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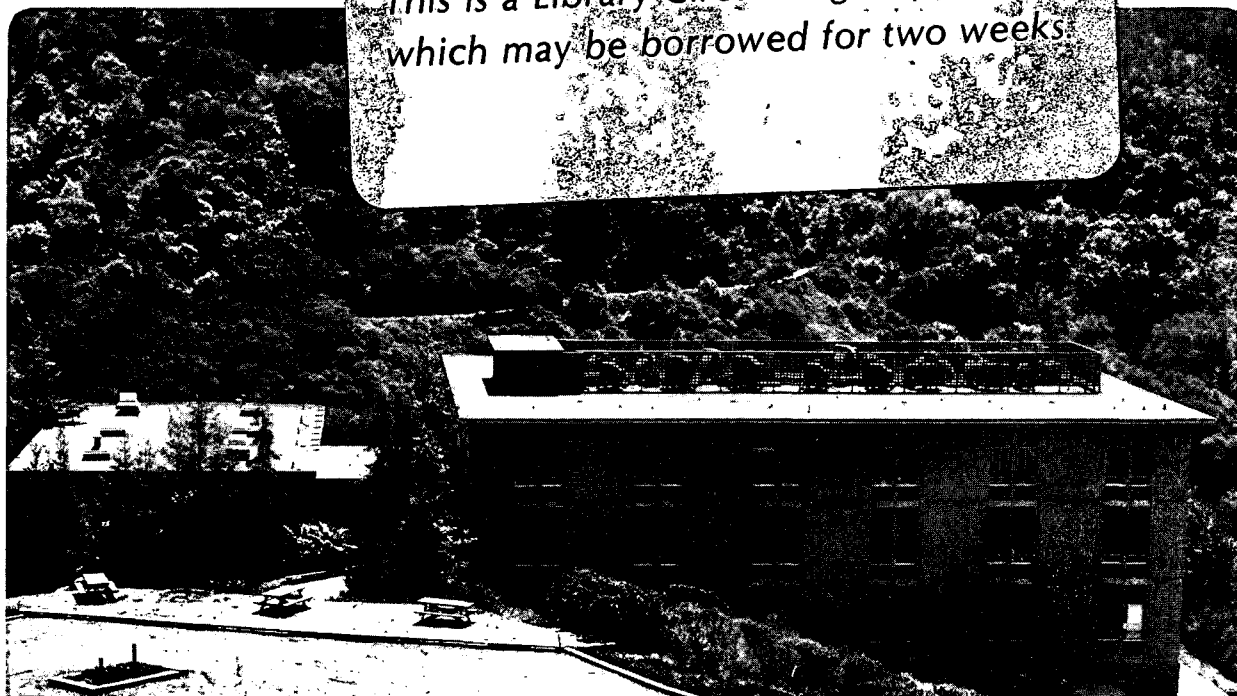
### REACTIVE SCATTERING OF ELECTRONICALLY EXCITED ALKALI ATOMS WITH MOLECULES

J.M. Mestdagh, B.A. Balko, M.H. Covinsky, P.S. Weiss, M.F. Vernon, H. Schmidt, and Y.T. Lee

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REACTIVE SCATTERING OF ELECTRONICALLY EXCITED  
ALKALI ATOMS WITH MOLECULES

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ABSTRACT

Representative families of excited alkali atom reactions have been studied using a crossed beam apparatus. For those alkali-molecule systems in which reactions are also known for ground state alkali and involve an early electron transfer step, no large differences are observed in the reactivity as Na is excited. More interesting are the reactions with hydrogen halides (HCl): it was found that adding electronic energy into Na changes the reaction mechanism. Early electron transfer is responsible of Na(5S, 4D) reactions, but not of Na(3P) reactions. Moreover, the NaCl product scattering is dominated by the HCl<sup>-</sup> repulsion in Na(5S, 4D) reactions, and by the NaCl-H repulsion in the case of Na(3P). The reaction of Na with O<sub>2</sub> is of particular interest since it was found to be state specific. Only Na(4D) reacts, and the reaction requires restrictive constraints on the impact parameter and the reactants' relative orientation. The reaction with NO<sub>2</sub> is even more complex since Na(4D) leads to the formation of NaO by two different pathways. It must be mentioned however, that the identification of NaO as product in these reactions has yet to be confirmed.

## 1. INTRODUCTION

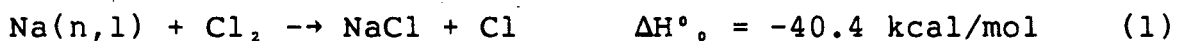
For a given elementary chemical reaction, specific forms of energy (i.e. translational, vibrational, rotational, and electronic) deposited in reactants are known to affect reactive scattering processes in different ways. Adding electronic energy to reactants is of special interest since in this way a relatively large amount of energy can be deposited in a single excitation step and, more importantly, the potential energy surface on which the reaction is initiated can be selected by exciting reactants to states of different symmetries. The reactivity and reaction dynamics of such excited reactants often differs substantially from that of the corresponding ground state molecules [1].

Reactive scattering of alkali atoms with molecules has been studied extensively over the past two decades [2]. A wide variety of experimental techniques have been used to determine the dynamics of these reactions, as well as the effect of reactant translational, vibrational and rotational excitation [3]. Until recently, the effect of electronic excitation remained unexplored [4-8].

The reactions of excited Na atoms with simple molecules have been systematically investigated in our laboratory using the crossed molecular beam method [4-7]. In this paper

some examples of excited Na atom reactions will be presented to illustrate the effect of electronic excitation on sodium reactivity.

First, systems are considered in which the reaction is exothermic and is initiated by an electron transfer from a sodium atom to a molecule; a representative example of this is the reaction:



In reactions (1),  $n,1$  represents the electronic state of Na: ground state 3S or excited states (e.g. Na(3P)). The  $\Delta H^\circ_0$  is for the reaction of Na(3S).

The second type of reaction is where ground state Na is known to react, but a simple electron transfer model cannot be used to account for observed features of the collision dynamics. The chosen example is:



where the excited state  $n,1$  is 3P, 5S or 4D.

The points which will be considered about processes (1-2) concern changes in the Na reactivity as well as changes in the reaction dynamics that are associated with depositing electronic energy into the Na.

The remainder of the examples concern reactions which are substantially endothermic and energetically unfavorable for ground state Na. The goal is to understand if and by what mechanism electronic excitation is able to turn on the reaction. One example that will be discussed is:



The somewhat more complicated process



will be described in greater detail.



## 2. EXPERIMENT AND ANALYSIS

The experimental set-up has been described elsewhere [5-7,9]. Briefly, two supersonic beams and one or two lasers are crossed orthogonally under single collision conditions. A mass spectrometric detector rotates about the collision region in the plane defined by two reactant beams as shown schematically in Fig. 1. Several types of experiments are performed:

i) product angular distributions are measured by rotating the detector,

ii) product velocity distributions are measured by a time-of-flight technique,

iii) the dependence of the chemical reactivity on the nature of the excited state of sodium is investigated for Na(3P), Na(4D), and Na(5S),

iv) the effect of collision energy is studied by changing the beam velocities.

