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The Reaction Dynamics of Sodium with Ozone

M.H. Covinsky, A.G. Suits, H.F. Davis, and Yuan T. Lee

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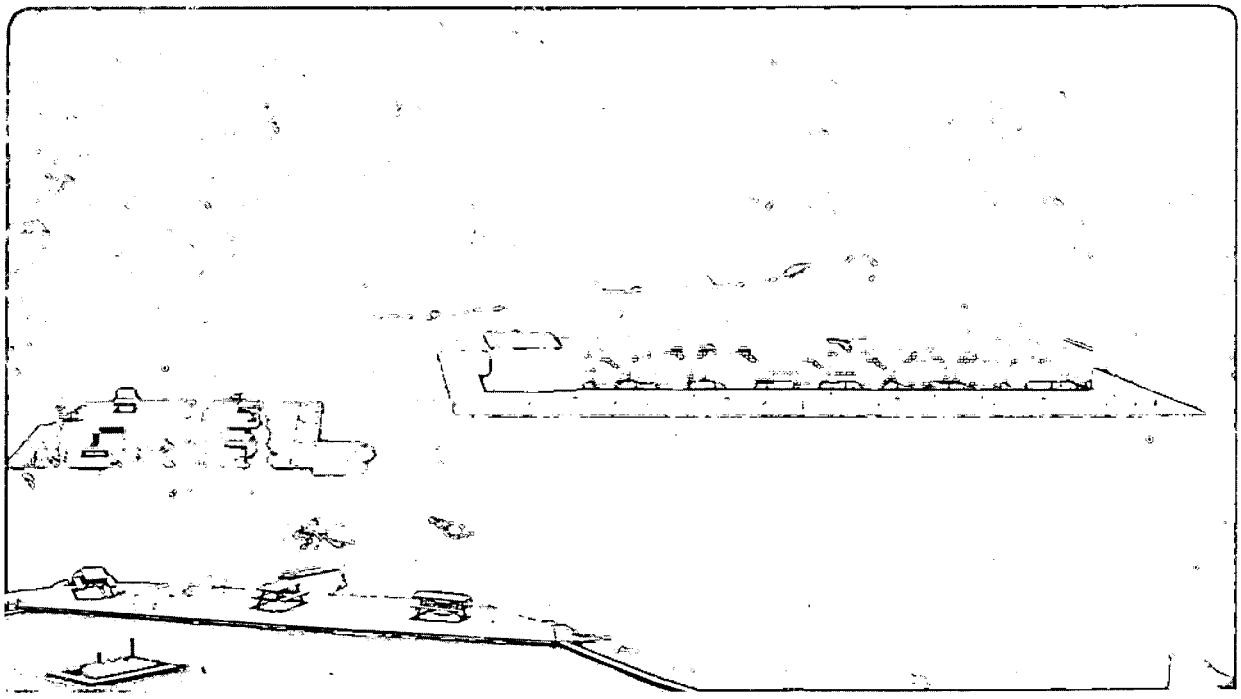

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Michael H. Covinsky, Arthur G. Suits,
H. Floyd Davis, and Yuan T. Lee

Department of Chemistry
University of California

and

Chemical Sciences Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720 USA

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Department of Chemistry
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Abstract

The reaction of sodium atoms (Na) with ozone (O_3) has been studied using crossed molecular beams at a collision energy of 18 kcal/mole. The only product observed was NaO. The reaction occurs via an electron-transfer mechanism that yields NaO which is forward scattered with respect to the sodium beam. The translational energy distribution peaks near the forward stripping limit but extends out to the maximum allowed by energy conservation. The fragmentation ratio of NaO upon electron bombardment ionization I(NaO+)/[I(NaO+) + I(Na+)] as a function of translational energy has been measured for an electron energy of 200V.

Introduction

The reaction of sodium atoms with ozone has been used to model the sodium D line nightglow in the mesosphere and in persistent meteor trains.[1-9] Chapman[1] proposed in 1938 that this reaction was the first step of a two step catalytic mechanism to explain the origin of the nightglow.

$$Na_{(g)} + O_{3(g)} \rightarrow NaO_{(g)} + O_{2(g)} \qquad \Delta H_0^0 = -35 \text{ kcal/mole} \quad (1)^{10}$$

$$NaO_{(g)} + O(^3P) \rightarrow Na(3^2P) + O_{2(g)} \qquad \Delta H_0^0 = -10 \text{ kcal/mole} \quad (2)^{11}$$

$$Na(3^2P) \rightarrow Na\ (3^2S) + h\nu\ (589 \text{ nm})$$

For many years the lack of accurate rate constant data hampered the modeling of the sodium layer.[6] Attempts were made to estimate a rate constant based on the $H + O_3$ reaction.[7,8] The rate constant of 6.5×10^{-12} cm^3/sec is too small to allow the Chapman mechanism to be valid. If the rate constant were this small then the three body recombination reaction

$$Na + O_2 + M \rightarrow NaO_2 + M \quad k = 5 \times 10^{-30}\ cm^6/sec^{12,13} \qquad (3)$$

would provide a major sink for Na. Additionally, incorrect rate constants lead to errors in the prediction of the height of the sodium layer and in the seasonal variation of the atmospheric sodium concentration. It was not until 1975 that Kolb and Elgin[14] pointed out that sodium can

react via a long range harpoon mechanism. Using a sodium atom ionization energy of 5.14 eV and an ozone electron affinity of 1.99 eV they calculated a cross-section of 65Å^2 for reaction (1) and a corresponding rate constant of 3.3 x 10^{-10} cm^3/sec at a temperature of 185°K.

The first gas phase measurement of the rate constant was performed by Husain, Marshall, and Plane in 1985.[15] They obtained a value of k = 4(+4,-2) x 10^{-10} cm^3/sec for reaction 1. Silver and Kolb[16] used fast flow cell methods to measure the rate constant. A value (3.1 ± 0.4) x 10^{-10} cm^3/sec at 295°K was found, in good agreement with the expected harpoon mechanism value. Using similar methods Ager, Talcott, and Howard[17] derived a rate constant of (7.3 ± 1.4) x 10^{-10} cm^3/sec at 286°K. They also measure a lower limit of 0.95 for $k_1/(k_1 + k_2)$. No explanation is given for this disagreement in the rate constant. However, it is interesting to note that both groups report the same total rate constant for the reaction

$$NaO + O_3 \rightarrow Na + 2O_2 \quad (4)$$

$$\rightarrow NaO_2 + O_2 \quad (5)$$

of 2 x 10^{-10} cm^3/sec which agrees with the harpoon model prediction in which the ionization potential of NaO is 6.5eV.[18]

This paper presents a crossed molecular beam study of the Na + O_3 reaction. Center of mass angular and translational energy distributions for the products are derived. These distributions are used to understand the dynamics of this reaction.

Experimental

These experiments were carried out in a crossed molecular beams machine that has been described previously.[19-22] A supersonic beam of sodium atoms is crossed orthogonally by a supersonic beam of ozone under single collision conditions at a 3mm x 3mm x 3mm collision volume. The collision chamber is liquid nitrogen cooled and pumped to 1 x 10^{-7} torr. (Fig. 1) Product is observed by a triply differentially pumped quadrupole mass spectrometer which has an electron bombardment ionizer and Daly detector. The mass spectrometer rotates in the plane defined by the two beams.

