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M.H. Covinsky, and Y.T. Lee

June 1985

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The State Specific Reaction of Electronically Excited Sodium Atoms
with Oxygen Molecules

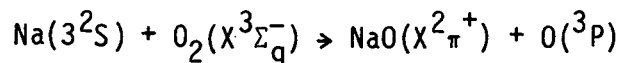
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ABSTRACT

The reaction of electronically excited sodium atoms with molecular oxygen has been studied in crossed molecular beams. The $\text{Na}(5^2\text{S}_{1/2})$ and $\text{Na}(3^2\text{P}_{3/2})$ states did not produce NaO at collision energies up to 18 kcal/mole, even though energetically allowed to do so. The $\text{Na}(4^2\text{D}_{5/2})$ state produced $\text{NaO} + \text{O}$ at center of mass collision energies higher than 16 kcal/mole, but not at 7 kcal/mole. The NaO produced was predominantly backwards scattered relative to the incoming sodium atoms in the center of mass frame of reference, implying that collinear and near collinear approach geometries are favored, and that the reaction proceeds directly with no collision complex formation. The $\text{NaO} + \text{O}$ produced were very highly internally excited, and it is likely that $\text{O}(^1\text{D})$ atoms were produced.

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The reaction:



is substantially endothermic, with $\Delta H = 58$ kcal/mole, but the electronic energy of the Na atoms in the 4D or 5S states, or with translational energy of at least 9.5 kcal/mole for Na atoms in the 3P states was more than enough to overcome this endothermicity. The purpose of this experiment was to study the effect of electronic energy and symmetry of the atomic wavefunction on chemical reactivity. We have chosen the $\text{Na}^* + \text{O}_2$ reaction since the endothermicity precludes reaction in the ground state. Moreover the positive electron affinity of O_2 , $E_a = 0.44$ eV, undoubtedly leads to an ionic intermediate, Na^+O_2^- , which plays an important role in the collision between Na^* and O_2 .

The experiment was performed in a modified universal crossed molecular beams machine described elsewhere.¹ Briefly, a seeded supersonic sodium atomic beam was crossed at 90° to a seeded or neat supersonic O_2 beam in a vacuum chamber under single collision conditions. The laser beams used for the excitation of sodium atoms crossed the atomic beam in this interaction region from the third perpendicular direction. Scattered product was detected with an ultrahigh vacuum quadrupole mass spectrometer equipped with an electron bombardment ionizer which could rotate in the plane defined by the atomic and molecular beams.

The laser excitation arrangement was similar to that of Reiland et al.² The Na($3^2P_{3/2}, F=3 \leftarrow 3^2S_{1/2}, F=2$) hyperfine transition of the Na D₂ line (589 nm) was optically pumped using a cw single frequency dye laser locked to the peak of the sodium fluorescence in the interaction region. Another single frequency cw dye laser was locked either to the green (569 nm) Na($4^2D_{5/2}, F=4 \leftarrow 3^2P_{3/2}, F=3$) transition, or to the red (616 nm) Na($5^2S_{1/2}, F=2 \leftarrow 3^2P_{3/2}, F=3$) transition. The optical pumping has been described in detail elsewhere,³ but Figure 1 shows the optical pumping scheme, and the approximate relative populations of the appropriate sodium levels when these transitions are saturated. Radiative transitions led to a significant steady state population in the Na(4^2S) and Na(4^2P) levels when either the Na(4^2D) or the Na(5^2S) levels were optically pumped as calculated from the Einstein A coefficients of Heavens.⁴

The laboratory angular distributions of products were measured for each of the three optically pumped Na levels, as well as for the ground state at three center of mass collision energies: 7, 16, and 18 kcal/mole. At the lower collision energy (7 kcal/mole) no reaction was observed for any of the Na levels. At the upper two collision energies (16 and 18 kcal/mole) reaction to NaO + O was observed only when the sodium atoms were optically pumped to the Na(4^2D) state. The measured laboratory angular distribution at a collision energy of 18 kcal/mole is shown in Figure 2. This distribution was taken with the mass spectrometer tuned to mass to charge ratio of 23 (Na⁺) because most of the product NaO fragments to Na⁺ in the electron bombardment ionizer.