The experimental angular and velocity distributions are fitted using a forward convolution method which varies assumed center of mass angular and translational energy distributions and averages over the variation in experimental conditions. For cases in which the reaction cross section was found to depend strongly on collision energy, the energy dependence of the reaction cross section is specifically taken into account in the convolution process.

### 3. RESULTS

#### 3.1 $\text{Na}(n,1) + \text{Cl}_2 \rightarrow \text{NaCl} + \text{Cl}$

Angular distributions of the NaCl products have been measured for Na(3S, 3P), and for three nominal collision energies: 3, 6, and 19 kcal/mol. Typical results are shown in figure 2 for 19 kcal/mol collision energy. The results for reactions of Na(3S) agree with the general understanding of ground state alkali - halogen reactions [2]. They show predominant forward scattering and narrow recoil energy distributions. The new feature brought out by figure 2 is that no large difference is observed between the product angular distribution associated with the reaction of Na(3S) and Na(3P), even though the electronic excitation lowers the ionization potential of Na by 2.1 eV.

The predominance of forward scattering and narrow recoil energy distributions allows one to derive center of mass distributions directly by fitting the laboratory angular distributions on the basis of an assumed center of mass distribution [10]. Best fits are shown in figure 2 for a 19 kcal/mol collision energy. A summary of features of the center-of-mass distributions is found in table 1.

3.2  $\text{Na}(n,1) + \text{HCl} \rightarrow \text{NaCl} + \text{H}$

The system was studied at collision energies of 3.4, 5.6 and 16.3 kcal/mol for reactions with  $\text{Na}(3\text{S}, 3\text{P}, 5\text{S}, 4\text{D})$ . The laboratory angular distributions of the product  $\text{NaCl}$  are shown in figure 3 for a 5.6 kcal/mol collision energy. As can be seen, there are important changes in the  $\text{Na}$  reactivity when switching from  $\text{Na}(3\text{S})$  to  $\text{Na}(4\text{D})$ .

These angular distributions along with the measured laboratory velocity distributions of the product  $\text{NaCl}$  allow one to extract a center-of-mass  $\text{NaCl}$  flux distribution. As discussed in references [5,7,9], all the reactions of excited  $\text{Na}$  exhibit with  $\text{HCl}$  predominant backward scattering with low recoil energy; these characteristics are most apparent in the reactions of the two most excited states, 5S and 4D.

3.3  $\text{Na}(n,1) + \text{O}_2 \rightarrow \text{NaO} + \text{O}$

Process (3) for Na(3S,3P,5S, 4D) has been studied over a wide range of collision energies: 8 to 22 kcal/mol. The most interesting feature of the results is the state specificity: no reaction was found for Na(3S,3P, 5S). Backwards scattered product was observed in the Na(4D) reactions when the average collision energy was larger than 11 kcal/mol [5]. The non-reactivity of Na(5S) is striking because process (3) has about the same exothermicity with either Na(5S) as the reactant or Na(4D) ( 36.9 kcal/mol vs. 41.5 ). The high activation energy for the reaction of Na(4D) is also surprising in view of the large exothermicity of the reaction. Representative results are shown in figures 4 and 5 for the reaction of Na(4D) at a collision energy of 18 kcal/mol.

### 3.4 $\text{Na}(n,1) + \text{NO}_2 \rightarrow \text{NaO} + \text{NO}$

Angular distributions for the  $\text{Na} + \text{NO}_2$  reaction were measured for  $\text{Na}(3\text{S}, 3\text{P}, 5\text{S}, \text{ and } 4\text{D})$ . The detected product in these experiments was the  $\text{Na}^+$  that fragmented from the  $\text{NaO}$  under electron bombardment; this meant that all the recorded distributions had a  $\text{Na}$  elastic scattering contribution. No  $\text{Na}(3\text{S})$  or  $\text{Na}(3\text{P})$  reaction was observed above this background. The  $\text{Na}(5\text{S})$  and  $\text{Na}(4\text{D})$  states, however, do react with  $\text{NO}_2$  as can be seen in figure 6. The product angular distributions for both these states are not the same. The most obvious distinction is in the reaction cross-sections which are in a ratio of approximately 12 to 1 in favor of  $\text{Na}(4\text{D})$ . The products also scatter differently. The  $\text{Na}(4\text{D})$  product is more backwards scattered and has a narrower energy distribution as evidenced by the sharper peak.

The nominal collision energy was varied between 5.5 and 19 kcal/mol so as to determine the  $\text{Na}(4\text{D}) + \text{NO}_2$  reaction threshold. The measured speed ratios of the reactant beams, which ranged from 3.2 to 5.2, allowed the spread in these energies to be calculated while the signal levels in the measured angular distributions gave an estimate of the relative reaction cross-sections at each nominal energy. A cross-section versus collision energy plot could then be constructed to match these observations. An adequate fit

was obtained when a step-function with a threshold of 20kcal/mol was selected. It must be mentioned however that this method is not very sensitive to the exact form this function.

Product velocity distributions were measured for the Na(4D) + NO<sub>2</sub> reaction at a collision energy of 19 kcal/mole. The laboratory angular and velocity distributions were calculated and fitted using an assumed product recoil energy distribution (P(E)) and center-of-mass angular distribution (T( $\theta$ )). The best T( $\theta$ ) and P(E) generated the contour map shown in figure 7.

Two different NaO products are apparent in figure 7. One (product 1) is very similar to the NaO observed in process (3). It is backwards scattered, has very little energy in translation, and has a very narrow distribution in velocity. The other type of NaO (product 2) is very different. It is forwards scattered, has much more energy in translation, and the velocity distribution is much broader. The relative cross-sections for production of each NaO have been estimated to be about equal. However, product 1 is kinematically enhanced for detection in the laboratory reference frame, and is therefore detected preferentially in the present experiment.

#### 4. DISCUSSION

In the reaction of alkali atoms with halogen containing molecules, some essential features can be modeled by the electron transfer "harpoon" mechanism. In this type of reaction, an ion pair complex is formed early by transfer of the Na valence electron into the Lowest Unoccupied Molecular Orbital (LUMO) of the molecule. This electron transfer is normally assumed to be rapid compared to the nuclear motions. The negative ion is formed on a dissociative repulsive region of the potential. When the ion dissociates, the negative fragment combines with  $\text{Na}^+$  via coulombic forces to form the reaction product [2].

##### 4.1 Reactions of excited Na atoms with halogen molecules.

The prominent feature seen in figures 2 and table 1 is that no large difference appears in the collision dynamics and, consequently, in the reaction mechanism when Na is excited. This observation is an indication that an electron transfer of the Na electron to the LUMO of the molecule is the initial step [2]. The shape of the LUMO is what determines the collision dynamics; it has been observed that the dynamics are very different when switching from halogen to organic halide molecules, but are only weakly sensitive to the identity of the alkali reactant [2]. This accounts for

the similarity in collision dynamics for reactions with different Na states; exciting Na affects the valence electron orbital, but not, of course, the LUMO of the molecule.