Primary Source

The source of the sodium beam is a resistively heated molybdenum oven that will be described in detail in a later publication.[23] The oven is divided into three parts. The inlet is a 9 inch long molybdenum tube. A molybdenum flow constrictor with a is placed inside this tube about 0.5 inches from the entrance to the reservoir to prevent sodium from backstreaming into the inlet tube and clogging

it. The Na reservoir consists of concentric cylinders designed for even heating and to be the coldest part of the oven. The nozzle diameter is .008 inches. The entire oven assembly is designed so as to permit the oven to be removed and replaced without the necessity of realigning the entire source.

The typical current and voltage used to heat the oven were 350 amps at 1.34V a.c. The temperature of the nozzle and reservoir were measured with an optical pyrometer. The temperature of the nozzle was 1100°C and the temperature of the reservoir was 700°C. At this reservoir temperature the vapor pressure of sodium is about 80 torr. The oven is backed with 500 torr of ultrahigh purity helium (99.999%). The Na-He mixture is expanded through the nozzle into the primary source chamber which is maintained at 2×10^{-4} torr.

After the expansion the beam passes through a molybdenum skimmer which is 0.30 inches downstream of the nozzle. The skimmer tip has a diameter of 0.030 inches. The skimmer is heated to 700°C conductively by passing current through four 3/16 inch diameter tantalum rods which pass through the body of the skimmer. The typical current and voltage is 95 amps at 2.2V a.c. The rods are electrically insulated from the skimmer by alumina tubes.

Secondary Source

The secondary source has been described in great detail previously.[21,22] The ozone used in this experiment was generated by an OREC model number 03V1-0 auto ozonator and held in a silica gel trap cooled in a dry ice/acetone slush. The trap was transferred to an FTS Systems Multicool model number MC-4-60A-1 constant temperature bath and the gas mixture was generated by passing helium through the trap. The ozone concentration was monitored by passing the gas mixture through a 1 cm quartz cell and measuring the absorption at 280 nm. No attempt was made to remove trapped oxygen. However, since there is not enough energy for O_2 and Na to react at the beam energies used this was not a problem. The total stagnation pressure of the beam was 240 torr and the mole fraction of ozone behind the nozzle was 0.12. The concentration of ozone was kept constant by adjusting the temperature of the constant temperature bath and continually monitoring the absorption through the quartz cell. The partial pressure of ozone was constant to within ±3% of the mean value. More importantly time of flight measurements of the velocity distribution of the beam taken with the ozone concentration at the extremes of ozone concentration allowed during the experiment varied by ±1% from the mean. The gas mixture was expanded into the source chamber which was maintained at 2×10^{-4} torr. The beam parameters are shown in table 1.

Data Acquisition

Data is acquired with programs run on an LSI-11/23 computer interfaced to a camac crate.[22] Both angular distributions and product time-of-flights (TOF) were measured. The TOF wheels were photoetched by PCM Products. Data is accumulated for at least a total of one hour at all angles measured. Beam velocity profiles are also measured with the time of flight technique however, single-shot wheels are used.

Results and Analysis

Angular and time of flight distributions were recorded at a collision energy of 18 kcal/mole. The newton diagram for this collision energy is shown in figure 2. The angular distribution (Fig. 3) is very broad and peaked forward of the center of mass. This angular distribution was recorded at m/e = 39 which corresponds to NaO^+ thus unambiguously identifying the signal as being the result of reactive scattering. This distribution is diagnostic of a long range electron transfer with the forward scattering of the NaO product.

The time of flight distributions at m/e=39 are shown in figure 4. The distributions are fit using an updated version of program CMLAB.[30] This program fits the data using the forward convolution method. The center of mass product flux distribution is expressed as a product of P(E),

the center of mass translational energy distribution and $T(\theta)$, the center of mass angular distribution. The P(E) and the $T(\theta)$ used to fit the data are shown in figures 5 and 6. One feature of the P(E) that becomes apparent is the unusual behavior at low translational energy. The distribution looks as if it has been cut away. The explanation is that we are detecting a diatomic product with a fragmentation ratio $I(NaO^+)/I(Na^+)$ that is very sensitive to the internal energy of the NaO product. Since NaO usually fragments to Na^+ upon ionization a small change in the fragmentation ratio of $I(NaO^+)/I(Na^+)$ will produce a large change in the intensity of NaO^+ detected. We assume in fitting the data that $I_{cm}(\theta,E) = P(E)\times T(\theta)$. However since fragmentation is important this is properly written

$$I_{cm}(m,\theta,E) = [F_m(E)\times P(E)]\times T(\theta)$$

where $F_m(E)$ is the ratio of the number of ions produced at fragment mass m to the total number of product molecules ionized as a function of the total relative translational energy of the products. In writing this equation an extra assumption is made in addition to the usual one about the separability of P(E) and $T(\theta)$. The extra assumption is that for a given relative translational energy E the state distributions of the products do not change drastically as a function of the center of mass angle θ such that the

fragmentation ratio will be angular dependent. If for example NaO were backscattered with relative translational energy E and all the available internal were in NaO vibration, then it would be expected that NaO ionization would strongly favor Na^+ production. If NaO were forward scattered with the same relative translational energy but the internal energy of NaO is much less with most of the internal energy stored in O_2 then NaO ionization would produce more NaO^+ than in the previous example. It is likely that any such breakdown in this assumption would also accompany a corresponding breakdown in the separability assumption which seems to be valid in our experimental observations. Therefore, it is unlikely that, for a given translational energy, there are large enough differences in the NaO quantum states produced as a function of the center of mass angle to cause a significant additional error.

To measure $F_m(E)$ time-of-flight data were taken 45° at both m/e=23 and m/e=39. This angle was chosen for two reasons. First, this angle is very close to the center of mass and therefore time-of-flight data taken at this angle sample the entire range of translational energies of products in the center of mass coordinate system down to below one kcal/mole. Second, this laboratory angle corresponds to a wide center of mass scattering angle for the elastic scattering of sodium off ozone. This wide scattering angle would require a low impact parameter

collision. Since it is known that this reaction has a very large cross-section as discussed in the introduction, these low impact parameter collisions will most likely lead to reaction rather than elastic scattering. Therefore the m/e=23 time-of-flight spectrum at 45° as mainly from reactive scattering and contains negligible contribution from elastic scattering.

The time-of-flight spectrum at 45° was taken by alternating between m/e=23 and m/e=39 after short intervals. The quadrupole resolution was set low to ensure that the transmission of the quadrupole mass filter was the same at both masses. The time-of-flight spectra were normalized to their counting time and added. The m/e=23 times of flight had to be shifted to be five microseconds slower to account for the different ion flight times through the quadrupole mass spectrometer. The individual measurements of m/e=23 and m/e=39 and the resulting sum are shown in figure 7. The $T(\theta)$ used to fit this TOF is derived from the m/e=39 data. The P(E) derived is shown in figure 8. The salient features of this distribution are shown in table 2. The integrated intensities of the normalized m/e=23 and m/e=39 times of flight were used to normalize the areas under the curves for both the m/e=39 P(E) and the total P(E). The m/e=39 P(E) was divided by the total P(E) to obtain $F_m(E)$ for m=39 as shown in figure 9. It should be emphasized that $F_m(E)$ is a function only of the total translational energy and thus it

is a quantity that averages over the range of combinations of O_2 internal energies and NaO vibrational and rotational energies that occur at a given relative translational energy. However if the internal excitation of the O_2 products are small, the fragmentation ratio shown will then largely reflect the dependence on NaO internal excitation. It is expected that $F_m(E)$ should also be dependent on the electron bombardment energy which was 200 volts in this experiment.

