and a 18 kcal/mol collision energy.

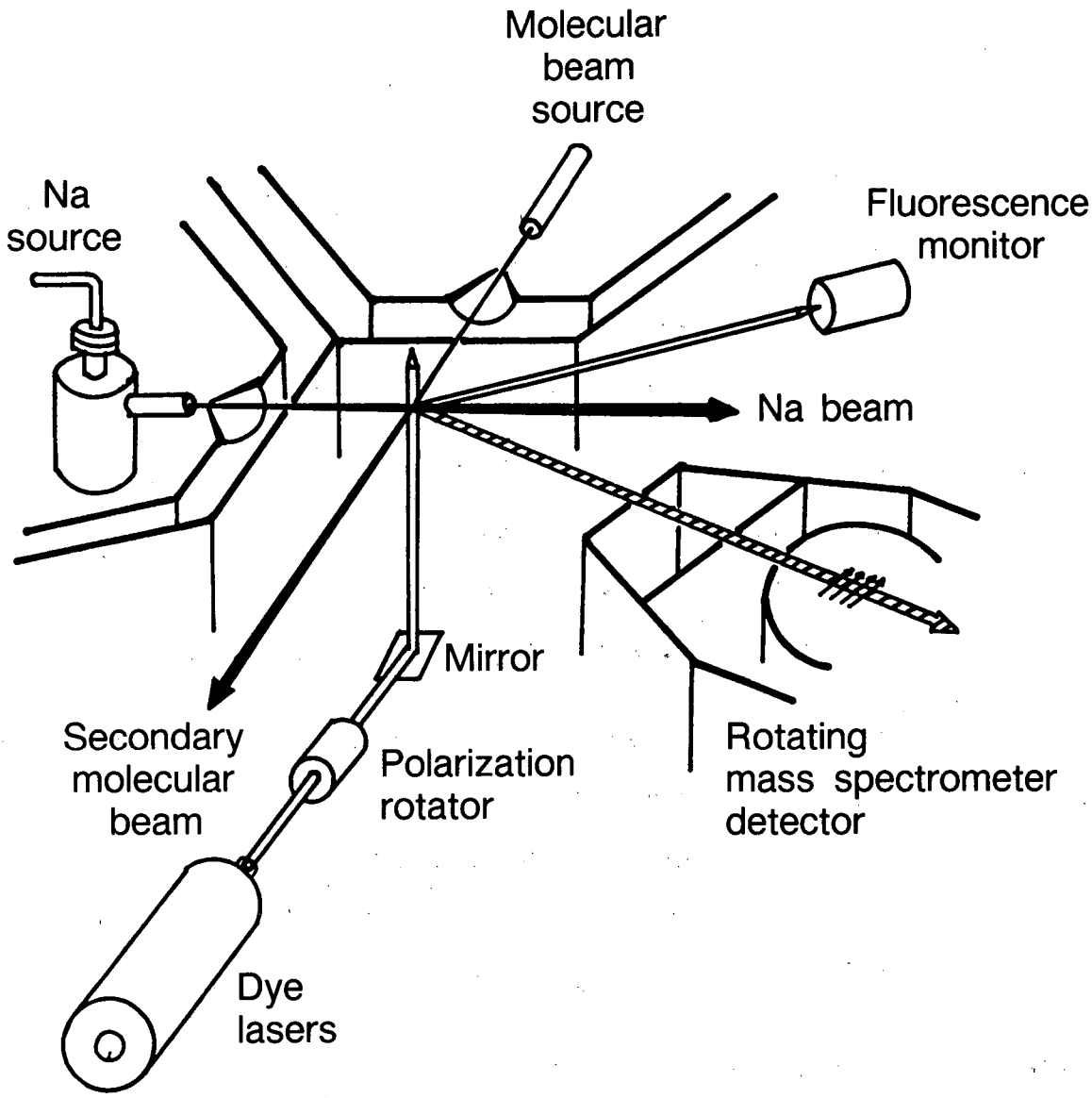

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