Experiments indicate that the total reactive cross section of process (1) does not increase very much when Na is excited. This result is somewhat surprising. The higher the Na excitation the lower the ionization potential; greater Na reactivity would then be expected since the electron transfer initiating the reaction should be possible at larger Na-molecule distances. The shift to large interatomic distances of the crossing between covalent and ion pair surfaces, however, reduces the interaction between them. This makes the excited states of Na less reactive than they would otherwise be. Such a reduction of the coupling element between covalent and ion pair surfaces as crossings move to larger distances has been demonstrated in a recent calculation using the DIM method on Alkali - Br<sub>2</sub> surfaces [11]. Apparently, these two factors, the earlier electron transfer and the lower coupling, compensate each other to some extent in these reactions.

No large change is observed in the center-of-mass recoil energies of NaCl produced in reaction (1) as Na is excited. The additional 48.4 kcal/mol corresponding to excitation of Na to the 3P level is thus released into internal



excitation of the product NaCl. This would suggest ion-pair formation occurring at a larger Na-Cl<sub>2</sub> distance which leads to the formation of more highly vibrationally excited NaCl.

#### 4.2 Reactions of excited Na atoms with hydrogen halides.

The dominant features of the excited Na + HCl reactions are the decreasing product recoil energy and the increasing reactive cross-section with increasing electronic energy. This can be observed directly in figure 3, and has been checked quantitatively by considering center of mass product angular and velocity distribution. For the reaction of Na(5S, 4D) most excess energy goes into the vibrational excitation of NaCl, in contrast to the reaction of Na(3P) where a large fraction of this energy goes into the translational energy of the products. Process (2) thus provides a situation where the reaction dynamics changes as the electronic excitation of the reactant is increased.

Reactions of ground state alkali atoms with hydrogen halides have never been adequately explained in terms of electron transfer "harpoon" models. The electron transfer in this case does not take place at long distance, because hydrogen halides have negative electron affinities [12]. However, excited Na atoms have much lower ionization potentials. This makes early electron transfer possible (see table 2), and such "harpoon" models should provide a useful framework to discuss reactions of excited Na atoms. HCl molecules are known to be dissociated into  $\text{Cl}^- + \text{H}$  by low energy electrons [13], so a dissociative electronic

attachment to HCl is expected to initiate the reactions of Na(3P,5S, 4D).

Let us consider the reaction of Na(5S, 4D) first. Based on the covalent and ion pair curve crossing, the electron transfer initiating the reaction occurs at large Na-HCl separations. The H atom departs very quickly after the electron transfer. The Na<sup>+</sup> and Cl<sup>-</sup> ions are then left at a separation approximately equal to the electron jump radius. The NaCl is thus formed with a large vibrational excitation, and the hydrogen atom is no longer present to release the excess energy. The early departure of H is thus able to explain the low product recoil energy found experimentally in reaction (2) for Na(5S, 4D).

Turning to Na(3P), the electron transfer occurs at a smaller distance, which is less than the sum of Van der Waals radii of HCl and Na, and the stages of electron transfer, H departure and NaCl formation are probably not well separated. The dynamics of H atom departure in this reaction are no longer dominated by the dissociation of HCl<sup>-</sup>. When the electron transfer occurs at a small distance between HCl and Na, the electronic configuration is closer to HCl-Na<sup>+</sup>. The repulsive departure between H and NaCl and the stronger coupling among all three atoms are thus responsible for a large fraction of the excess energy

in reaction (2) for Na(3P) going into product recoil energy.

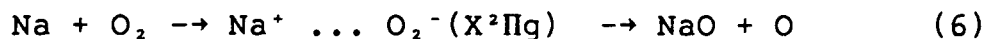
When the electron is to transfer at a long distance, a model such as the Direct Interaction model with Products Distributed as In Photodissociation (DIPR-DIP) should be able to describe the reaction dynamics well [14]. This model characterizes the reaction by sequential two body steps: electron transfer from Na to HCl, departure of H from Cl<sup>-</sup>, and, finally, association of Na<sup>+</sup> and Cl<sup>-</sup> to form NaCl. The above discussion for process (2) suggests that the DIPR-DIP model should explain Na(5S, 4D) reactions well, but not the reaction of Na(3P) with HCl. This has been confirmed more quantitatively in references [5,7,9].

#### 4.3 Reactions of excited Na atoms with O<sub>2</sub> molecules.

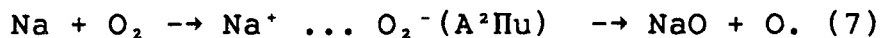
The most prominent feature in reaction (3) was that Na(4D) reacts with O<sub>2</sub>, but not Na(5S). Since the radiative decay of the 5S state populates the 4P,4S ... levels, it is clear that these levels also do not react to produce NaO.

The strong back scattering of the NaO products with respect to the incoming Na atoms is evidence of a direct (i.e. no long lived collision complex is formed) reaction. The especially narrow NaO center-of-mass angular range seen in figure 5 suggests that there are restrictive constraints on the impact parameter and relative orientation required for reaction to proceed. The narrow product recoil energy distribution in figure 5 shows that very little of the excess energy of this reaction goes into translation. It has been proposed in reference [6] that electronic excitation of NaO, O, or both carries away most of the excess energy.

Alexander has derived analytic forms for the lowest diabatic potential surfaces of the Na<sup>+</sup>-O<sub>2</sub><sup>-</sup> system [15]. Two reactive pathways have been proposed in this work as possibly involved in Na + O<sub>2</sub> reactions:



and



It was suggested in reference [6], that pathway (6) is probably not involved in the reaction since this "harpoon"-like pathway would be unlikely to be associated with a large activation barrier as was observed experimentally for process (4).

Recently, calculations have been performed where the reaction pathways (6) and (7) are included in a multiple ionic-covalent curve crossing model [16]. These calculations point out that pathway (6) is actually associated with much smaller reactive cross sections than pathway (7). The competition of the inelastic channel  $\text{Na}(4D \rightarrow n,1)$  with the reactive channel along pathway (6) is one of the main reasons why (6) makes such a small contribution to the reaction. Consistent with experimental results, the cross section associated with pathway (7) has a large threshold energy, and involves impact parameters smaller than  $1\text{\AA}$ . This makes pathway (7) a likely candidate to explain process (4). It is worthwhile to recall that dissociative electronic attachment on  $\text{O}_2$  molecules giving  $\text{O}^- + \text{O}$  fragments is a resonant process which proceeds through the same  $\text{A}^2\Pi_u$  level of  $\text{O}_2^-$  as that involved in reactive pathway (7) [17].

#### 4.4 Reactions of excited Na atoms with NO<sub>2</sub> molecules.

Process (4) is different from all the others that have been discussed so far in that two products are formed from the reaction of Na(4D). One of these products, product 1, is very similar to the NaO formed in reaction(3). Both exhibit backward scattering and have a small, narrow recoil energy distribution. This suggests that, as with the oxygen reaction, product 1 formation is a direct reaction with certain strict impact parameter and orientation requirements.

The other product observed in the Na(4D) + NO<sub>2</sub> reaction is very different from product 1. This is most apparent in the angular distributions. Product 2 is forward scattered suggesting a direct reaction with a large impact parameter. The recoil energy distributions also differ. Product 2 is formed with a much broader distribution of recoil energies and the mean translational energy of this distribution is approximately 5.5 kcal/mole larger than that of product 1.