There are four very striking features of these measurements. First, the reaction only proceeded from the Na(4^2D) state, even though the Na(5^2S) state (only 1350 cm^{-1} lower) and the Na(3^2P) state (if collision energy is included) were energetically allowed to react. The fact that significant steady state populations in the Na(4^2S) and Na(4^2P) levels were produced when we optically pumped the Na(5^2S) level allows us to conclude that the reaction also did not proceed for these states at the measured collision energies.

Secondly, the NaO product angular distributions were strongly backwards peaked relative to the incoming sodium atoms in the center of mass frame of reference. This implies that a collinear or near collinear approach geometry was favored, and that the reaction proceeded directly with no collision complex formation. The theoretically determined lowest energy state of the NaO₂ system, which has C_{2v} symmetry, has the Na atom at the apex of an isocetes triangle, and is 1.6 eV more stable than ground state reactants (Na(3^2S) + O₂($X^3\Sigma_g^-$)).⁵ Infrared, Raman, and ESR Spectroscopies of NaO₂ trapped in low temperature rare gas matrices have also shown the triatomic to be an isocetes triangle.^{6,7,8} Had NaO been produced via collision partners in a C_{2v} approach geometry and/or via long-lived collision complexes the NaO product angular distributions would have shown a much greater intensity in the forward direction relative to the incoming Na atoms in the center of mass frame of reference. Electron transfer from Na* to O₂ in the entrance channel is likely to form NaO₂ long-lived complexes, but apparently they did not lead to NaO production.

The collinear approach geometry and the reaction only for Na(4D) imply that a $C_{\infty V}$ NaOO(Δ) transition state led to NaO + O. Table I shows that in a nearly collinear approach geometry only a $C_{\infty V}$ NaO₂(Δ) transition state is accessible to the Na(nD) states and not to Na(nS) and Na(nP) states. Figure 3 shows a diabatic correlation diagram for Na + O₂ in $C_{\infty V}$ symmetry for states of spin multiplicity 2. No attempt has been made to accurately portray the energies of the transition states other than the lowest energy NaO₂ state as calculated by M. Alexander.⁵ A B₂ state in C_{2V} symmetry (isocetes triangle) is also accessible only to Na(nD), but we can exclude this possibility since we know that NaO was produced via a collinear NaOO geometry. Any state in C_s symmetry (non-collinear, and not isocetes triangle) can through curve crossings, go to low energy NaO₂ complexes which would most likely decay to quenching products -- Na(3S) + O₂($X^3\Sigma_g^-, a^1\Delta$), the lowest energy decay channels for NaO₂ complexes. It appears that only those collinear collisions between Na(4D) and O₂ which do not involve charge transfer in the entrance channel are responsible for NaO production.

Thirdly, the very small angular range over which the reactively scattered NaO was detected shows that the products were very highly internally excited (>2 eV). While our detector is not state selective, we are able to determine the product translational energy, and thus by using thermochemical information and invoking conservation of energy, we are able to determine the total product internal energy. Figure 4 shows the Newton circles for the production of various excited products from Na(4²D) and ground state molecular oxygen at a collision energy of 18 kcal/mole. Since

reaction products correlate adiabatically only to the ionic reactants $\text{Na}^+ + \text{O}_2^-$, there must be hops among the potential energy surfaces in order to produce NaO from neutral reactants. As figure 4 shows, the NaO product angular range falls completely within the Newton circle for the production of $\text{NaO}(A^2\Sigma^+) + \text{O}(^1D)$. While we cannot conclude with certainty that these were the product states, it seems very likely that $\text{O}(^1D)$ atoms were produced, and that the majority of the remainder of the excess energy was deposited into the internal degrees of freedom of NaO.

Lastly, the lack of reaction at low collision energy shows that there must be an entrance channel barrier of at least 7 kcal/mole, but less than 16 kcal/mole. This also suggests that the harpoon mechanism of electron transfer in the entrance channel does not lead to chemical reaction.