Fig. 1

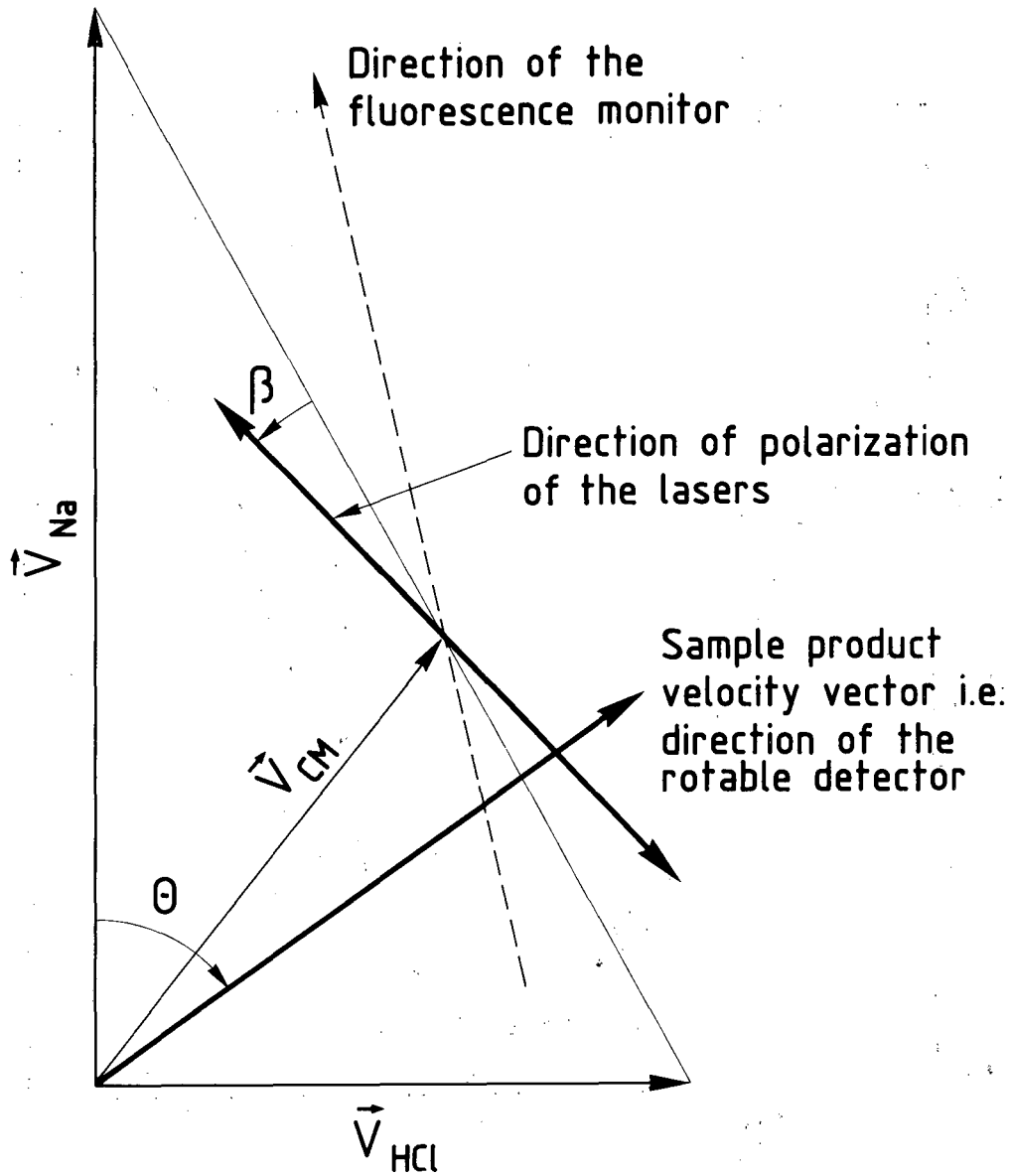

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Fig. 2

