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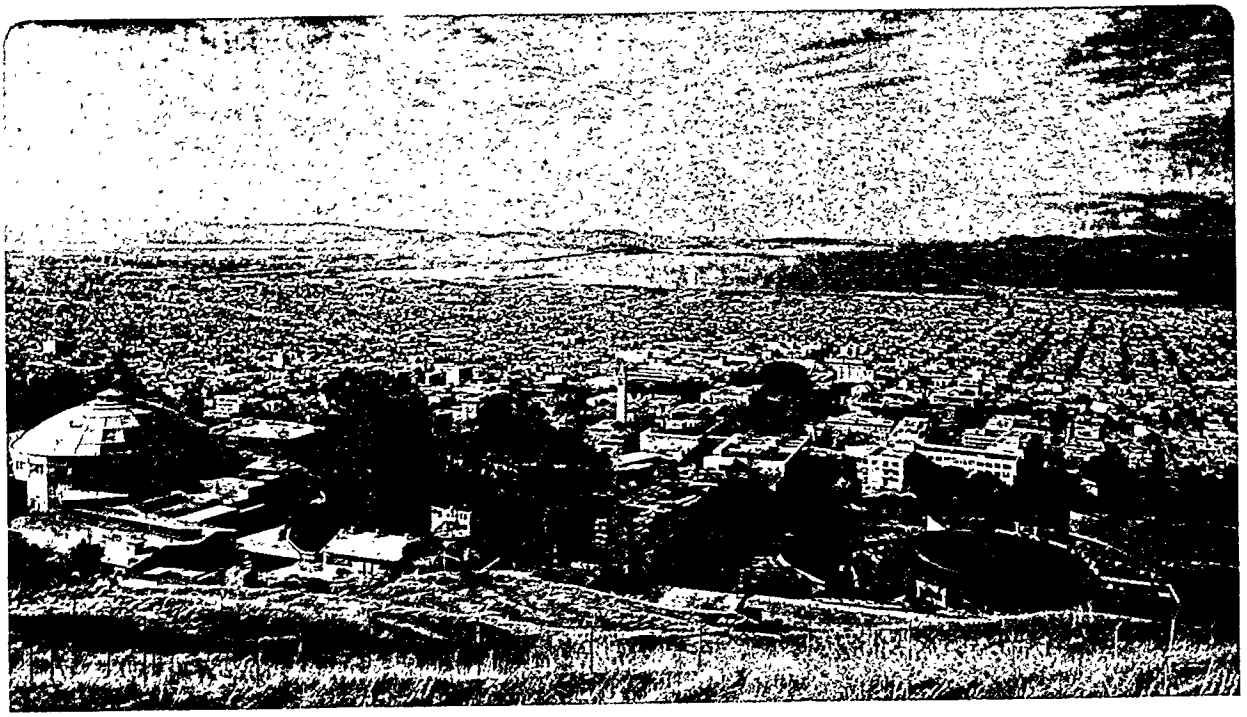

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The Reactions of Na_2 with O_2

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I. Abstract

The reactions of Na_2 with O_2 were studied in a crossed-beam experiment at collision energies (E_c) of 8 and 23 kcal/mol. The formation of NaO_2 + Na was observed at both collision energies, with the angular distributions of NaO_2 in the center of mass coordinates peaking strongly forward with respect to the direction of the O_2 beam, suggesting that the reaction is completed in a time scale that is shorter than one rotational period of the molecular system. From the velocity distribution of the products, we found that the newly formed NaO_2 molecules are internally excited, with less than 20% of the available energy appearing in the translational motion of the separating products. These results indicate a "spectator stripping" mechanism for the reaction, with the O_2 stripping one Na off the Na_2 molecules. At E_c = 23 kcal/mol the cross section for this reaction channel, σ_{NaO2}, is estimated to be 0.8 $Å^2$. Another reaction channel which produces NaO + NaO was seen at E_c = 23 kcal/mol. The angular distribution for NaO is broad and forward-backward symmetric in the center of mass frame. A substantial fraction of the available energy is released into the relative motion of the products. This reaction is likely to proceed on an excited potential energy surface since a charge transfer to the excited O_2^- orbitals seems necessary for breaking the O-O bond. The measurement yields a bond energy of 60 kcal/mol for the Na-O molecule, and a total cross section of 2 $Å^2$ for this reaction channel at E_c = 23 kcal/mol.