The differences between the two products formed in process (4) suggest that two different mechanisms are involved in their production. This is supported by the observation that Na(5S) seems to react with NO<sub>2</sub> to produce product 2 but not 1. This can be seen from the Na(4D) and Na(5S)

product angular distributions in figure 6. What is most noticeable is the large difference in the reaction cross-sections. Since the Na(4D) and Na(5S) states are very close in energy (98.8 vs. 94.9 kcal/mole) and both put the reactions well above the reaction endothermicity and threshold barrier of 20 kcal/mole, this difference in reactivity could be the result of different reaction pathways. This point is furthered by the different peak positions and widths in the two angular distributions.

Sholeen and Herm have studied the reaction  $\text{Li}(2\text{S}) + \text{NO}_2$ , which is similar to process (4) for ground state Na [18]. The reaction products they found share many of product 2's characteristics. Their experiments showed the formation of  $\text{LiO}(X^2\Pi)$  and  $\text{LiO}(A_2\Sigma)$  which was forward scattered and exhibited a large, broadly distributed recoil energy (the peak energy was 45% of the reaction exothermicity or 3.8 kcal/mol). They saw no low translational energy, backward scattered product, although they did not try the experiment using electronically excited Li. Sholeen and Herm proposed a  $\text{Li}^+\dots\text{NO}_2^- (^3\text{B}_1 \text{ or } ^1\text{A}_1)$  intermediate to explain their data. The  $\text{Li}^+\dots\text{NO}_2^- (^3\text{B}_1)$  ion-pair seemed more plausible. It does not provide as deep a well in the reaction potential surface as the  $\text{Li}^+\dots\text{NO}_2^- (^1\text{A}_1)$  intermediate. Also, this choice could explain the large product recoil energies observed;  $\text{NO}_2^- (^3\text{B}_1)$  results from the



transfer of the Li electron to an antibonding orbital ( ${}^2b_1\pi$ ) on  $\text{NO}_2$ . Sholeen and Herm, however, did not choose one pathway over the other [18].

The mechanism proposed in both the  $\text{Li} + \text{NO}_2$  and  $\text{Na} + \text{O}_2$  experiments is reaction through an excited ion-pair intermediate. Since one of the  $\text{Na} + \text{NO}_2$  products is similar to that of the  $\text{Na} + \text{O}_2$  and the other to the  $\text{LiO}$ 's, it seems possible to propose that process (4) proceeds through the following intermediates:



Based on the comparison of the 2 products found to those found by others, the  $\text{Na} + \text{NO}_2$  reaction might proceed via intermediate (10) to give product 1 and through (9) to form product 2.

Since  $\text{NO}_2$  is a bent molecule, a near collinear collision between the Na and the O-N bond in the  $\text{NO}_2$  would result in a forward scattered product with a fairly large impact parameter. This approach geometry, then, is consistent with the observations for product 2 formation. Problems, however, arise when one attempts to determine the  $\text{Na}(4D)-\text{NO}_2$  collision geometry necessary to form product 1.

A small impact parameter, which was what was seen experimentally, would put the Na away from the oxygen it is supposed to be colliding with. Also, one would expect forward scattering for this type of collision. Physically, how is the product 1 NaO formed?

One answer that must be considered is that NaO is not being formed. As mentioned, in the experiment, Na<sup>+</sup>, not NaO<sup>+</sup>, is detected. The possibility, thus, exists that Rydberg sodium atoms are being produced. If this is true, the similarity between product 1 and the Na + O<sub>2</sub> product would cast some doubt on the Na + O<sub>2</sub> mechanistic assignment. Another explanation is that NaN + O<sub>2</sub> is forming. The Na(4D) + NO<sub>2</sub> → NaN + O<sub>2</sub> reaction channel is energetically possible (ΔH is approximately -30 kcal/mole). If the Na approached the N along the C<sub>2v</sub> symmetry axis, one could expect the product to be backwards scattered as is observed. Experiments done thus far have not given a definitive answer to the question of what this backward scattered product is. Future experiments are being planned to resolve this.

#### 4.5 Other Interesting Features

The experiments reported here have been extended in order to study how rotating the laser polarization, and thus the excited Na(P or D) orbital, affects the Na reactivity. Due to space limitations, only a few of these results are summarized below (see [7,9] for more details).

The Na(4D) + HCl reaction is enhanced when the Na(4D) orbital is aligned along the relative velocity vector. This behavior is expected if the reaction proceeds through a long range electron transfer mechanism in collinear Na...Cl-H geometry. For the Na(4D)+O<sub>2</sub> system, the favourable alignment for the reaction changes with the scattering angle, and corresponds to the Na(4D) orbital perpendicular to the molecular axis Na-O-O. Finally, the polarization effects encountered in the Na(4D)+NO<sub>2</sub> reaction suggest that product 1 but not product 2 formation is affected by the Na(4D) orbital alignment. This reinforces the conclusion reached in section 4.4 that products 1 and 2 are formed by different reaction mechanisms.

## 5. CONCLUSION

Representative families of excited alkali atom reactions have been studied using a crossed beam apparatus, and the reactivity of various excited states of Na has been investigated.

For those systems in which reactions are also known for ground state alkali and involve an early electron transfer step, (e.g. reactions of Na with  $\text{Cl}_2$ ), no large differences are observed in the reactivity as Na is excited. This can be understood in terms of two competing effects: the lower ionization potential of excited Na increases the Na reactivity which is compensated by a lower coupling between the covalent and ion pair diabatic curves of the Na-halogen system. The dynamics of the reaction remain unaffected by the Na electronic excitation, since the reaction behavior is entirely determined by the shape of the LUMO of the molecular reactant. Similar observations, which are not reported here, have been done for reaction of excited Na atoms with organic halide molecules. [4]

More interesting are the reactions of Na atoms with hydrogen halides. For ground state Na and Na(3P), the reaction does not proceed via early electron transfer, and the NaCl-H repulsion dominates the product scattering. The

excitation of Na to the 5S and 4D levels changes the reaction mechanism. The reaction then proceeds via an early dissociative electron attachment of the Na valence electron on HCl, and the HCl<sup>-</sup> repulsion dominates the NaCl product scattering.

The reactions of excited Na with oxygenated compounds, are of particular interest. The reaction with O<sub>2</sub> was found state specific, only Na(4D) reacts with O<sub>2</sub>, and seems to involve electron transfer to O<sub>2</sub>, so as to form the excited state A<sup>2</sup>Π<sub>u</sub> of O<sub>2</sub><sup>-</sup>, i.e. the state responsible for dissociative electronic attachment on O<sub>2</sub>. The reaction with NO<sub>2</sub> is even more complex since Na(4D) leads to the formation of NaO by two different pathways. It must be mentioned however, that the identification of NaO as product in these reactions has yet to be confirmed.

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TABLES

Table 1 Features of the center of mass distributions fitted to the laboratory angular distributions for Na(3S,3P) + Cl<sub>2</sub> reactions. Energies are in kcal/mol.