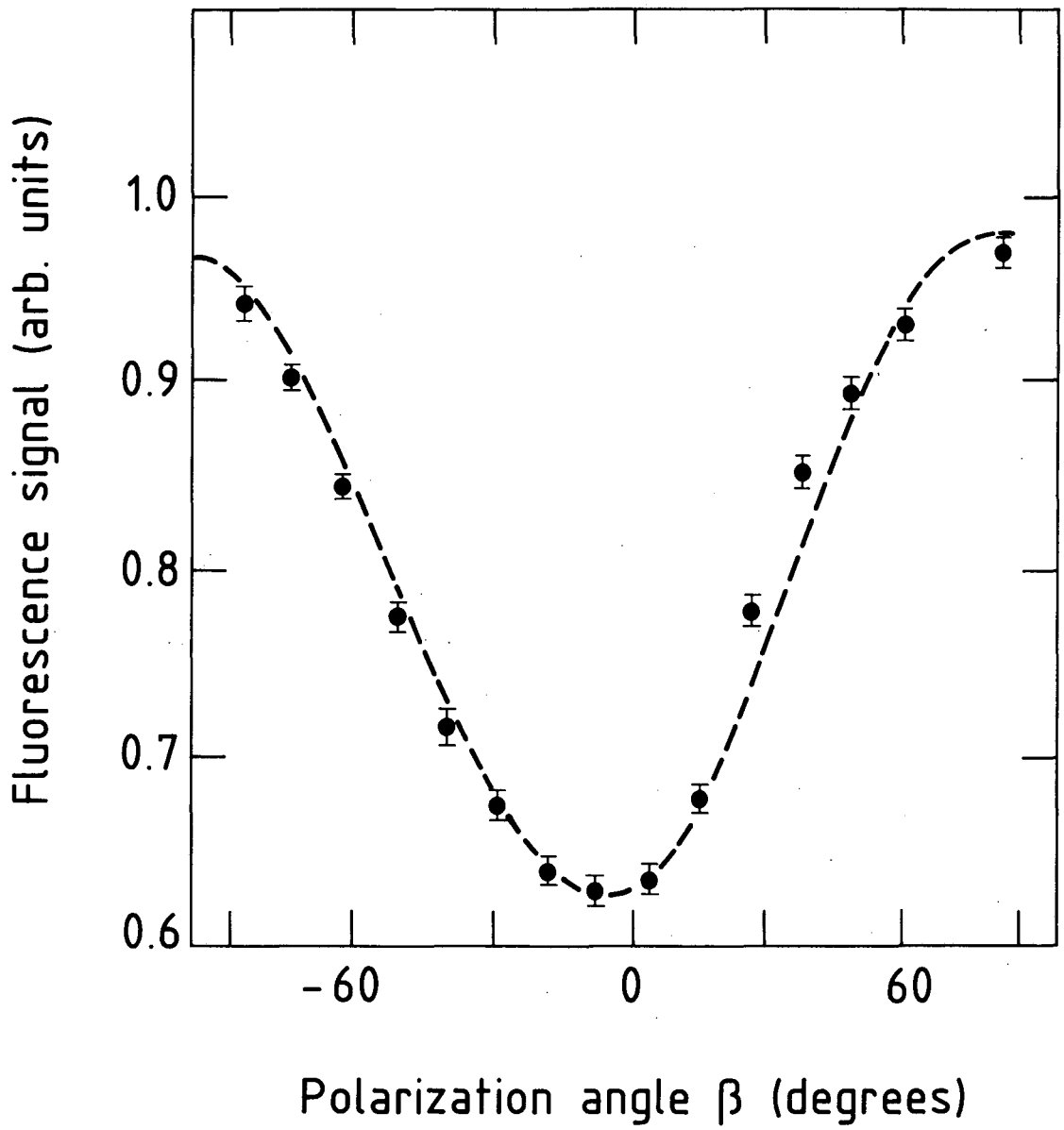

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Fig. 3