II. Introduction

The reactions of alkali metals (M) with oxygen molecules have been studied for decades. In combustion processes, alkali atoms can rapidly form superoxides, MO_2, in an oxygen rich flame through recombination reactions such as $M + O_2 + N \rightarrow MO_2 + N$ (where N is a third body).[4][5][6] The knowledge of the rate constants for these reactions and that for the unimolecular decomposition of MO_2 is essential for modelling the kinetics of the combustion processes and calculating the composition of the free radicals in the flame. However, the alkali dimer reactions, which also produce MO_2, were often neglected in kinetics modelling because there was less information for these reactions. Although the concentration of the dimers in the flame is much lower than that of the monomers, it is still appreciable owing to the covalent bonding in the alkali dimer molecules, which is nearly 1 eV in strength. Further more, reactions of the dimers could be significant also because they produce MO_2 via direct bimolecular reactions, which is expected to be faster than the three body recombinations between M and O_2. Therefore taking the dimer reactions into consideration could make substantial improvements over the existing kinetics models.

The various collisional processes of alkali atoms with oxygen molecules have been investigated extensively during the past fifteen years, especially the electronic excitations of the alkali atoms $M + O_2 \rightarrow M^* + O_2$ at collision energies of 2 ~ 10 eV.[7] In the $Na + O_2$ collision, Na D-line fluorescence was observed as the collision energy was increased above the $3P \leftarrow 3S$ excitation energy of 2.1 eV, with its inten-

sity becoming stronger as the collision energy was increased. The cross section for this process was found to be 26 $Å^2$ at a collision energy of 5 eV. When the collision energy was above 8 eV, fluorescence from higher electronic states appeared. The inelastic scattering experiment of Na(4D) + O_2 carried out in our lab[8] showed that the translational energy of the reactants could effectively promote Na to long-lived Rydberg states ($\tau \geq 320$ μs). Kleyn and coworkers carried out landmark investigations of the charge transfer processes $M + O_2 \rightarrow M^+ + O_2^-$ at collision energies ranging from 4 to 2000 eV.[9][10] In their experiment, the relative velocity of the reactants was so fast that the "collision time" was comparable with the vibrational period of the O_2^- ($\omega_e = 1089$ cm^{-1})[11]. Because the electron transfer probability and the critical distance vary strongly as a function of the internuclear distance of O_2^-, these authors observed oscillations in the differential cross sections. These results clearly demonstrated that the measurements of angular distributions of the scattered molecules could reveal not only the average lifetime of the collision complexes using the picosecond rotational period as an inherent clock, but also in the cases of charge transfer the vibrational motions of the reaction intermediates on the time scale of ~100 femtoseconds. In all these processes mentioned above, charge transfer from alkali metal to O_2 molecules was undoubtedly the essential first step to account for the change of the electronic states of the alkali atoms in these experiments; and the behavior of the ionic intermediate $M^+O_2^-$ determines the outcomes of the scattering. The chemical reaction $M + O_2 \rightarrow MO + O$ however, was not seen in the previous studies.

Alkali dimers have many interesting properties[11][12][13] that make their chemistry very unique. The ionization potentials of the dimer molecules are lower than those of the corresponding monomers such that when dimers interact with electron accepting molecules, the ionic and covalent potential energy surfaces cross at larger intermolecular distances, which could strongly affect the charge transfer probabilities and the overall reaction cross sections. The bond lengths of M_2 and M_2^+ are extraordinarily long (e. g. 3.0 Å for Na_2, 3.5 Å for Na_2^+.) and although the bond length of M_2^+ is longer, the bond dissociation energy of M_2^+ ion is ~50% higher than those of M_2 neutrals. The covalent bonds of the alkali dimers are abnormally weak, with the bond dissociation energies lower than 1 eV, making many chemical reactions involving the cleavage of the alkali dimer bonds exoergic.

Figger and coworkers[14] observed chemiluminescence in their crossed-beam experiment of alkali metal dimers with oxygen molecules. In the reactions of Cs_2, Rb_2, K_2 and Li_2, D-line emissions as well as continuous chemiluminescence from the collision zone were recorded. They attributed them to the formation of electronically excited products from the reactions $M_2 + O_2 \rightarrow MO_2 + M^*$ and $M_2 + O_2 \rightarrow MO_2^* + M$. No emission was observed for the Na_2 reactions due to their lower exothermicities.

Very recently, Goerke and coworkers[15] reported the results of their studies on the reactions of sodium clusters with oxygen molecules using photoionization and ion time-of-flight as detection methods. $Na_nO(2 \leq n \leq 4)$ and $Na_mO_2(2 \leq m \leq 6)$ products were detected for the reactions of $Na_x(3 \leq x \leq 8)$ with O_2. Angular distributions of $Na_nO(2 \leq n \leq 4)$ and $Na_mO_2(2, 3, 5)$ showed strong forward scattering with respect to the sodium cluster beam in the center of mass frame. Although the energy distributions of the products were not measured, their experimental data suggested that most of the exothermicity remained in the internal degrees of freedom of the products. The cross sections for the reactions were determined to be 50 ~ 80 $Å^2$, which led to their conclusion that electron harpooning[16][17][18][19] was the first step in the course of the reactions. However, these authors didn't include Na_2 reactions into their consideration. Meanwhile, due to the high ionization potential of NaO and NaO_2 they were not able to detect these molecules with the photon energy used in their experiments, although the presence of these molecules was almost certain.