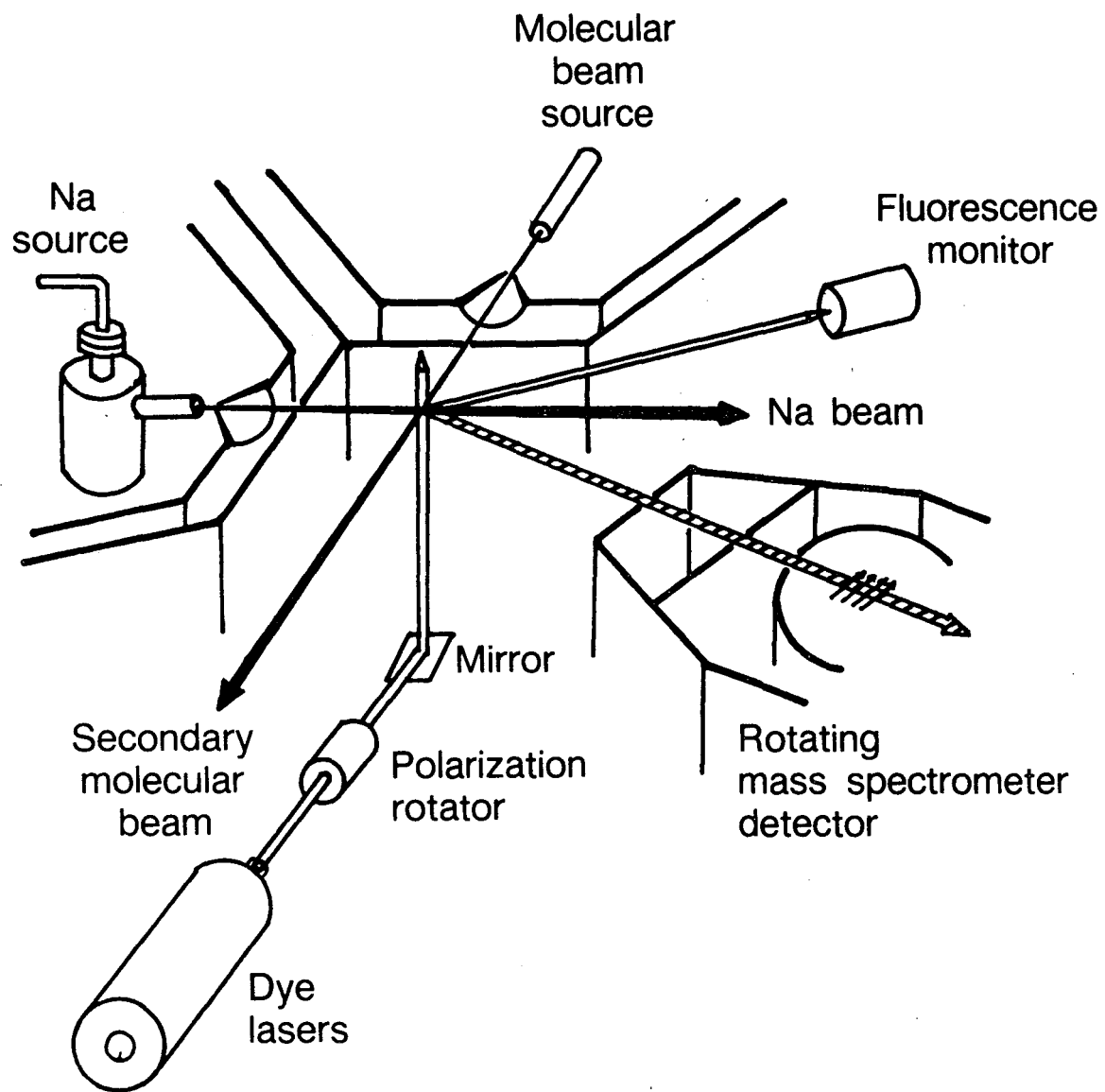
Na Level	Collision Energy	% of forward scattering	Peak Recoil energy	$\sigma(3P)/\sigma(3S)$
3S	6.	83	0.6	
3P	6.	76	1.2	1.58
3S	19.	85	0.8	
3P	19.	82	1.0	1.16

Table 2 Covalent-ion pair diabatic curve crossing radii for various electronic states of Na for the Na+HCl system. The electron affinity of HCl is taken to be -0.82eV [14].

Na Level	Ionization Potential(eV)	Crossing Radius (Angstrom)
3S	5.1	2.4
3P	3.0	3.7
5S	1.0	7.8
4D	0.8	8.6