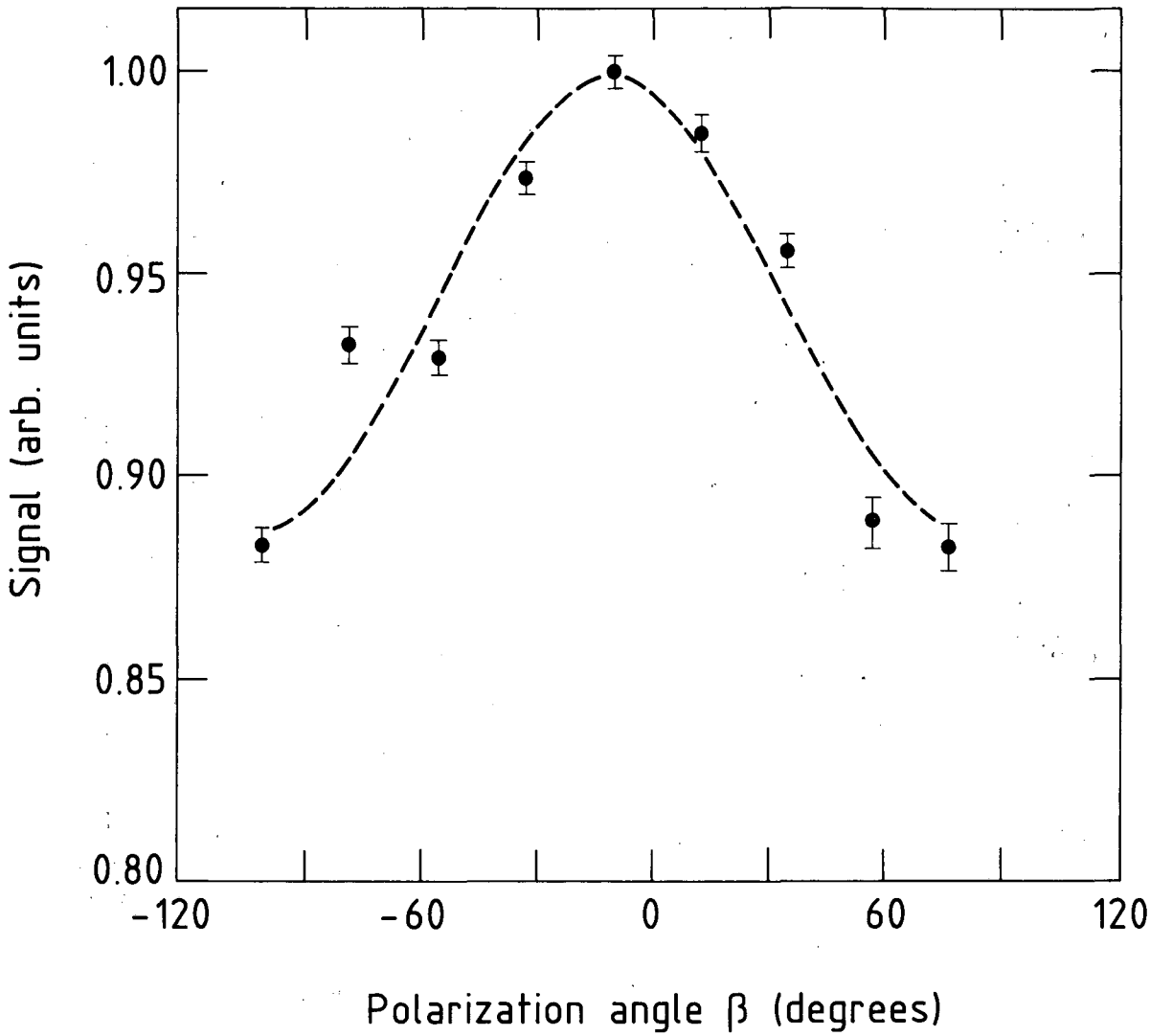

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Fig. 4

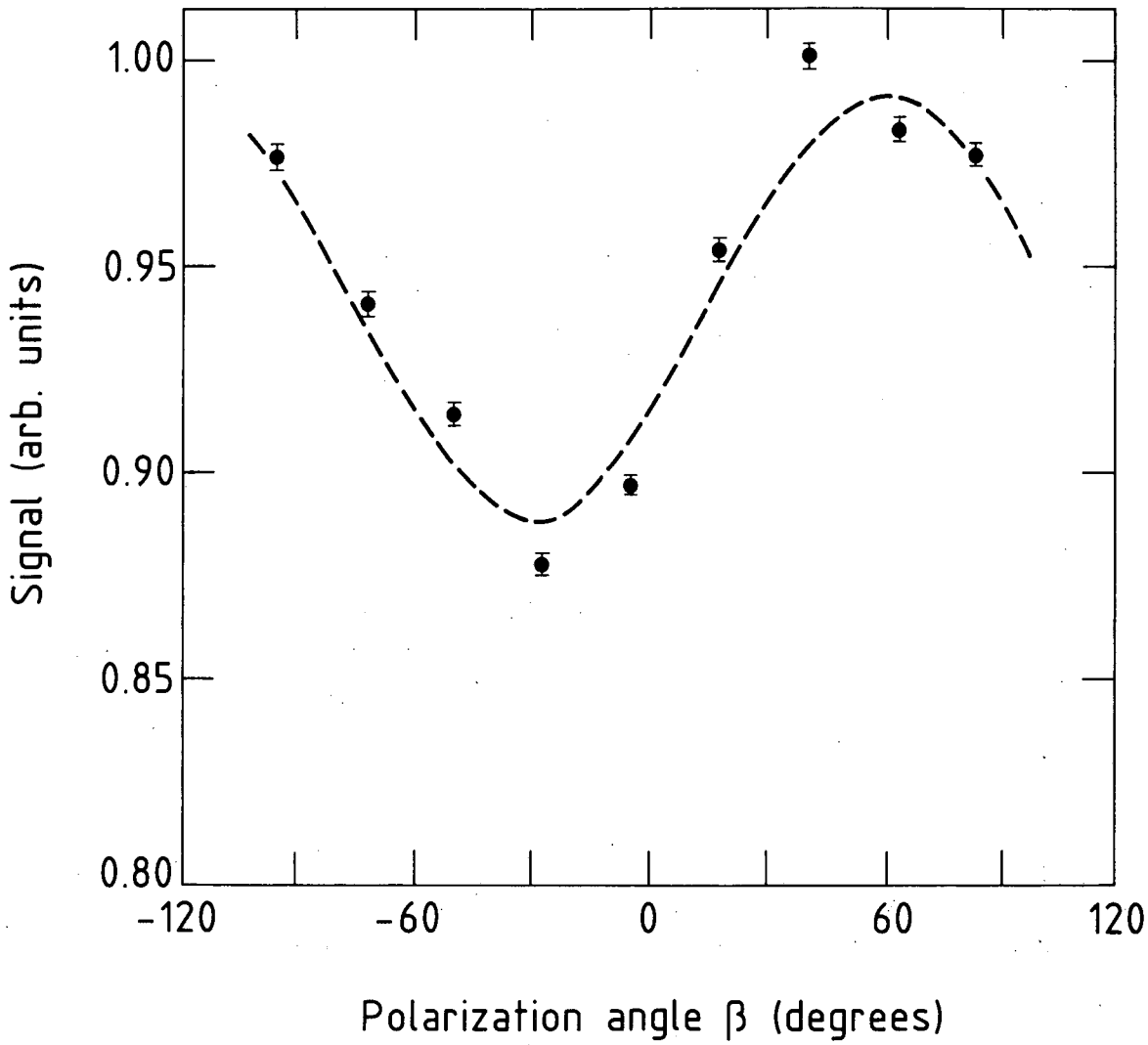