This paper presents our results from crossed-beam studies of the reactions of sodium dimers with oxygen molecules. For this seemingly simple chemical system, there are at least four distinct reaction pathways that were energetically accessible under our experimental conditions:

$$Na_2 + O_2 \rightarrow NaO_2 + Na, \quad \text{(i)}$$

$$Na_2 + O_2 \rightarrow Na_2O + O, \quad \text{(ii)}$$

$$Na_2 + O_2 \rightarrow NaO + NaO, \quad \text{(iii)}$$

$$Na_2 + O_2 \rightarrow Na + Na + O_2. \quad \text{(iv)}$$

The energetics for these reactions[11][12][13] are plotted in Fig. 1. Reaction (i) is the only exothermic reaction and it becomes Reaction (iv) in the case when the internal excitation of NaO_2 along the Na–O_2 bond exceeds its dissociation limit. In our experiment, we measured the angular and velocity distributions of the products at two collision energies, which enabled us to identify the important reaction channels and learn the dynamics underlying these molecule-molecule collision processes.

III. Experimental

The details of the crossed-beam apparatus used in our experiment can be found in many earlier publications.[20][21] Briefly, the alkali dimer source consisted of a resistively heated molybdenum oven and nozzle assembly, with the temperatures of the nozzle and the oven being controlled independently by different heating elements. Sodium vapor carried by an inert gas, which was either He or Ne, expanded out of the 0.2 mm diameter nozzle to form a supersonic beam of Na/Na_2/inert gas mixture. Na_2 concentration was about 5% molar fraction of the total sodium in the beam when He was used as carrier gas. The beam quality dropped severely when we seeded Na_2 in Ne so the dimer intensity became much weaker. No substantial amount of trimers or larger clusters was detected under our experimental conditions. Na_2 beam was crossed at 90° by a neat oxygen supersonic beam in the main collision chamber under single collision conditions. The O_2 source nozzle was heated to 473°K to prevent cluster formation. Both sources were doubly differentially pumped. The beams were skimmed and collimated to 2° FWHM in the collision chamber. Under these conditions, the collision energies for the reaction could be varied from 8 kcal/mol to 23 kcal/mol.

A rotatable detector combining a quadrupole mass spectrometer and a Daly type ion counter was used to measure the angular and velocity distributions of the products in the molecular beam-defined plane. A fraction of the neutral products entering the detector were ionized by 200 eV electron bombardment. Ions formed in the ionization region were extracted into a quadrupole mass filter which was set to have unit mass resolution. The products were modulated at the entrance of the detector with a double-sequence pseudorandom mechanical chopping wheel.[21] The number density of a certain mass was recorded as a function of the flight time that the molecules spent to travel through the distance from the chopping wheel to the ion counter. Neutral time-of-flight spectra were obtained by deconvolving the recorded signal over the chopper gating function and substracting the ion flight time from ionizer to the ion counter. Under our experimental conditions, we were unable to measure the signal close to the Na_2 beam. At these angles, the number density of elastically scattered Na was very high such that a certain fraction of scattered Na could be excited to long-lived Rydberg states by electron bombardment and subsequently field-ionized in the ion counting region. The mass spectrometer was "transparent" to these Rydberg atoms so they became strong interference at all the masses of interest. We also

recorded the spectra for O and O_2 but the effort to extract any information related to reactions was not successful because of the high background of oxygen in the mass spectrometer and the intense nonreactive scattering of the O_2.

IV. Results and kinematic analysis

In our experiment, we observed NaO^+ (m/e = 39) signal which was unambiguously from the reactive scattering since it contains both Na and O. The monomer reaction $Na + O_2 \rightarrow NaO + O$ has very large endothermicity (ΔD_0 = + 58 kcal/mol[12]). Under our experimental conditions, even the highest collision energy for $Na + O_2$ was not sufficient for this reaction to happen. Thus the observed NaO^+ signal must be from the reactions of sodium dimers with oxygen molecules. This result is in contradiction with that reported by Goerke et al.[15] who explicitly ruled out the possibility of the dimer reactions in their similar experiment. Neither NaO_2^+ nor Na_2O^+ signal was seen under our experimental conditions. However this does not necessarily mean that only Reaction (iii) took place. In the ionization region, electron impact fragmentation is severe, especially for the internally excited molecules. Both NaO_2 from Reaction (i) and Na_2O from Reaction (ii) could fragment completely and both molecules could form NaO^+. Additional analysis on the kinematics and dynamics of the reactions have to be made in order to identify the actual reaction pathway(s).