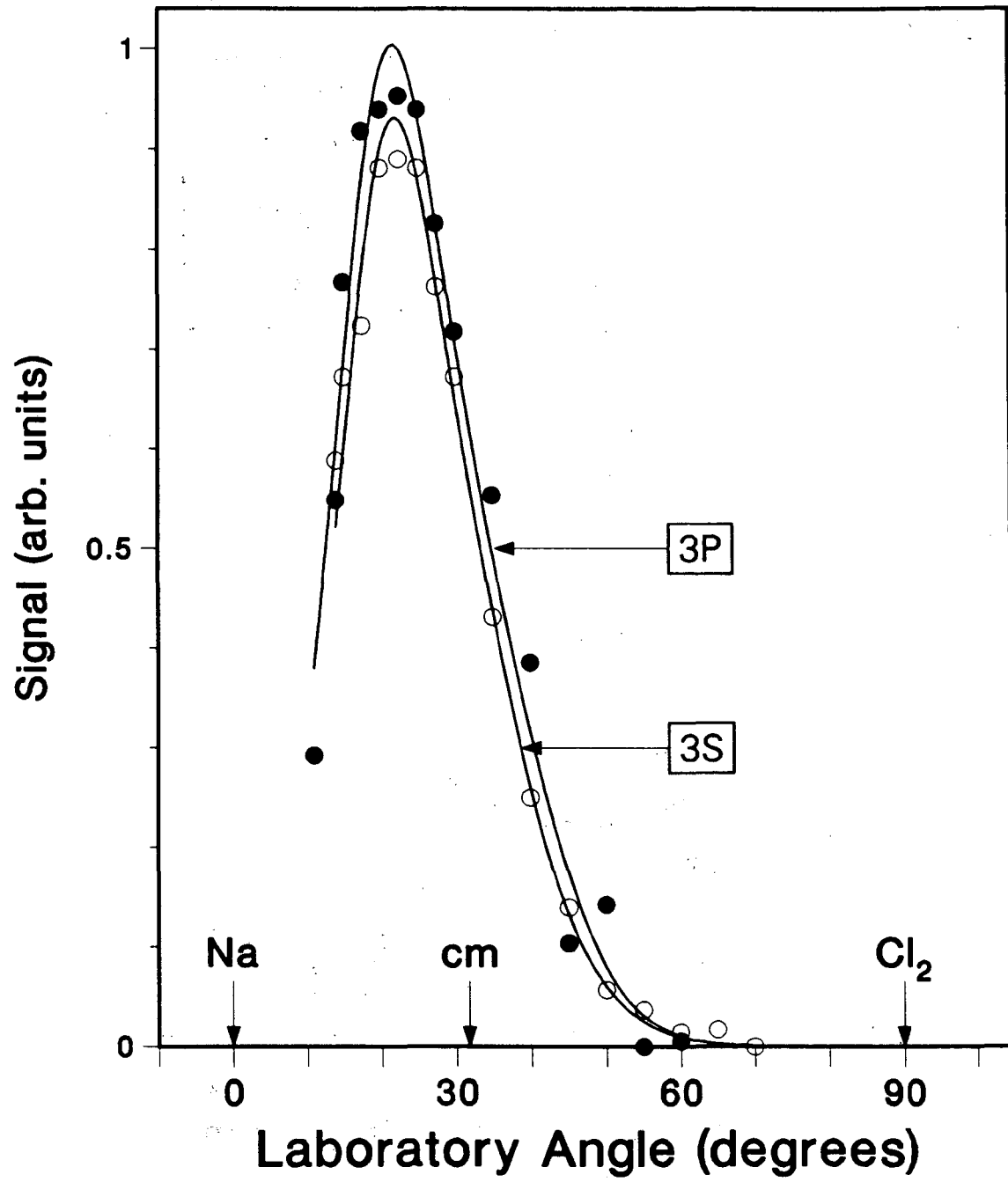
FIGURE CAPTIONS

- Figure 1 Schematic of the crossed molecular beam apparatus.
- Figure 2 NaCl product angular distribution for the reaction  $\text{Na}(3\text{S},3\text{P}) + \text{Cl}_2$  at 19 kcal/mol collision energy. The solid lines are the best fit to the data generated from center of mass angular and recoil energy distributions.
- Figure 3 NaCl product angular distributions for the reaction  $\text{Na}(3\text{S},3\text{P},5\text{S},4\text{D}) + \text{HCl}$  at 5.6 kcal/mol collision energy. The solid lines are just for guiding the eyes.
- Figure 4 NaO product angular distribution for the reaction  $\text{Na}(4\text{D}) + \text{O}_2$  at 18 kcal/mol collision energy. The solid lines are the best fit to the data generated from center of mass angular and recoil energy distributions.
- Figure 5 Best fit center of mass angular distribution (full line, left and lower scale) and recoil energy (dashed line, right and upper scale) of NaO in  $\text{Na}(4\text{D}) + \text{O}_2$  reactions at 18 kcal/mol collision energy.
- Figure 6 NaO product angular distributions for the reaction  $\text{Na}(3\text{S},3\text{P},5\text{S},4\text{D}) + \text{NO}_2$  at 19 kcal/mol collision energy.
- Figure 7 NaO product center of mass contour plot for the reaction of  $\text{Na}(4\text{D}) + \text{NO}_2$  at 19 kcal/mole collision energy.



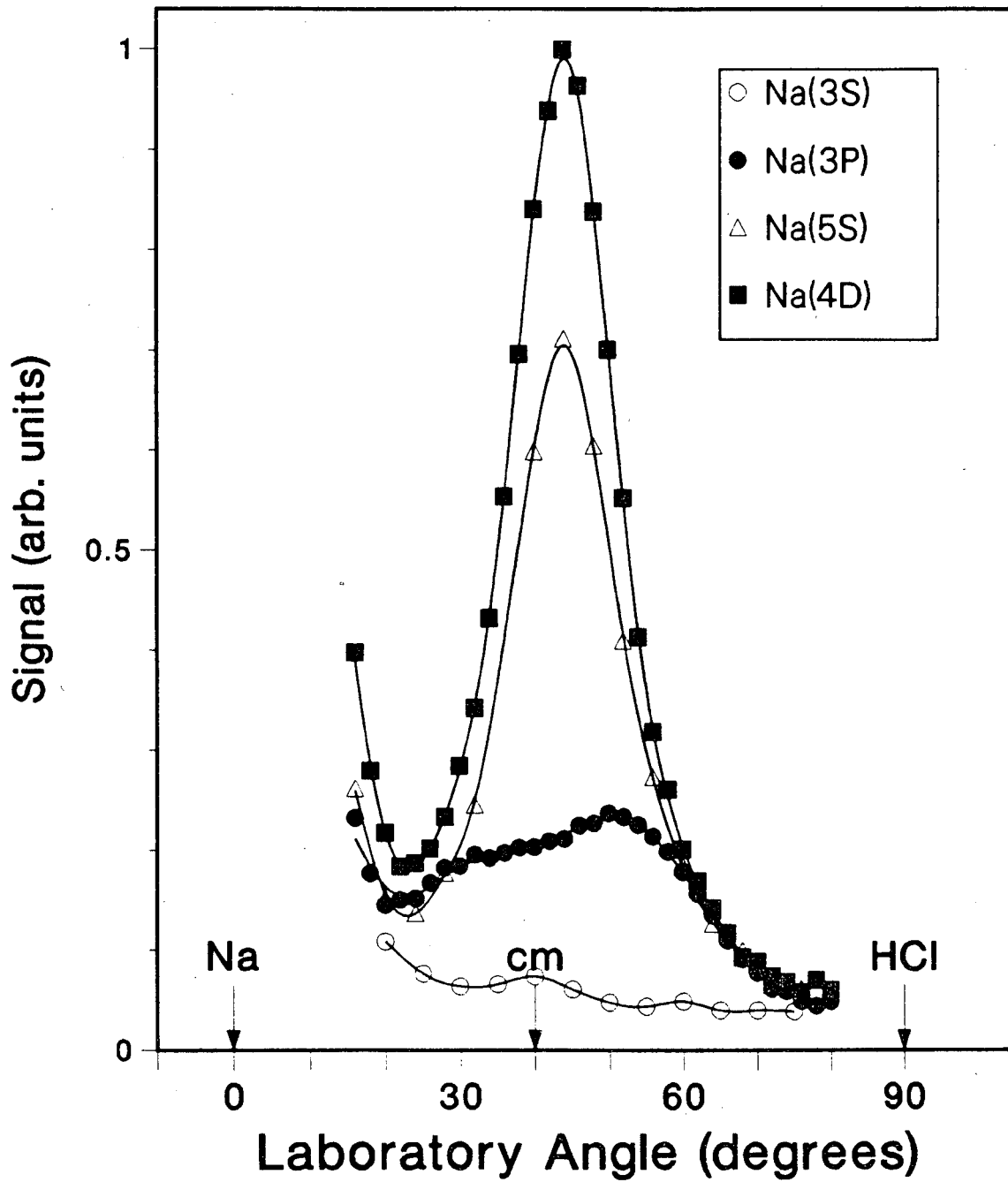
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Fig. 1