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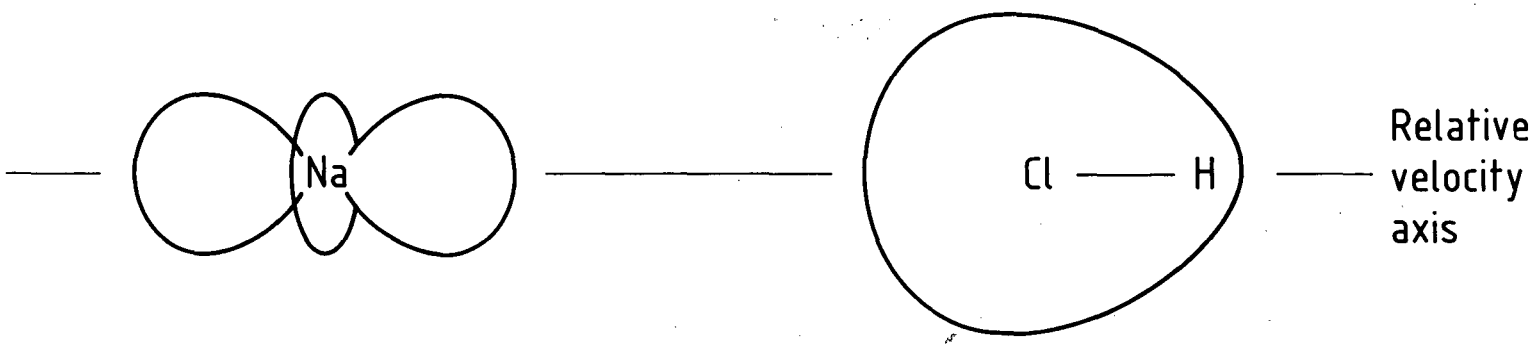
Fig. 5