A. Collision Energy at 8 kcal/mol

The Newton diagram[22][23][24] for $Na_2 + O_2$ at a nominal collision energy of 8 kcal/mol is shown in Fig. 2. Θ_{CM} denotes the laboratory angle of the center of mass velocity vector for $Na_2 + O_2$. For future discussions, we also plotted the center of mass velocity (dotted line) for $Na + O_2$, which extends an angle of Θ_m from the Na_2 beam. The direction of the Na_2 velocity in the center of mass frame is defined as 0^o hereafter. At this collision energy, only Reaction (i) could take place, so the observed NaO^+ signal was entirely due to the fragmentation of NaO_2 products. The solid circle in Fig. 2 encloses the zone within which NaO_2 might appear. Fig. 3 shows the NaO^+ time-of-flight spectra recorded at several laboratory angles. Beyond the range of these angles, the signal became too weak to observe the time-of-flight peaks. It was observed that most NaO_2 products appeared around Θ_m. Signal intensities obtained by integrating the time-of-flight spectra are plotted in Fig. 4 to give the laboratory angular distribution for NaO_2. Compared with the range that the NaO_2 circle extends to in the Newton diagram, the NaO_2 angular distribution was very narrow.

In Fig. 3 and Fig. 4, the solid lines are the computer simulation of the data obtained by assuming certain center of mass translational energy distribution (P(E)) and angular distribution ($T(\theta)$) shown in Fig. 5. Peaking at the direction of the O_2 beam (180^o), the angular distribution shows remarkable anisotropy, with all the NaO_2 products scattered into the hemisphere towards the O_2 beam. This anisotropy indicates that the reaction takes place during a time that is shorter than the rotational period of the molecular system so that the products are separated before they lose the information of the well defined approaching direction of the reactants.[24] At this collision energy, the total available energy for the reaction ($E_c + \Delta D_0$) is 34 kcal/mol, among which only an average of 2.6 kcal/mol appears in the translational motion of the products (cf. P(E) in Fig. 5). The rest of the energy has to become the internal excitation of the NaO_2 molecules. When NaO_2 is ionized to form NaO_2^+, the binding energy between Na^+ and O_2 becomes weaker and the internal excitation initially stored in NaO_2 is likely to remain in NaO_2^+ and causes the complete dissociation of NaO_2^+ into Na^+ and O_2. This is probably the reason why NaO_2^+ parent ion was not detected. However when NaO_2 is excited to higher electronic states during the electron impact ionization, the dissociative ionization could produce a stable NaO^+ ion.

B. Collision Energy at 23 kcal/mol

All the dimer reactions (i) ~ (iv) became energetically accessible at a collision energy of 23 kcal/mol. The Newton diagram for this collision energy is shown in Fig. 6. For Reaction (ii), the available energy was only 5 kcal/mol. The heavier products Na_2O (compared with O) have to be limited in the small circle. On the other hand, NaO molecules produced by Reaction (iii) are much less confined because there was slightly more available energy (9 kcal/mol) and no disparity in the masses of the products. The time-of-flight spectra of NaO^+ recorded at different laboratory angles are plotted in Fig. 7, and the laboratory angular distribution of the NaO^+ intensity is shown in Fig. 8. There are clearly two features in the time-of-flight spectra. Both features exist well out of the Na_2O limit which indicates clearly that the observed signal was not from Reaction (ii). The slow peaks which appear at ~120 μs have a very narrow angular distribution, with the intensity peaking sharply around Θ_m. The angular and velocity distributions of this slow signal bear such strong resemblances to those of the NaO_2 products we saw at low collision energy that it is with little doubt to assign this signal to the same reaction channel. The fast peaks, arriving at ~70 μs, have very different characteristics than those of the NaO_2 products. Appearing weak at all angles and becoming only slightly stronger at small angles, these fast peaks have much less variation in the intensity, an indication of products with larger recoil velocities and broader laboratory angular distributions. Therefore this fast signal is, without any doubt, the NaO products from Reaction (iii).

The simulation of the time-of-flight and angular distribution data was done by assuming an independent set of P(E) and T(θ) for each reaction channel. An additional parameter γ was assigned to each reaction channel to weight its contribution to the observed signal. The total fits are plotted in solid lines in Fig. 7 and Fig. 8. The dotted lines and the dashed lines show the contributions from Reaction (i) and Reaction (iii), respectively. Fig. 9 shows the P(E) and T(θ) for Reaction (i). As mentioned above, these distributions are similar to those at low collision energy. T(θ) again peaks sharply at the direction of O_2 beam with all the NaO_2 scattered into the O_2 hemisphere, showing strong anisotropy. Among the 49 kcal/mol available energy, only an average of ~8 kcal/mol was released into the translational energy of the separating products. The P(E) has a sharp rising edge at ~7 kcal/mol, which indicates that the internal energy of NaO_2 could not exceed 42 kcal/mol or else the NaO_2 molecule could not be held together. The subsequent result is the collisional dissociation making Na + Na + O_2. Therefore this sharp rising edge in P(E) marks the onset of Reaction (iv), which requires at least the energy to break the Na-Na bond. The collision energy of 23 kcal/mol less the cut off energy of 7 kcal/mol in the P(E) is then our experimental measurement of the Na-Na bond dissociation energy. The result of 16 kcal/mol is in agreement with the well known value in the literature.[12]