Discussion

The center of mass angular distribution of NaO is very strongly forward peaked. Additionally although the translational energy distribution extends out to the maximum allowed by conservation of energy the energy distribution peaks at low values. These distributions are characteristic of a reaction that proceeds via a long range harpoon mechanism[31]. An electron is transferred from Na to O_3 at a distance of 4.6Å. This distance is calculated using an ionization potential of Na of 5.1 eV and an electron affinity of O_3 of 1.99 eV. Similar to halogen molecules, O_3^- can dissociate into O_2 and O^- after the electron is transferred. The Na^+ then "reels in" an O^- and NaO proceeds in the same direction as the initial Na velocity thus yielding a forward distribution. If there is only a small interaction between the departing NaO and O_2 molecules then

this reaction approaches the forward stripping limit. In this limit the velocity of O_2 formed is the same as the initial velocity of O_3. Under the conditions used in this experiment the stripping limit would result in a product translational energy of 7 kcal/mole close to our peak in the energy distribution which is around 10 kcal/mole. Support for this mechanism can be found in the large gas phase rate constants previously measured for this reaction.[13-15] Additionally the proposed charge transfer state $Na^+O_3^-$ has been detected in rare gas matrices.[32,33]

Bates and Ojha[34] argued that in the gas phase reaction once the electron is transferred from Na to O_3 an intimate collision takes place between the Na^+ and the O_3^- exciting the internal modes of the anion before separating into products. This argument is certainly correct if O_3^- is a strongly bound species which will not dissociate before the coulomb attraction draws the Na^+ and the O_3^- together. Our results suggest another possible explanation. NaO is strongly forward scattered which implies that Na and O_3 spend less than 1/2 a rotational period together. This means that the oxygen-oxygen bond must be broken very quickly. Our previous work on ground and excited state sodium reactions it has been found that the course of a reaction between sodium and a given molecule can be predicted in a very rough and broad manner by examining the gas phase electron scattering data of the molecule in

question.[35] The feature that has proved most important is the existence of broad low energy dissociative attachment resonances. Such processes have been seen in ozone.[36,37] The processes in question are

$$O_3 + e^- \rightarrow O_2 + O^- \qquad \Delta H = -9 \text{ kcal/mole} \quad (4)$$

$$O_3 + e^- \rightarrow O + O_2^- \qquad \Delta H = 15 \text{ kcal/mole} \quad (5)^{38}$$

The threshold for reaction 4 was found to be at an electron kinetic energy of 0 eV. The threshold for reaction 5 was 0.4 eV within experimental error. The cross-section for O^- production was found to be greater than the cross-section for O_2^- production at the peaks of the resonances. The existence of the broad zero volt resonance implies that when an electron is transferred from Na to O_3 the O_3^- will fall apart into O_2 and O^- rapidly. The bond can then be formed between the Na^+ and the O^- ion. The higher threshold for the production of O_2^- is consistent with the fact that no NaO_2 was seen. The O_3^- is formed in the strong field of the Na^+. The manner in which this can drive the dissociation in can be thought of in two ways. First, the Na^+ creates a 6.7×10^7 V/cm field at a distance of 4.6Å. As pointed out by Birely and Hershbach this can initiate the field-induced dissociation of O_3^-.[39,40] Alternatively, as the electron is

transferred the Na^+-O^- coulombic interaction can provide the energy necessary to dissociate the O_3^-.

The Bates and Ojha model might still be consistent with the data especially since our collision energy is high and the crossing distance of 4.6Å is not much larger than the sum of the radii of the product molecules. It is possible for Na^+--O_3^- to have a strong collision after electron transfer occurs and for the reaction to be complete in less than one rotational period. However it seems likely that O_3 will behave like a halogen and dissociate without the hard collision when the impact parameter is relatively large.

There is an exception to the rapid dissociation model that is due to the fact that in the ozonide anion the electron is unable to transfer freely among all three oxygens in a manner consistent with the formation of O_2 and O^-. If Na lies along the C_{2v} axis of O_3 with the apical oxygen pointed toward the Na when electron transfer occurs, the dissociation of O_3^- and the coulombic attraction of Na^+ and O^- will oppose. This will lead to longer lived intermediates than is found in alkali-halogen reactions and is consistent with the larger amount of backward scattering than is typically seen for stripping reactions.

The fact the translational energy distributions are so broad might indicate strong coupling between the departing NaO and O_2. The NaO formed by the "harpoon" with high vibrational energy can relax if an intimate encounter

between nascent NaO and O_2 occurs and the energy goes into translation as the molecules separate.

Normally it is difficult to make conclusions about the distributions of excess energy between two product molecules and the partitioning of the internal energy between vibrational and rotational degrees of freedom in crossed molecular beam experiments that make only angular and time of flight distribution measurements. For all but the lightest molecules in triatomic reactions the rovibrational energy levels are too closely spaced to be resolved. These conditions are true in this experiment. However, the fragmentation pattern results do allow us some qualitative insights into the internal energy distribution. If all the internal energy went into O_2 and NaO were formed cold the $F_m(E)$ would be flat. The fact that it is strongly dependent on the product translational energy means that there is considerable variation in the internal excitation of the NaO bond. In other words, O_2 formed might not contain as much variation in the internal excitation. At very low translational energies the $F_m(E)$ turns slightly upward in favor of m/e=39. If NaO is formed electronically excited then it can fluoresce during the 125 microsecond flight time and thus increase the probability of NaO^+ production upon electron impact ionization. NaO fluorescence from an electronically excited state has been found by Gole and coworkers in an Na + O_3 flame at 6700Å.[41,42] From the lack of

structure in the translational energy distribution or a substantial anomaly in $F_m(E)$ one can conclude that electronically excited NaO is a small fraction of the NaO produced.

Conclusions

The reaction of Na + O_3 yields NaO + O_2. No NaO_2 was observed. It occurs via a long range electron transfer with the NaO forward scattered. Although the translational energy distribution extends out to the maximum allowed by energy conservation there is a great deal of energy in the internal modes of the products a substantial amount of which is in NaO vibration. For a large fraction of reactive encounters O_2 is not a spectator; intimate encounters between nascent products seem to be important. The angular distribution of the products shows some of the products are from longer-lived intermediates likely to be NaO_3 with C_{2v} symmetry and the negative charge on the central O atom.

Acknowledgement

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Table 1

Beam Parameters

	peak velocity (cm/sec)	beam spread $v/\Delta v$
Na	2.80×10^5	11.3
O_3	1.43×10^5	10.4

Table 2

P(E) Features

	$\langle E_{trans} \rangle$	E_{peak}
m/e=39	28.7 kcal/mole	38 kcal/mole
m/e=23 + m/e=39	22.4 kcal/mole	10 kcal/mole

Figures

Figure 1: Schematic of the crossed molecular beams apparatus.