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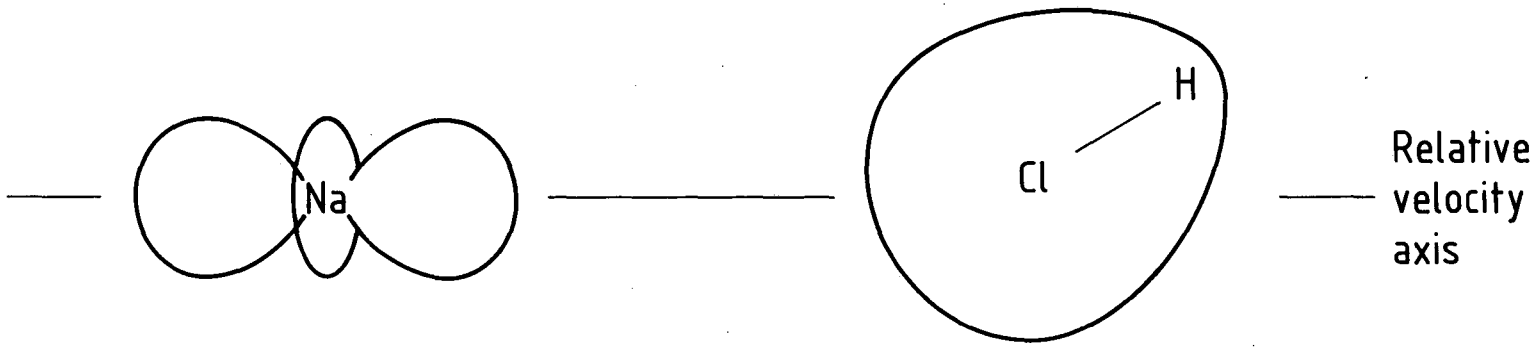
Scheme 1



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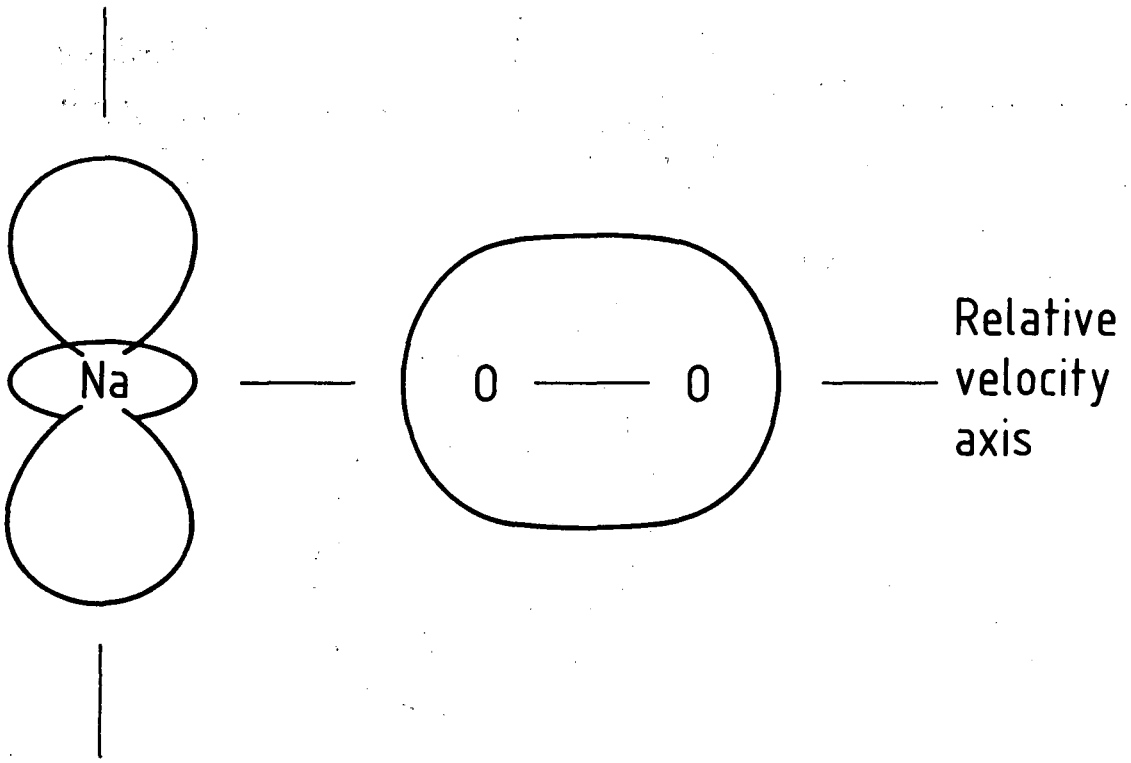
Scheme 2