Fig. 10 shows the P(E) and T(θ) used in the simulation of Reaction (iii). The angular distribution is quite broad. The forward-backward symmetry in the product angular distribution is a prerequisite rather than an experimental result because in this reaction two identical molecules are always produced with exactly opposite center of mass velocities. Under such conditions the angular distribution does not tell us the time duration of the reaction, which is the important information for dynamics studies. The P(E) shows that an average of 3 kcal/mol is released in the translational motion of the products. The high energy cut off at 5.5 kcal/mol in the P(E) allows us to estimate Na-O bond strength. From the conservation of energy, there is the following relation between the energies of the reactants and the products:

$$E'_{trans} + E'_{int} = E_{trans} + E_{int} + \Delta D_0 \qquad (1)$$

where E_{trans} and E'_{trans} are the center of mass translational energies of the reactants and products, respectively. Similarly, E_{int} and E'_{int} are the internal energies, i.e. the total electronic, vibrational and rotational energies, in the reactants and the products, respectively. ΔD_0 is the change of the bond dissociation energy for the reaction. E_{int} is assumed to be negligible for the supersonic beams. E'_{trans} reaches its maximum value when E'_{int} is the minimum, which will be assumed to be zero, namely at the highest translational energy release, both NaO products are assumed to be in the ground state. From Equation (1) and the maximum translational energy release in the P(E), we calculated the change of bond dissociation energy ΔD_0 for Reaction (iii) to be -17 kcal/mol. Using the accurately known values of D_0(O-O), 119 kcal/mol, and D_0(Na-Na), 18 kcal/mol,[12] we obtained D_0(Na-O) = 60 kcal/mol, which can be compared with the literature value of 61.2 ± 4.0 kcal/mol.[12]

From the best fit, the relative contributions of these two reactions to the observed signal at m/e = 39 are:

$$\gamma_i : \gamma_{iii} = 1 : 1.8. \qquad (2)$$

In Equation (2), we use the subscripts to denote the reaction channels.

In order to estimate the cross sections for the reactions, we also measured the time of flight spectra for the Na^+ signal under the same experimental conditions. It is known that both NaO and NaO_2 dissociate heavily to Na^+ under electron impact.[25][26] The collisional dissociation Reaction (iv), if present, would also generate Na^+. But most Na^+ detected came from elastic/inelastic scattering of the Na monomer with O_2 because the number density of the monomers at the collision zone was roughly 20 times higher than that of the dimers. Na^+ time-of-flight spectra at 25° and 30° are given in Fig. 11. At these angles, the nonreactive scattering of Na_2 was negligible. For comparison, the scattering signal of Na from N_2 at corresponding angles was also measured and is plotted in the same figure. The differences due to the reactions are obvious. We can fit the Na^+ spectra for $Na/Na_2 + O_2$ scattering with four different channels: the elastic scattering from $Na + O_2$, the inelastic scattering from $Na + O_2$, Reaction (i) from $Na_2 + O_2$ and Reaction (iii) from $Na_2 + O_2$. We use the same translational energy and angular distributions as those for the NaO^+ signals to fit the reactive signals in the Na^+ spectra although we have to use different weights (γ') to account for the different fragmentation patterns of NaO and NaO_2 in the ionization region. The results are also plotted in Fig. 11, where the solid lines show the overall fit and the broken lines indicate the contribution from each individual channels, as described in detail in the figure captions. The discrepancies between the fit and the data are possibly due to the collisional dissociation Reaction (iv), which is difficult to account for because it is a three body event. Nevertheless, leaving Reaction (iv) out will not affect our final results of obtaining the cross sections for Reaction (i) and Reaction (iii) because we are comparing these reaction channels with the nonreactive signal only. From the fit, the relative weight for each channel is:

$$\gamma'_{elastic} : \gamma'_{inelastic} : \gamma'_{i} : \gamma'_{iii} = 105 : 171 : 0.5 : 3.0. \qquad (3)$$