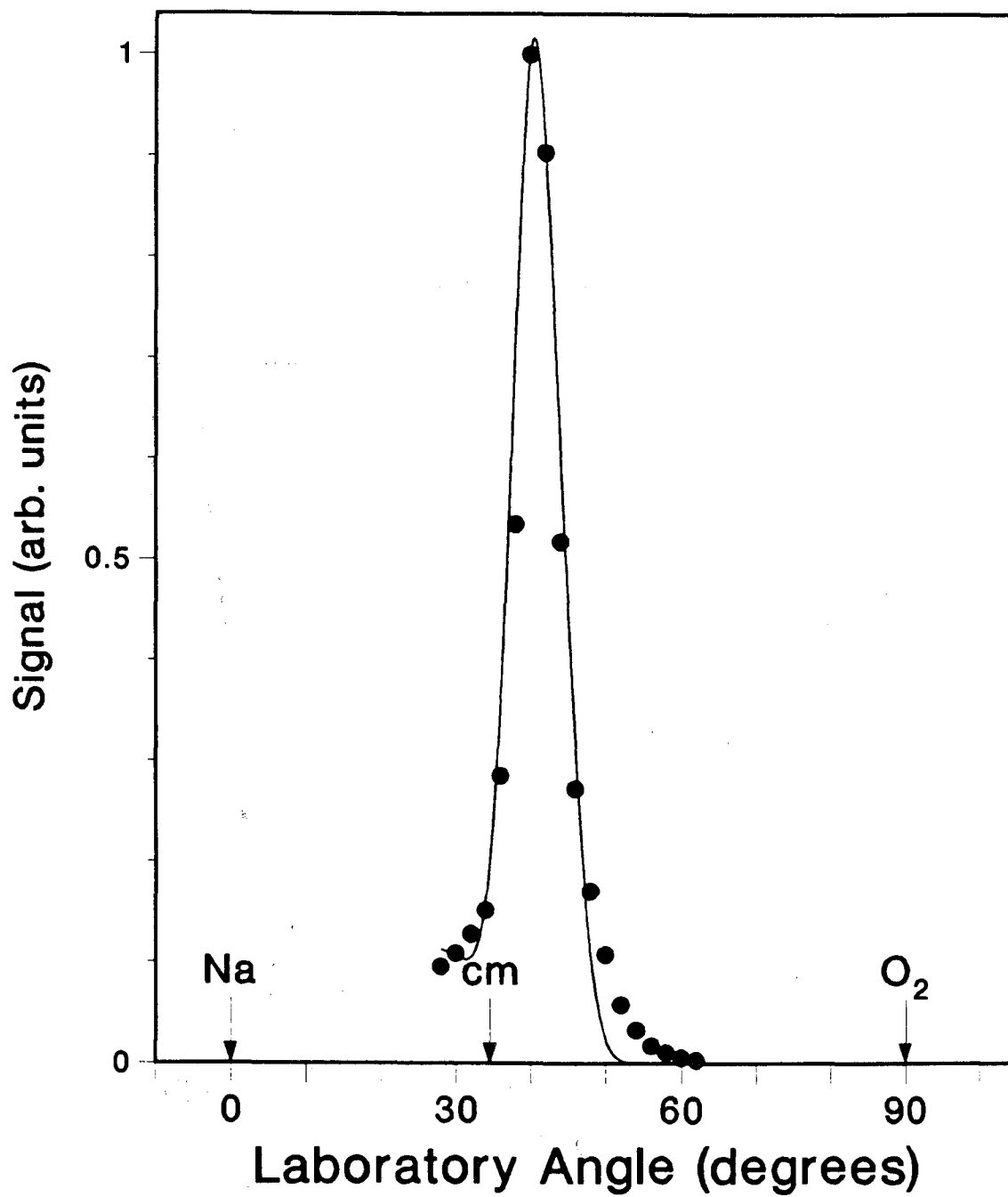
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Fig. 2



XBL 863-883

Fig. 3



XBL 863-850

Fig. 4

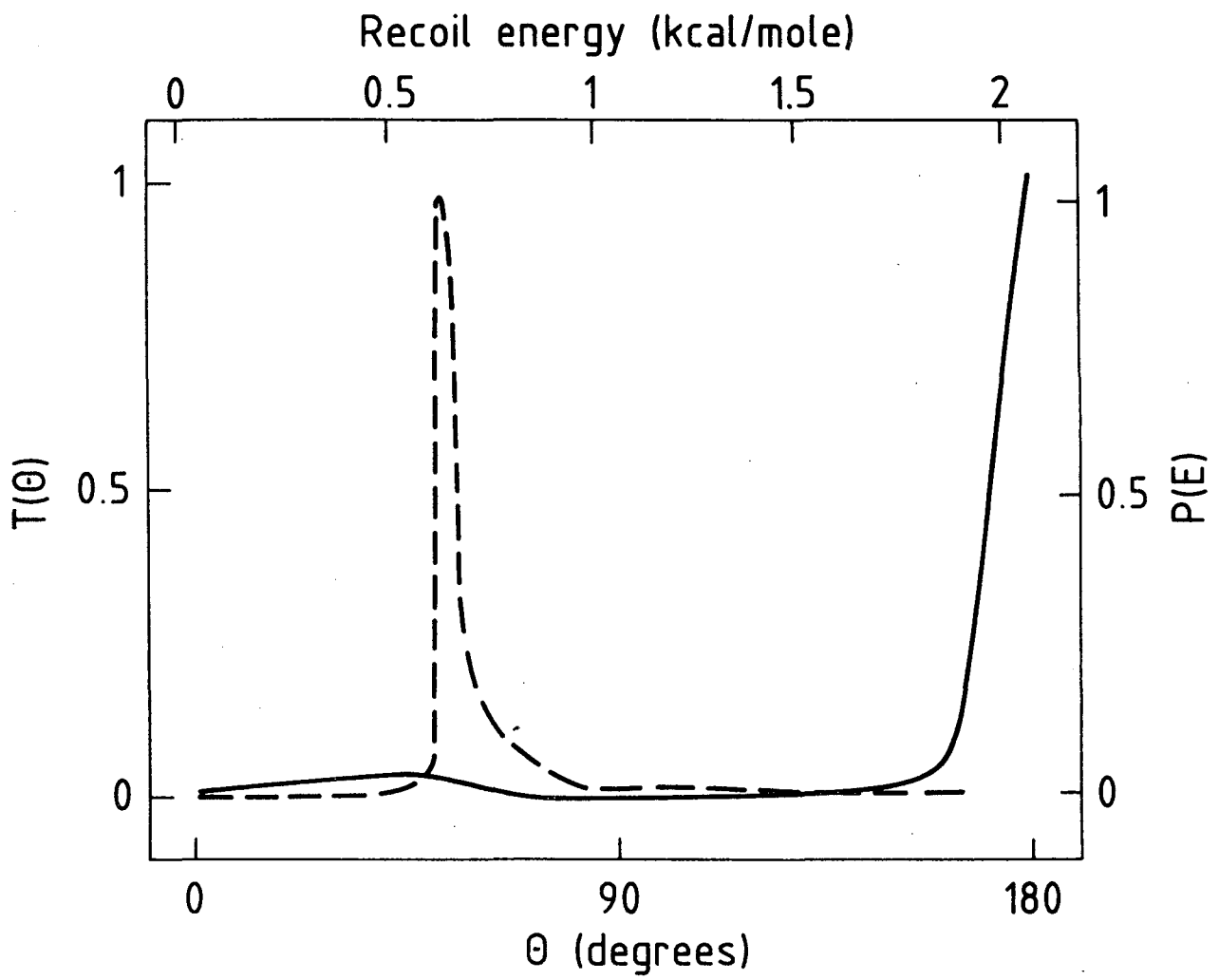
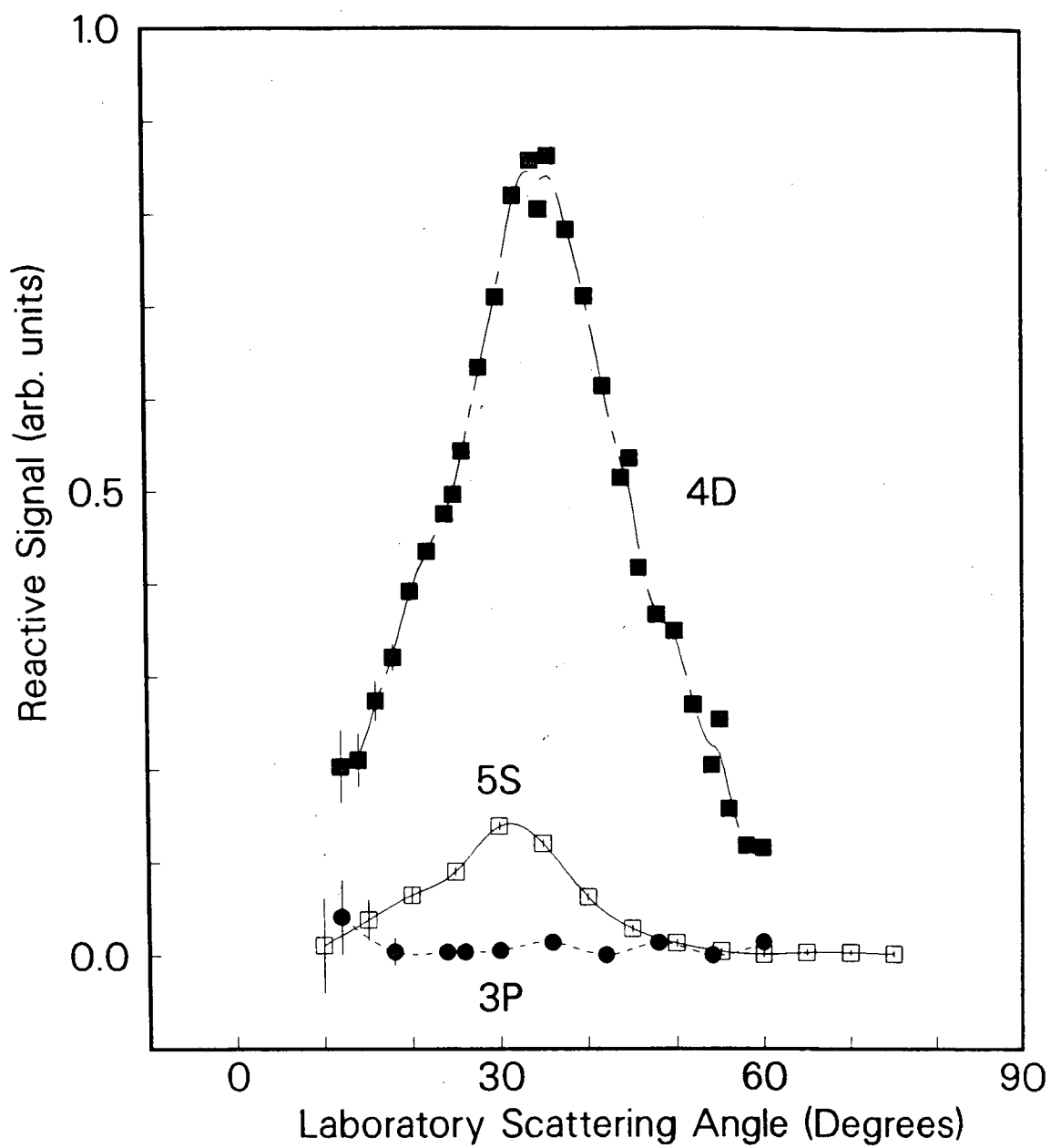