Figure 2: Newton diagram for the reaction

$Na + O_3 \rightarrow NaO + O_2$ E_{coll} = 18 kcal/mole.

Figure 3: Laboratory angular distribution at m/e=39. The points are the measured distribution. The line is the best fit to the distribution.

Figure 4: Time of flight distributions at m/e=39. The dots are the data. The lines are the best fit to the data.

Figure 5: P(E) m/e=39 used for best fit.

Figure 6: T(θ) m/e=39 used for best fit.

Figure 7: Time of flight for the sum of m/e=23 and m/e=39

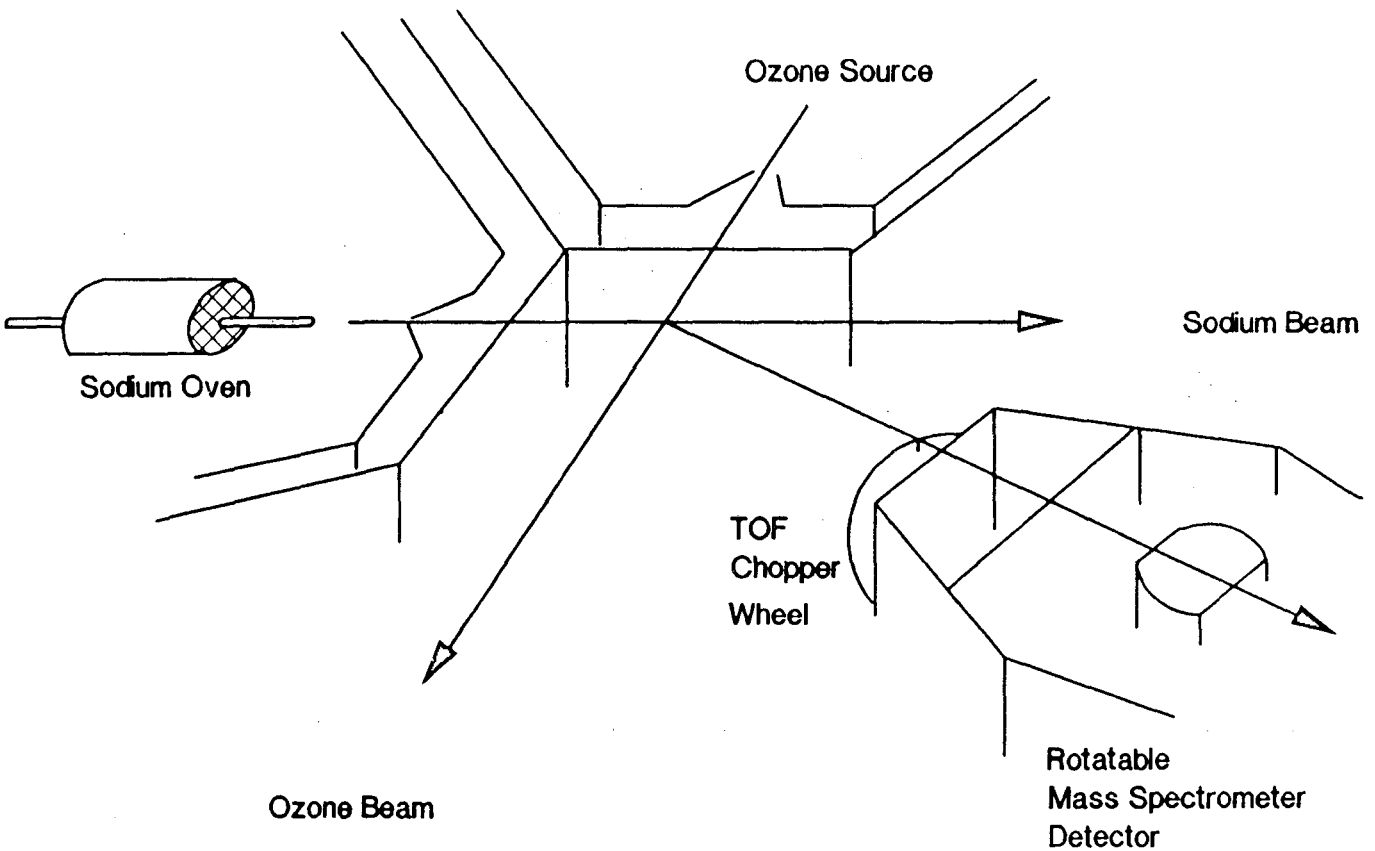
_____ total calculated fit.

----- contribution from m/e=23.

____...___ contribution from m/e=39.

Figure 8: P(E) derived for the sum of m/e=23 and m/e=39.

Figure 9: $F_m(E)$ Fragmentation of NaO to NaO^+ as a function of total translational energy.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Sodium Oven
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Mass Spectrometer
Detector
Ozone Beam