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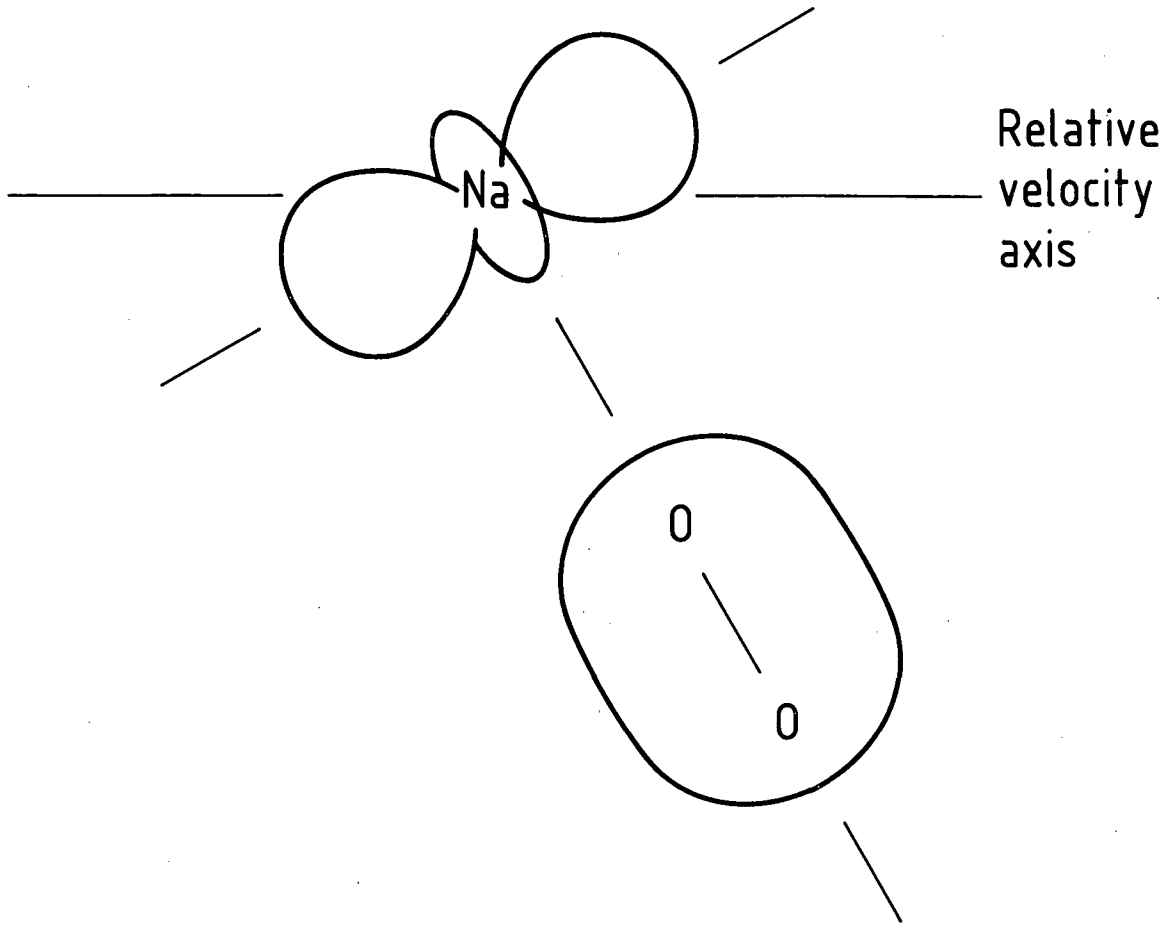
Scheme 3



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Scheme 4

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720