We are currently investigating the angular and velocity distributions of the NaO product, and are also investigating the dependence of the reactive scattering cross sections upon the direction of the laser polarization, and thus upon the Na orbital alignment. A detailed calculation of the excited NaO_2 potential surfaces would provide great insight into the mechanism of this reaction, and it is hoped that this work will stimulate such a theoretical treatment.

ACKNOWLEDGMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Two of the lasers used in this research were on loan from the San Francisco Laser Center supported by the National Science Foundation under Grant No. CHE79-16250 awarded to the University of California at Berkeley in collaboration with Stanford University.

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Table I. Symmetries of important reactant and intermediate states for Na + O₂ collisions.

| <u>System</u> | <u>Symmetry</u> | | | <u>Multiplicity</u> |
|---|-----------------------|----------------------|-----------------------|---------------------|
| | <u>C_{∞v}</u> | <u>C_s</u> | <u>C_{2v}</u> | |
| Na(ns ² S)+O ₂ (X ³ Σ _g ⁻) | Σ ⁻ | A'' | B ₁ | 2,4 |
| Na(np ² P)+O ₂ (X ³ Σ _g ⁻) | Σ ⁻ | A'' | A ₂ | 2,4 |
| | π ⁺ | A' | A ₁ | 2,4 |
| | π ⁻ | A'' | B ₁ | 2,4 |
| Na(nd ² D)+O ₂ (X ³ Σ _g ⁻) | Σ ⁻ | A'' | B ₁ | 2,4 |
| | π ⁺ | A' | A ₁ | 2,4 |
| | π ⁻ | A'' | A ₂ | 2,4 |
| | Δ ⁺ | A' | B ₂ | 2,4 |
| | Δ ⁻ | A'' | B ₁ | 2,4 |
| NaO ₂ (lowest 2 states) | π ⁻ | A'' | A ₂ | 2 |
| | π ⁺ | A' | B ₂ | 2 |
| Na ⁺ (¹ S)+O ₂ ⁻ (X ² π _g) | π ⁺ | A' | B ₂ | 2 |
| | π ⁻ | A'' | A ₂ | 2 |
| Na ⁺ (¹ S)+O ₂ ⁻ (a ⁴ Σ _u ⁻) | Σ ⁻ | A'' | A ₂ | 4 |
| Na ⁺ (¹ S)+O ₂ ⁻ (² Δ) | Δ ⁺ | A' | A ₁ | 2 |
| | Δ ⁻ | A'' | B ₁ | 2 |

FIGURE CAPTIONS

- 1 Optical pumping scheme for the two step laser excitation of the $\text{Na}^*(4^2D_{5/2})$ [$\text{Na}^*(5^2S_{1/2})$] level, and the populations of various levels when the lasers saturate the transitions shown.
- 2 Laboratory angular distributions of NaO at a center of mass collision energy of 18 kcal/mole. The upward trend at low laboratory angle is elastic scattering as the detector is moved closer to the Na beam. This is observed because product NaO fragments in the electron bombardment ionizer to Na^+ .
- 3 Diabatic correlation diagram for $\text{Na} + \text{O}_2$ in a collinear approach geometry for states of spin multiplicity 2.
- 4 Newton circles vs. observed product NaO angular range at 18 kcal/mole.