Because we did not observe any NaO_2 signal, it is safe to assume that NaO_2 molecules, if ionized, dissociated completely to either NaO^+ or Na^+. Fig. 12 illustrates the relations between the parent molecules directly from the scattering and the measured signal, which will serve as a road map for our discussions in the following sections. Here σ_i and σ_{iii} are the reaction cross sections for Reaction (i) and Reaction (iii), respectively. $\sigma_{elastic}$ and $\sigma_{inelastic}$ are the cross sections for the elastic scattering and

the inelastic scattering of Na + O_2. $\sigma_{ion}(X)$ denotes the ionization cross section of molecule X by electron bombardment. The ions so formed undergo further dissociation to give the observed signal. We define ξ as the fraction of NaO^+ among the total Na-containing positive ions produced by electron bombardment. According to the assumption that NaO_2 dissociate completely upon electron bombardment, the fraction of Na^+ from NaO_2 is $(1-\xi)$. In a similar way, we define the fraction of Na^+ among the total Na-containing positive ions produced from ionization of NaO products to be η. Accordingly the branching ratio between Reaction (i) and Reaction (iii) can be obtained. From Equation (2), we have:

$$\gamma_i : \gamma_{iii} = [\sigma_{ion}(NaO_2)\times\sigma_i\times\xi] : [2\times\sigma_{ion}(NaO)\times\sigma_{iii}\times(1-\eta)] = 1 : 1.8. \quad (4)$$

The factor "2" accounts for the fact that two NaO were produced in Reaction (iii). Similarly, from Equation (3), we draw another relation between σ_i and σ_{iii}:

$$\gamma'_i : \gamma'_{iii} = [\sigma_{ion}(NaO_2)\times\sigma_i\times(1-\xi)] : [2\times\sigma_{ion}(NaO)\times\sigma_{iii}\times\eta] = 0.5 : 3.0. \quad (5)$$

In order to compare the cross section for each channel, we need the knowledge of the ionization cross sections for Na, NaO and NaO_2 by 200 eV electron bombardment. The ionization cross section of Na is known[27], $\sigma_{ion}(Na) = 2.46$ Å^2. The ionization cross section of NaO can be estimated[28] from the ionization cross section of O_2, and the ratio of the polarizabilities(α's) of O_2[12] and NaO using the following equation:

$$\sigma_{ion}(O_2) : \sigma_{ion}(NaO) = \alpha_{O2} : \alpha_{NaO} = 1.58 : 3.05, \quad (6)$$

where α_{NaO} was obtained by adding the polarizability of Na^+, $\alpha_{Na+} = 0.155$ Å^3, and the polarizability of O^-, $\alpha_{O-} = 2.85$ Å^3. The result is $\sigma_{ion}(NaO) = 5.2$ Å^2. Similarly, we can calculate the ionization cross section for NaO_2, which gives $\sigma_{ion}(NaO_2) = 6.5$ Å^2.

Covinsky[25] measured η as a function of internal excitation of NaO in the Na + O_3 experiment. η is roughly 0.8 for internally cold NaO (which was the case in this experiment because there is very little excess energy for Reaction (iii) and a considerable amount of this excess energy was released into the translational motion of the products). Using this value, we obtained $\xi = 0.45$ and $\sigma_i : \sigma_{iii} = 1 : 2.5$.

The next step is to compare the reactive signal with the total nonreactive scattering. From Equation (3), we have the following relations:

$$\frac{\gamma'_i}{\gamma'_{elastic}+\gamma'_{inelastic}} = \frac{\sigma_{ion}(NaO_2)\times\sigma_i\times(1-\xi)}{20\times\sigma_{ion}(Na)\times\sigma_{Nonreactive}} = \frac{0.5}{276}, \quad (7)$$

and

$$\frac{\gamma'_{iii}}{\gamma'_{elastic}+\gamma'_{inelastic}} = \frac{2\times\sigma_{ion}(NaO)\times\sigma_{iii}\times\eta}{20\times\sigma_{ion}(Na)\times\sigma_{Nonreactive}} = \frac{3.0}{276}, \quad (8)$$

where $\sigma_{Nonreactive}$ is the sum of the cross sections of elastic scattering and inelastic scattering of Na + O_2. We added factors "20" in Equation (7) and Equation (8) because the number density of the monomers in the collision zone was roughly 20

times higher than that of the dimers. The interaction between Na monomer and O_2 becomes strong at the crossing of the covalent and ionic surfaces because of the charge transfer. If we neglect the long range van der Waals interaction, the internuclear distance at the surface crossing could be estimated using the following equation which is based on simple "Harpoon Mechanism":[16][17][18][19]

$$R_c = \frac{14.4}{IP_{Na}(eV) - EA_{O_2}(eV)} \quad (Å), \qquad (9)$$

where IP is the ionization potential of Na[12] and EA is the electron affinity of O_2[12], both in the units of electron volts. Equation (9) gives a value of 3.1 Å for R_c, which is larger than the averaged hard sphere radius between Na and O_2. Since there is no reaction between Na monomer and O_2, we can assume R_c to be the nonreactive collision radius. Therefore we obtained the total nonreactive scattering cross section to be: $\sigma_{Nonreactive} = \pi R_c^2 = 30$ Å^2. Using these numbers in Equation (7) and Equation (8), we obtained the cross sections for Reaction (i), $\sigma_i = 0.8$ Å^2 and Reaction (iii), $\sigma_{iii} = 2$ Å^2.