Figure 1

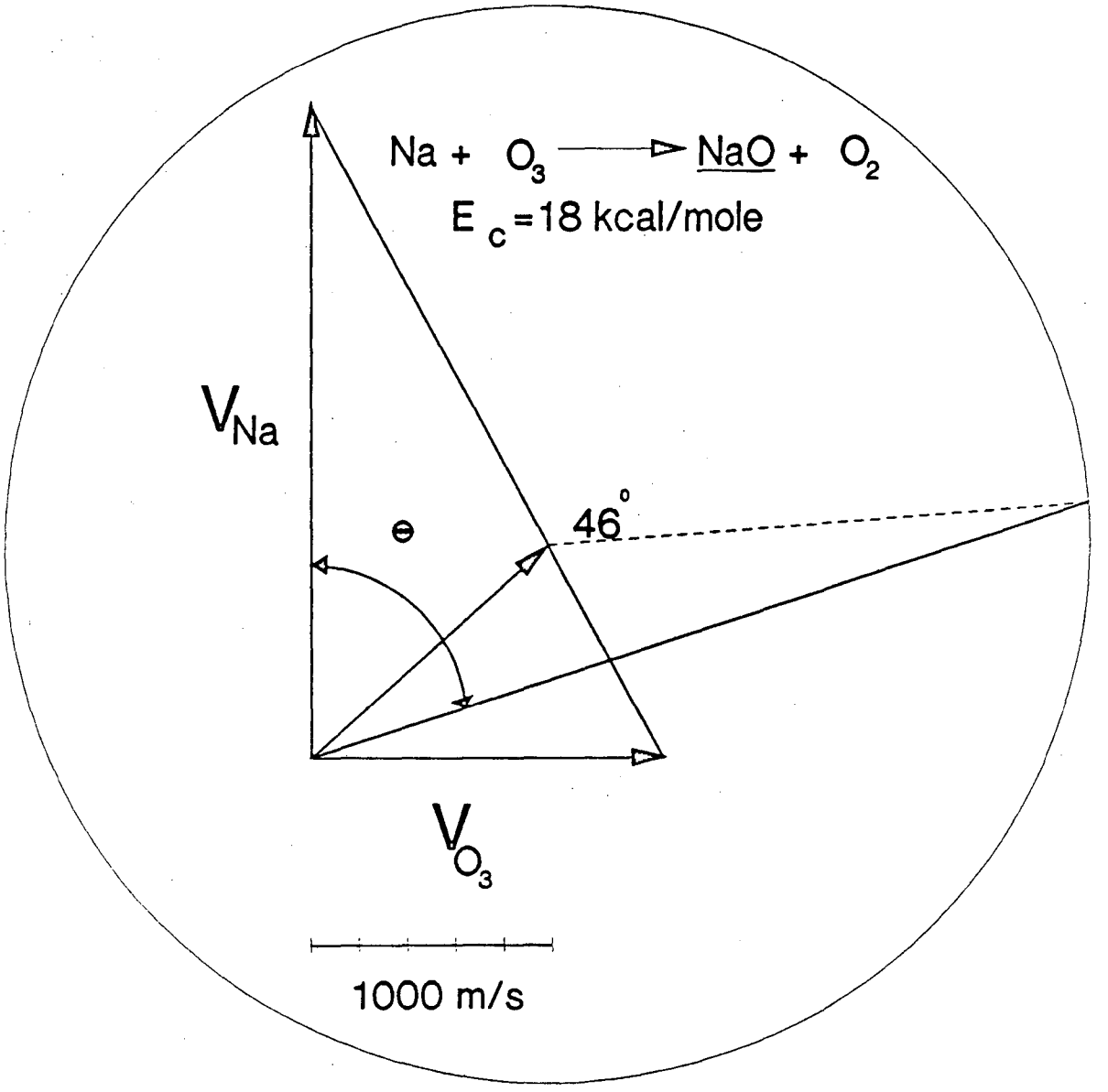

Figure 2

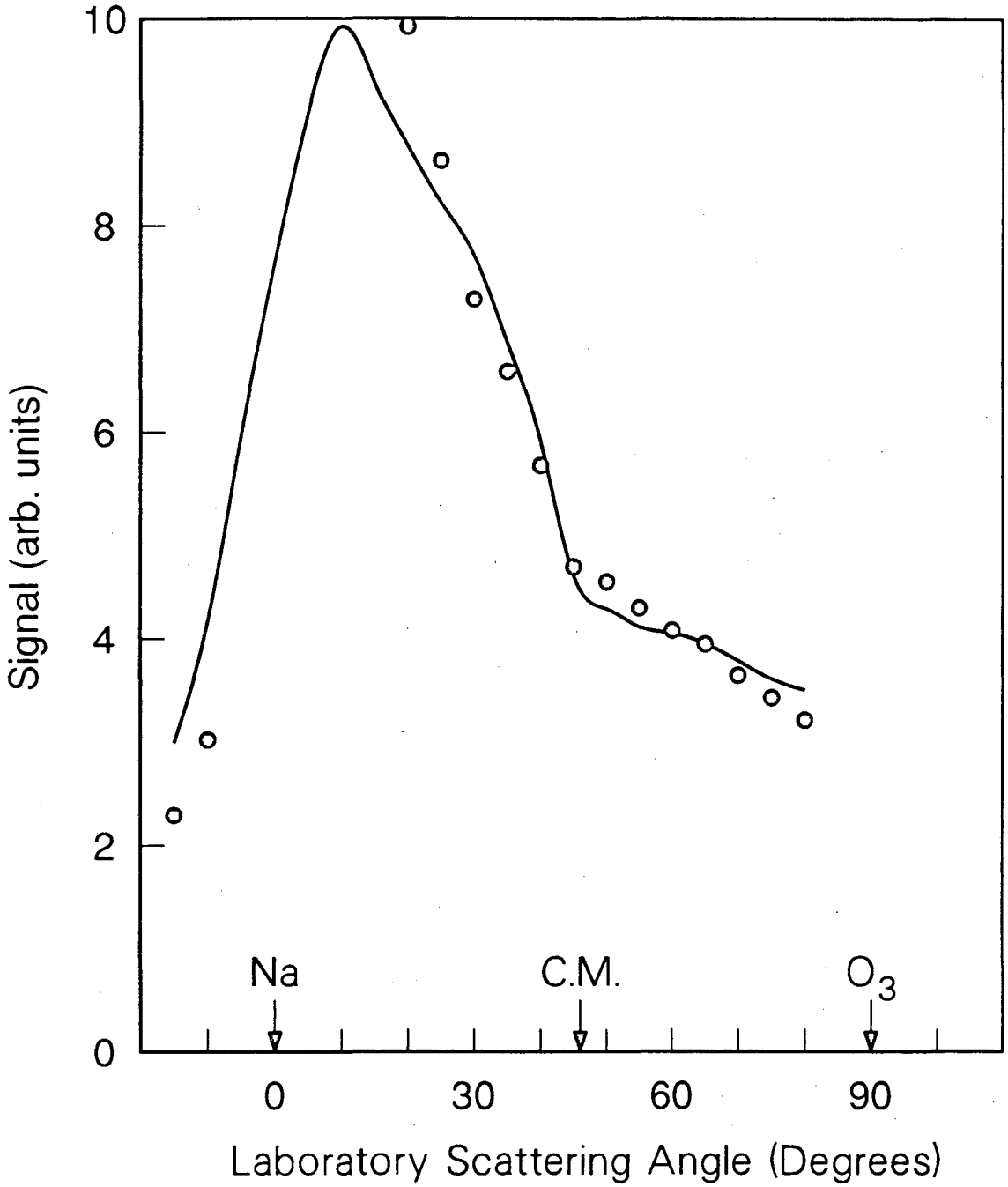

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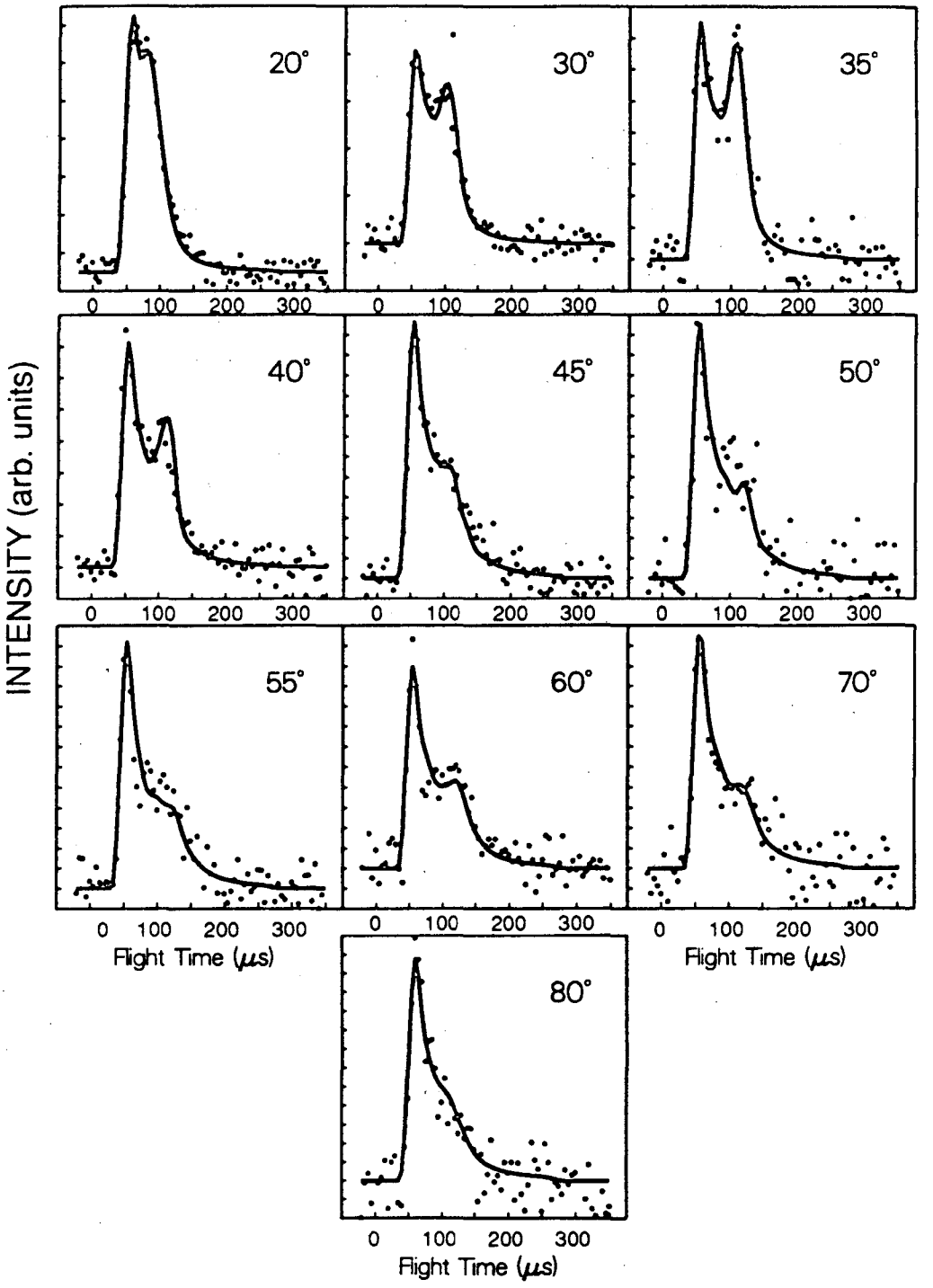