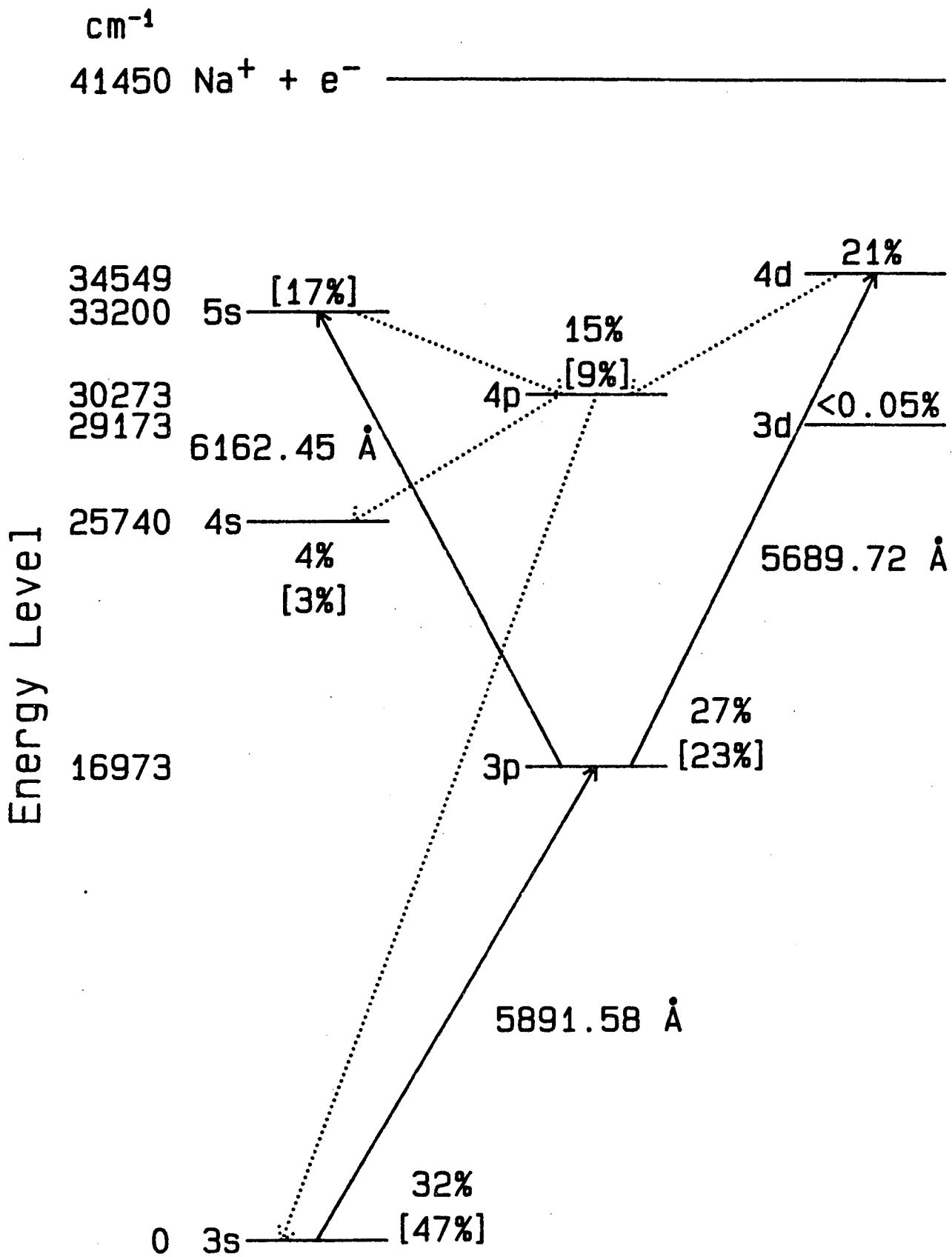


Fig. 1

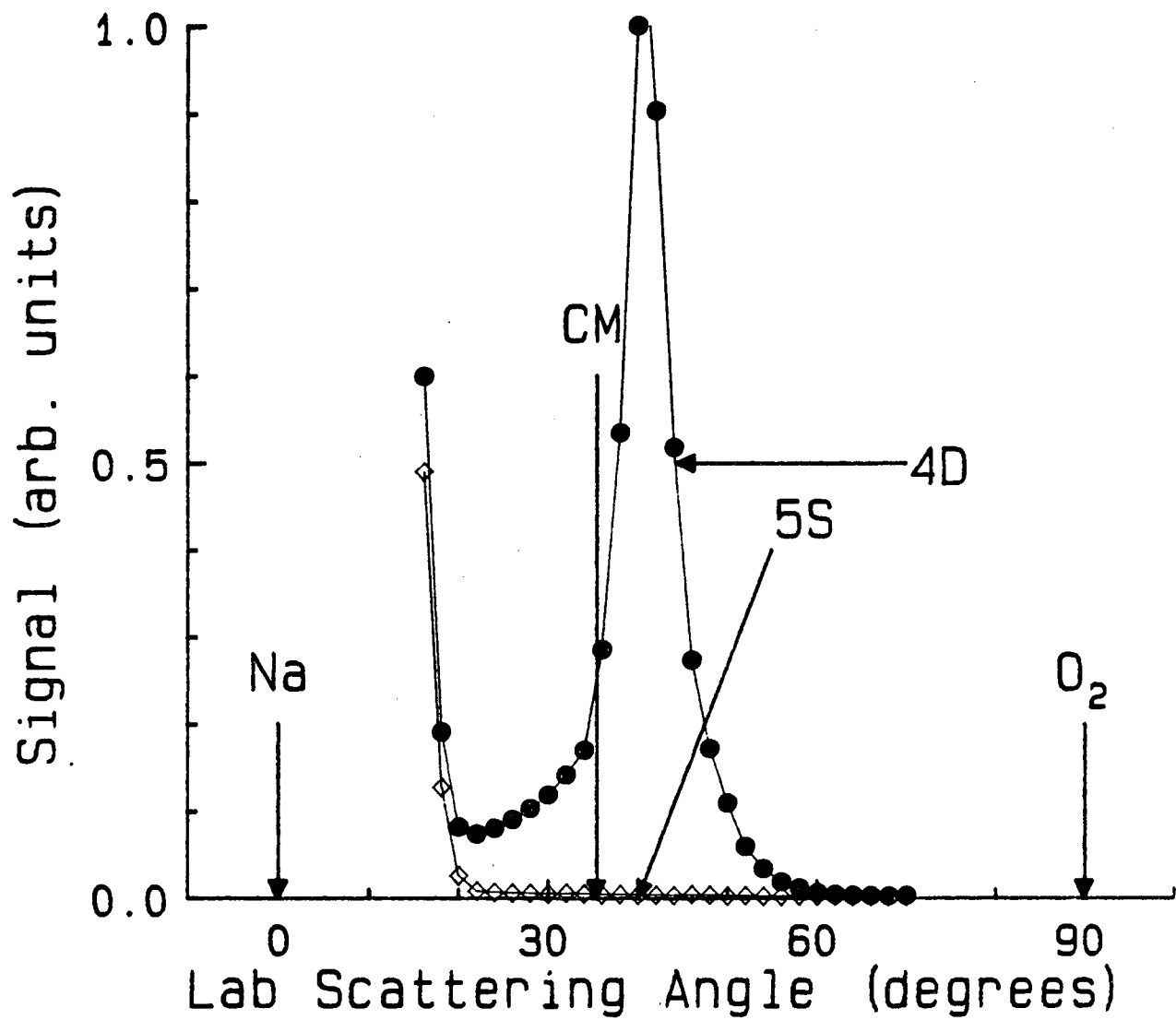