V. Discussion

The MO_2 molecules have been studied quite extensively in the past. Alexander generated semiempirical potential energy surfaces for LiO_2 and NaO_2.[29] He showed that the ground state NaO_2, which was 1.6 eV more stable than the separated ground state Na and O_2, had C_{2v} geometry with Na at the apex of an isosceles triangle. The interaction within the molecule could be best described as $Na^+...O_2^-$ singly charged ionic bonding. This is in accord with the Infrared and Raman[30][31] or ESR[32] spectroscopy results in low temperature matrices. Calculations on the NaO molecule also indicates that it is singly ionic, $Na^+...O^-$.[33] These results suggest that during the course of Reaction (i) and Reaction (iii), the $Na_2 + O_2$ system has to experience a change from covalent character to ionic nature. This resembles the well known M/M_2 + Halogen molecules (XY) reactions and was commonly characterized by the Harpoon Mechanism. Nevertheless, the $Na_2 + O_2$ reaction shows very different results than the M/M_2 + XY system. In the case of M_2 + XY,[34] for example, the main pathways have both M_2 and XY dissociate to form MX + M + Y or MX + MY with the total cross sections larger than 100 Å^2. For the MX + M + Y channel, the MX product peaked strongly toward the M_2 direction in the center of mass velocity space.

M_2 + XY reactions are model systems that proceed via a long range electron transfer mechanism. Due to the low ionization potential of M_2 and high electron affinity of XY, the potential energy surfaces of the ionic state ($M_2^+...XY^-$) and the covalent state ($M_2...XY$) intersect at intermolecular distance R_c = 7-8 Å (Equation (9)) which is much larger than the "hard sphere" radius. At this internuclear distance, there is a fair chance for the valence electron to "jump" from M_2 to the XY. A vertical ionization from the outer turning point of ground state M_2 puts M_2^+ in the attractive well and vertical ionization from the inner turning point sets M_2^+ on slightly repulsive (1 eV/Å) surface. Because the M_2^+ is almost 50% more strongly bound than M_2,[13] along with the fact that both M_2 and M_2^+ have very low vibrational frequencies, the two alkali nuclei will separate only very slowly after electron transfer. On the other hand the XY^- bonding is much weaker than that of XY neutral molecule. Vertical Frank-condon transition puts XY^- on a very strong repulsive wall (6 eV/Å) above its dissociation limit primarily due to the strong antibonding orbital σ_{pz}*. As a result, X^- and Y separate promptly after the vertical electron transfer while the M and M^+ will linger together for longer time. The reaction proceeds as if the M_2^+ "strips" the X^- off to form the M_2X molecules which peak preferentially towards the M_2 direction, leav-

ing the other halogen atom Y as a "spectator". The highly vibrationally excited M_2X nascent molecule then boils off an M atom to form the final MX product. The initial repulsive force between the two halogens is offset by their attraction at longer distance as the two halogen atoms separate. consequently, the spectator Y does not carry away much of the excess energy.

For the $Na_2 + O_2$ system, the scenario is quite different. O_2 has a much lower electron affinity of 0.44 eV[12] so that the nominal crossing distance R_c calculated from Equation (9) is only 3.2 Å and only collisions with impact parameter smaller than R_c will experience the electron transfer. This limits the total cross section for charge transfer to be 32 $Å^2$ at most. Nevertheless, at such short intermolecular distance, the interaction between the ionic surface and the covalent surface is very strong. Once the system arrives at this region, it will have an almost unit probability to switch from covalent surface to ionic surface adiabatically. The final outcome of the reaction is determined by the interaction between Na_2^+ and O_2^- after the electron transfer. Unlike the case of XY, the O_2^- bond is only slightly longer than that of O_2 and the binding energy is almost as large. Vertical transition from O_2 to the ground state of O_2^- would put O_2^- in the deep potential well. It takes some extra 90 kcal/mol in order to break O_2^- to form $O + O^-$. On the other hand, the weakly bound Na_2^+ is much more vulnerable to dissociate into $Na + Na^+$ under the influence of the strong Coulomb attraction. In the case when the impact parameter is large, there is little chance to cleave the O_2^- molecule during the time when two molecules glance off each other. Strong Coulomb interaction between Na^+ and O_2^- leads to the formation of NaO_2 molecules that are highly excited along the newly formed bonds. The departing Na atom should hardly be affected during the collision because the interaction between Na^+ and Na is relatively weak compared with the Coulomb interaction between Na^+ and O_2^-. Therefore it acts similarly as the "spectator" in the cases of the halogen reactions. The most important role for this Na atom is to carry away the excess energy partly through the breaking of the na-Na bond, much like a "third body" as in the recombination reactions, which is the reason why the NaO_2 products are most likely to appear at Θ_m — the result is just like a simple recombination of Na and O_2. Using this "spectator stripping" model, we can calculate the translational energy releases for E_c = 8 and 23 kcal/mol to be 2.4 and 6.6 kcal/mol, respectively, matching well with the peaks in the corresponding P(E)'s.