Figure 3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0 100 200 300
Flight Time (μs)

Figure 4

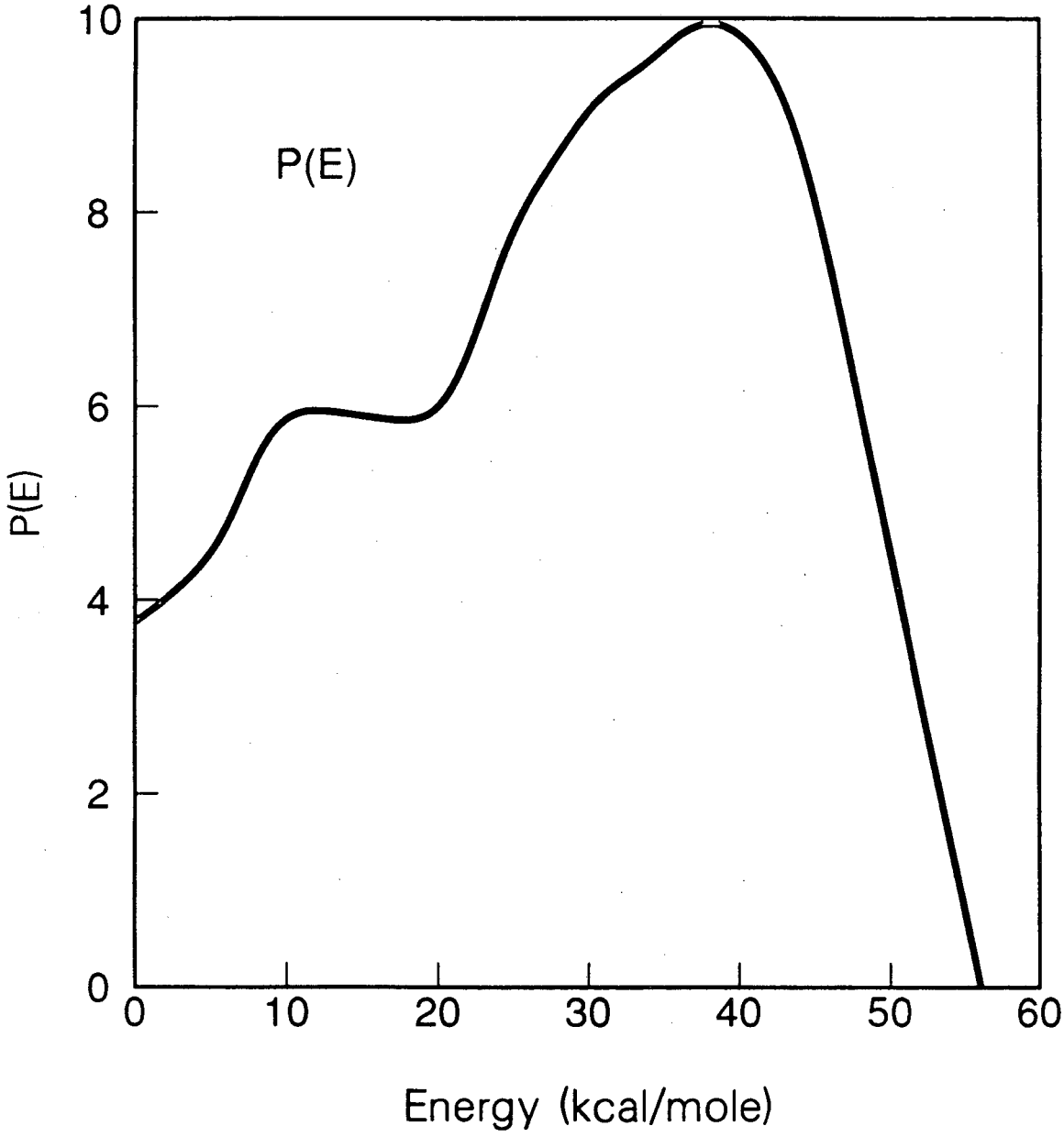
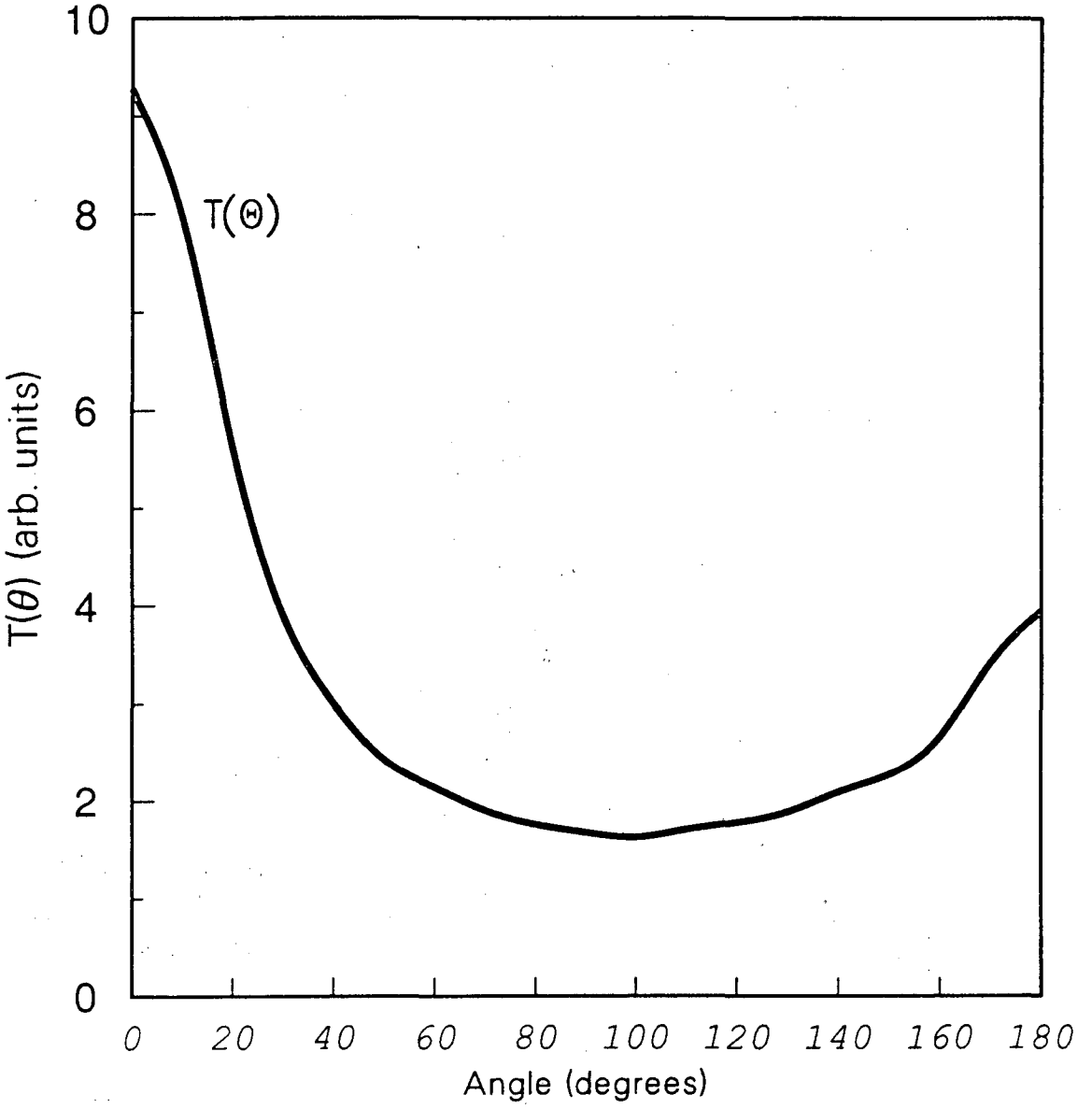