Fig. 2

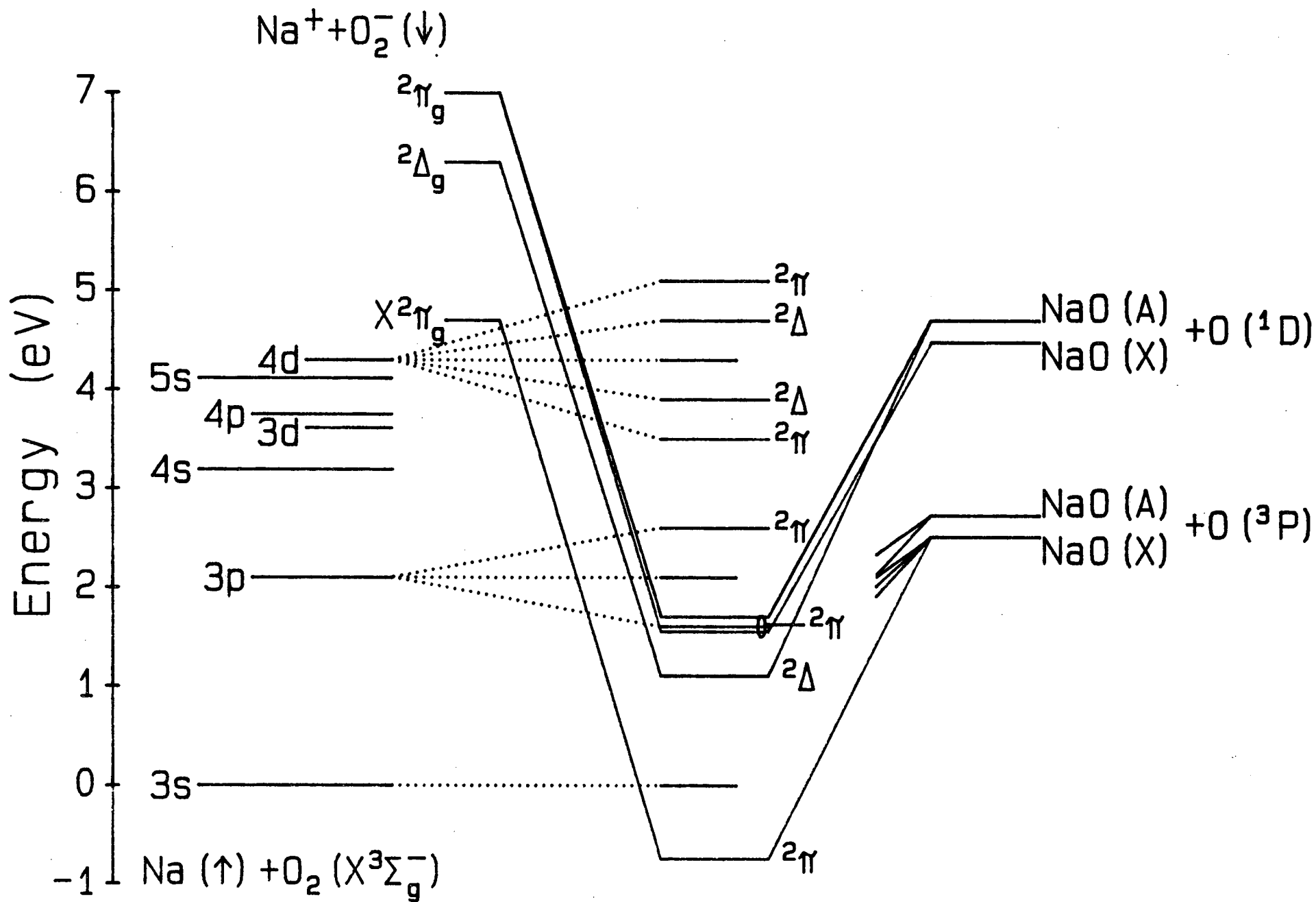