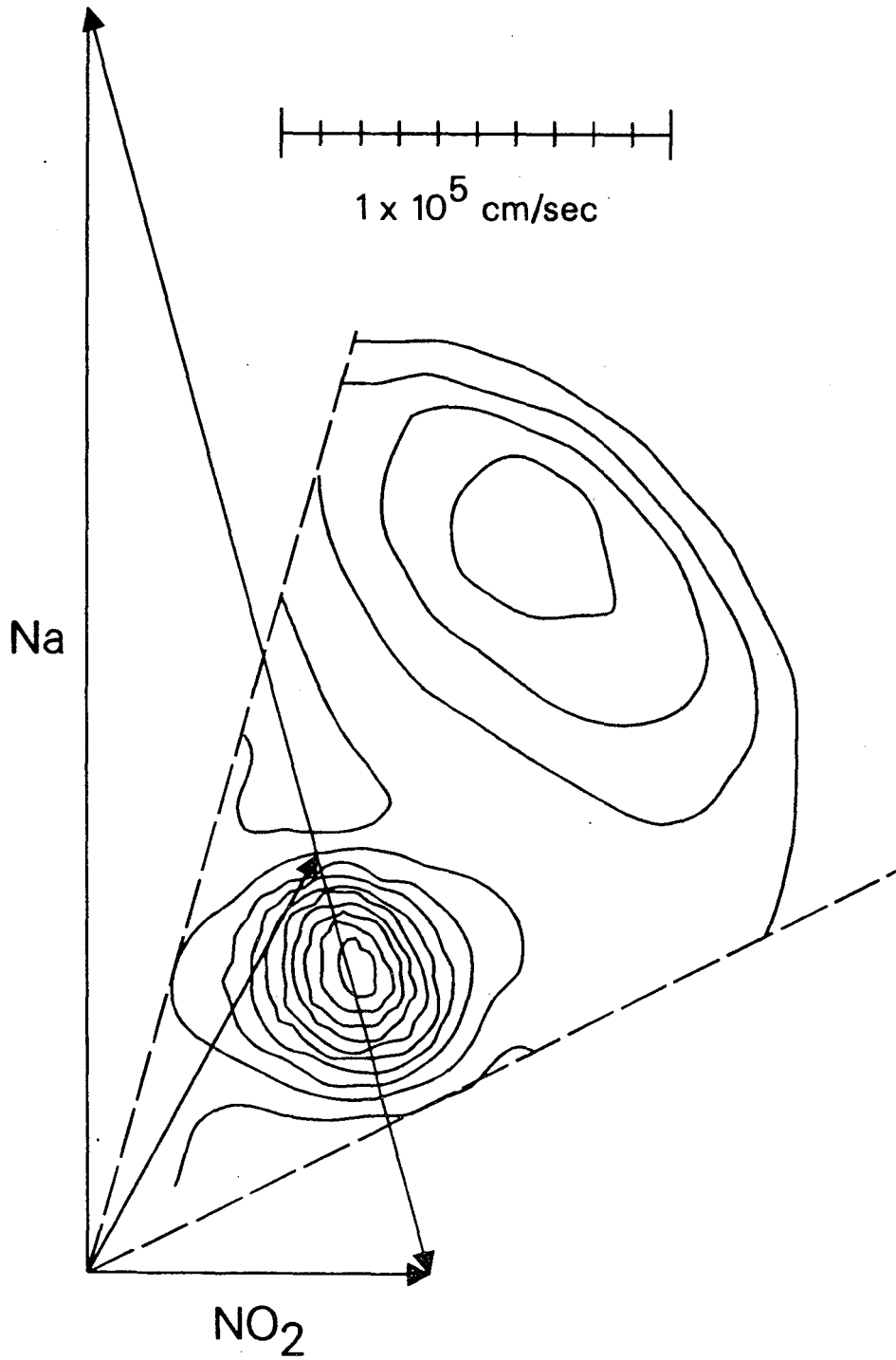
Fig. 5



XBL 875-2018

Fig. 6





XBL 875-2019

Fig. 7

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