Figure 5



XBL 913-621

Figure 6

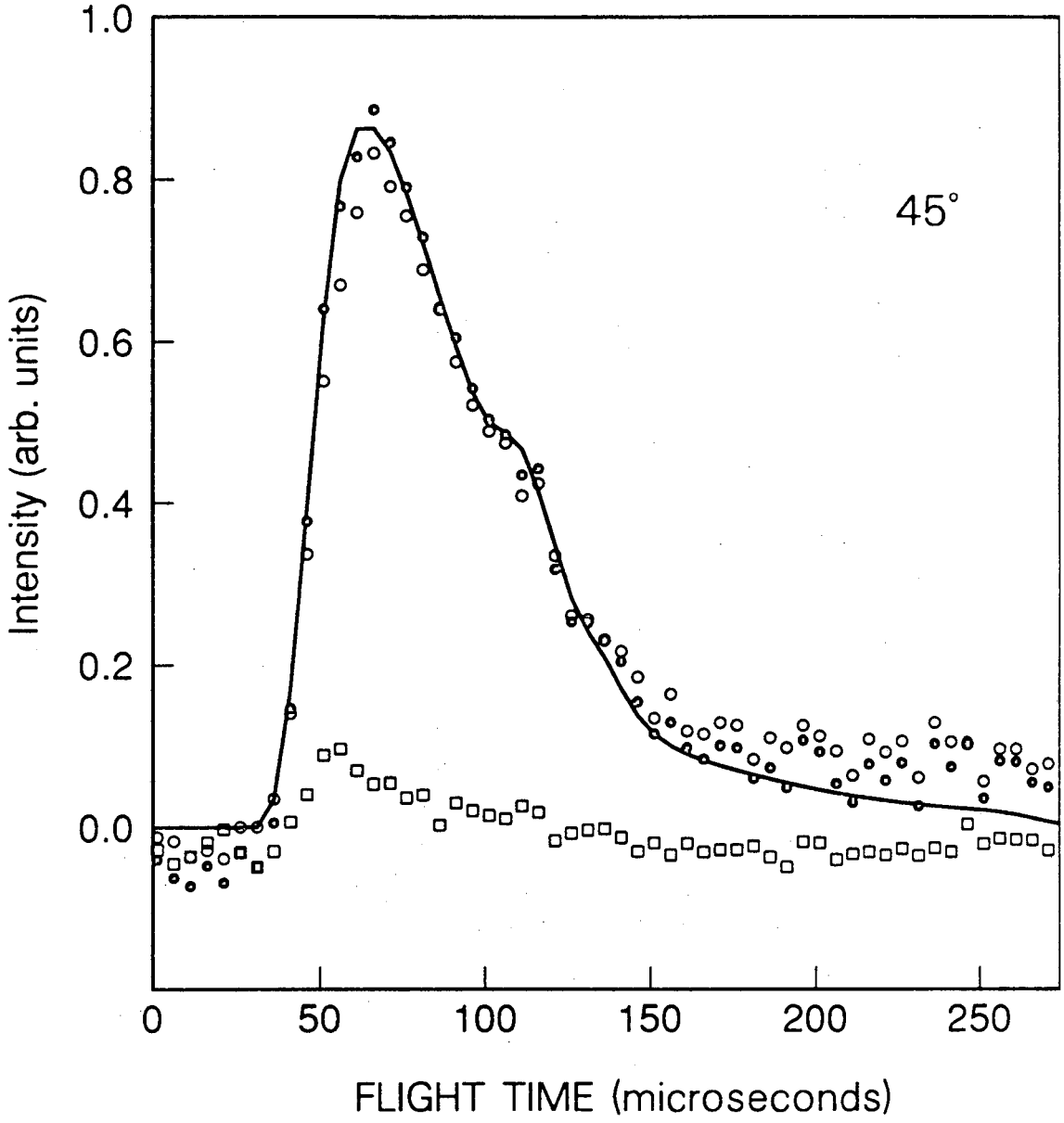

1.0
0.8
0.6
0.4
0.2
0.0
Intensity (arb. units)
45°
0
50
100
150
200
250
FLIGHT TIME (microseconds)