Fig. 3

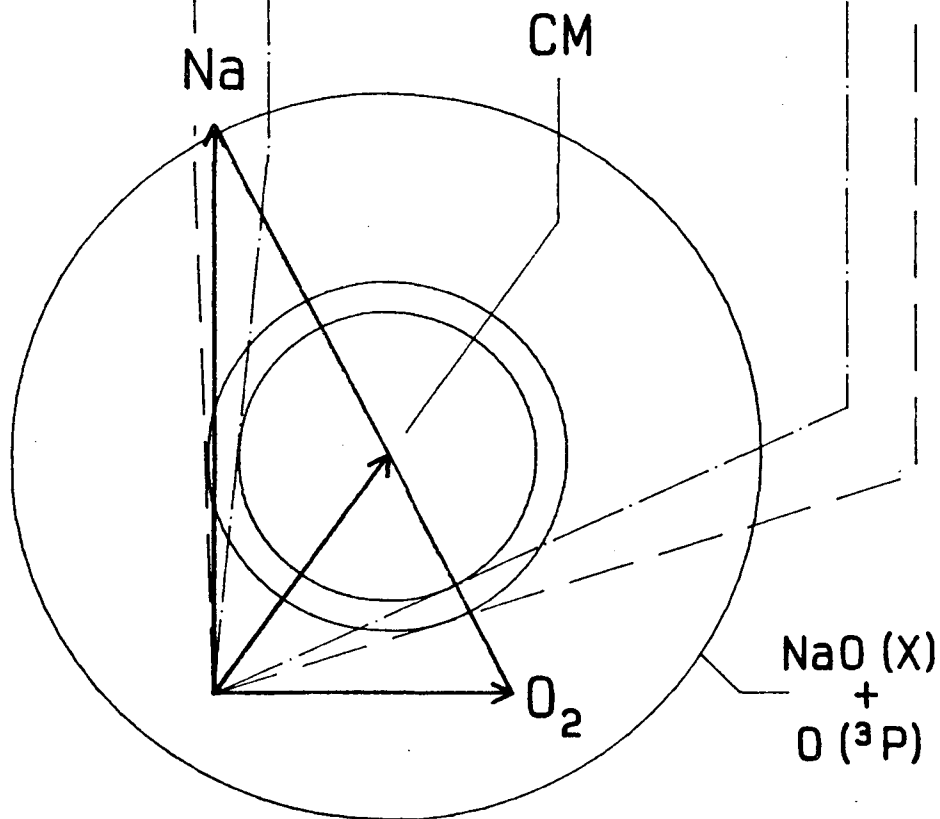
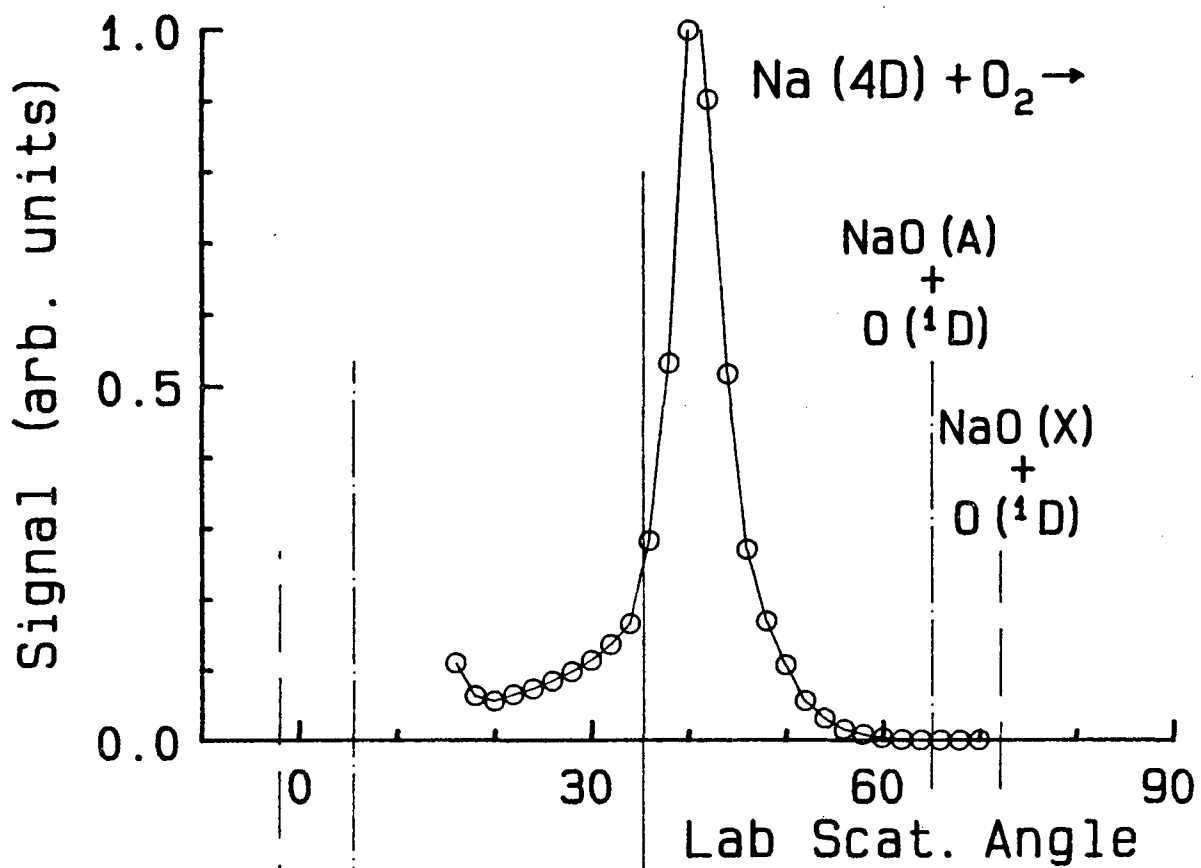


Fig. 4

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