Figure 7

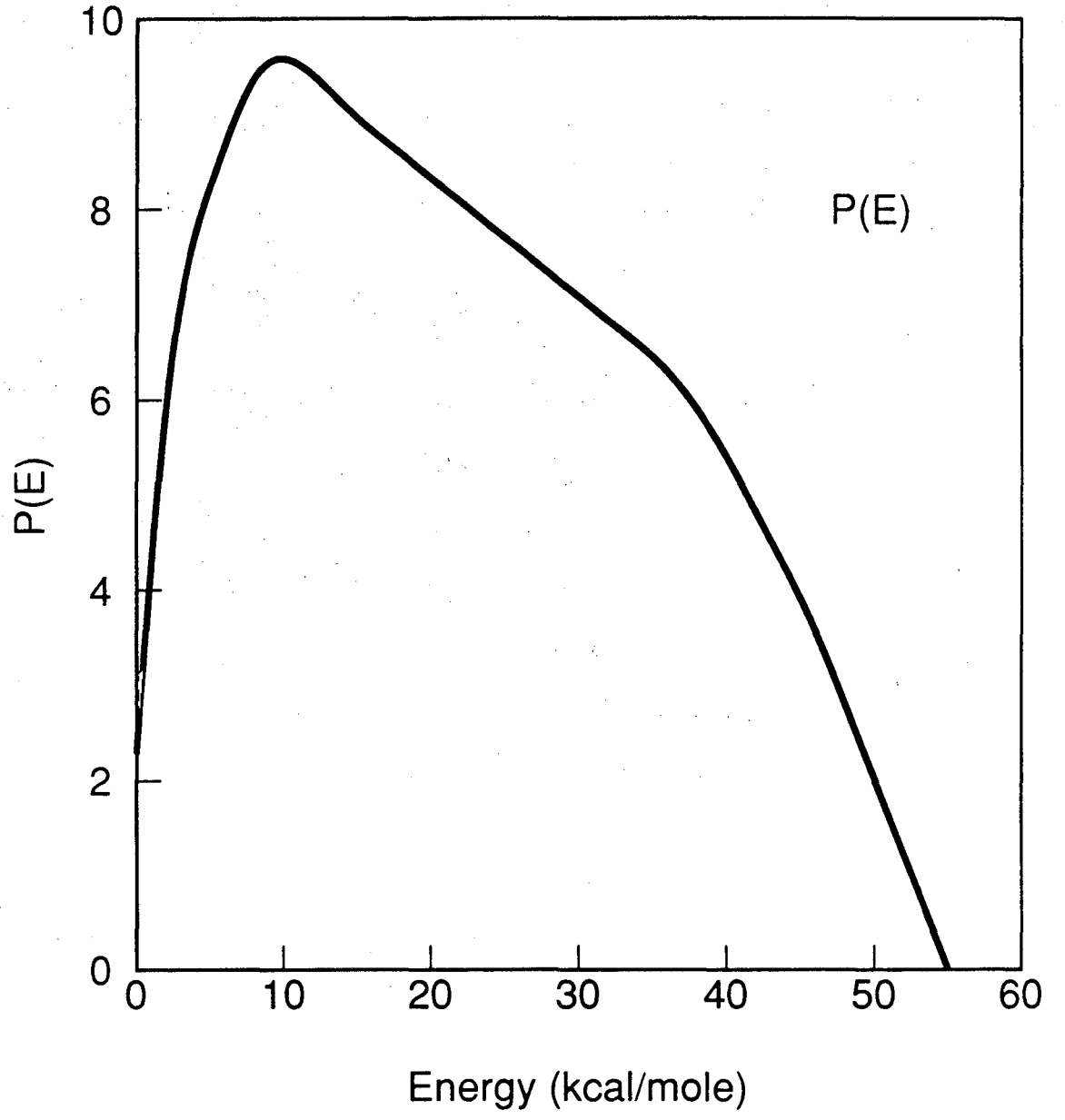


Figure 8

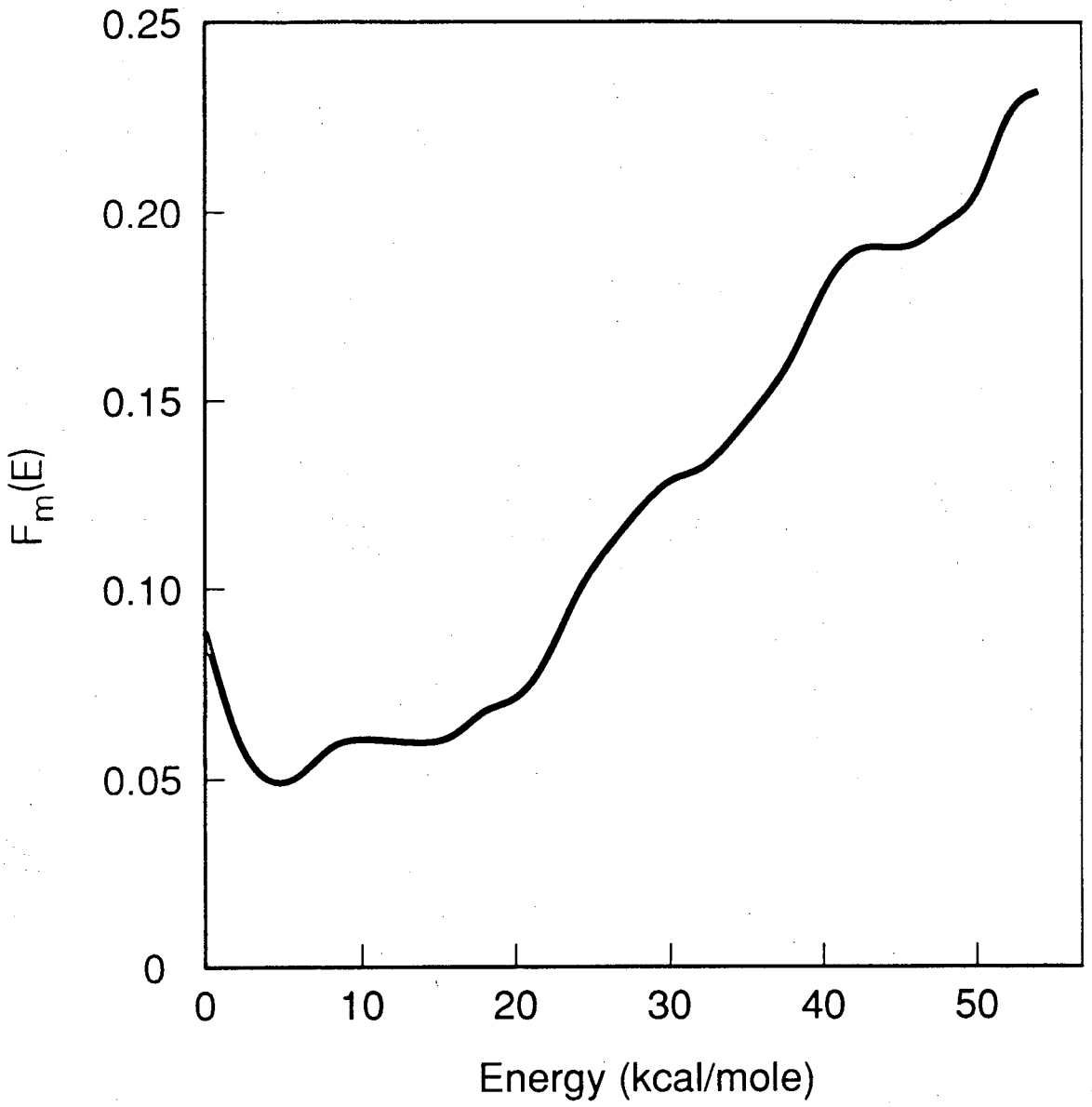


Figure 9

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