It is worth pointing out that the formation of NaO_2 results from the transfer of only one electron from Na_2 to O_2. If both valence electrons are transferred to O_2, the molecular system is likely to sample the deep well on the potential energy surface, forming Na_2O_2 complex (cf. Fig. 1). Since Na_2O_2 complex dissociates mainly through the low energy channel, forming $NaO_2 + Na$, we would expect to see for the NaO_2 products a forward-backward symmetric angular distribution, which is a characteristic for the complex formation. However in the experiments we observed a very anisotropic angular distribution. Therefore the complex formation mechanism can be excluded.

Contrary to the spectator mechanism of Reaction (i), Reaction (iii) requires considerable rearrangement of the electronic configuration of the system. First of all, both valence electrons have to be transferred because each NaO molecule has $Na^+...O^-$ singly ionic character. This requires a close collision and a favorable approaching geometry between the reactants. This was not directly observed for this reaction because the symmetric angular distribution determined by the kinematics does not provide us much information of the scattering. But evidence could be found from the chemi-ionization reaction $Ba + Cl_2 \rightarrow BaCl^+ + Cl^-$ in which case $BaCl^+$ is backward scattered with respect to the Ba beam, demonstrating that the favored geometry for transferring two electrons is a collinear head-on collision.[36] Second, the strong O-O bond has to be broken. The exact pathways leading to the breaking of the O-O bond could not be deduced from our data, but some insights could be gained

by looking at the early results of dissociative attachment of O_2, and the results of our recent *Ab initio* calculations[37] using *Gaussian 92* . The formation of O + O^- by electron attachment was studied in great detail and a single electronically excited state $^2\Pi_u$ was found to be responsible for this process, although there are many other states in the vicinity. The state specificity is largely due to the symmetry restriction which could be removed in the case of chemical reaction with the presence of the Na atoms. But the results do suggest that the breaking of the O-O bond is likely initiated by an electron transfer to the excited O_2^- orbital, which will result in a substantial bond stretching in O_2^-. The argument that the excited O_2^- orbital is important to the NaO + NaO reaction is further supported by our recent calculations in which we computed the energetics for the molecular system at various geometries. It is found that for all the potential energy surfaces with ground state O_2 characteristics, NaO_2 is the dominant product in the exit channel. The details of the calculations will be reported in a forthcoming paper.

VI. References

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[4] E. Bulewicz, C. G. James, and T. M. Sugden, Proc. R. Soc. London **235**, 89, (A1956).

[5] M. J. McEwan,and L. F. Phillips, Combust. Flame **9**, 420 (1965); *ibid.* **11**, 63, (1967).

[6] C. H. Muller, K. Schofield, and M. Steinerg, J. Chem. Phys. **72**, 6620, (1980).

[7] V. Kempter, W. Mecklenbrauck, M. Menzinger, and Ch. Schlier, Chem. Phys. Lett. **11**, 353, (1971).

[8] H. Hou, K. T. Lu, A. G. Suits, and Y. T. Lee, Unpublished results.

[9] A. W. Kleyn, Ph. D. Thesis, Stichting voor Fundamenteel Onderzoek der Materie, Amsterdam, The Netherlands, (1982).

[10] A. W. Kleyn, M. M. Hubers, and J. Los, Chem. Phys. **34**, 55, (1978).

[11] JANAF Thermochemical Tables, 3rd ed., J. Physical and Chemical Ref. Data, 14, (1985), Supp. No.1.

[12] D. R. Lide, Editor-in-Chief, *CRC Handbook of Chemistry and Physics*, 74th edition (1993-1994).

[13] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold Company (1979).

[14] H. Figger, W. Schrepp, and X. Zhu, J. Chem. Phys. **79**, 1320, (1983).

[15] A. Goerke, G. Leipelt, H. Palm, C. P. Schulz, and I. V. Hertel, Z. fur Physik D **32**, 311, (1995).

[16] Magee, J. Chem. Phys. **8**, 687, (1940).

[17] A. W. Kleyn, in: *Alkali Halide Vapors*, edited by P. Davidovits and D. L. McFadden, Academic Press, (1979).

[18] D. R. Herschbach, Appl. Opt. Supp. 2, 128 (1965).

[19] R. D. Levine and R. B. Berstein, *Molecular Reaction Dynamics and Chemical Reactivity*, Oxford University, New York (1987).

[20] Y. T. Lee, J. D. McDonald, P. R. LeBreton, and D. R. Herschbach, Rev. Sci. Instrum. **40**, 1042, (1969).

[21] H. F. Davis, A. G. Suits, and Y. T. Lee, J. Chem. Phys. **96**, 6710, (1992) and the references therein.

[22] D. R. Herschbach, Disc. Faraday Soc. **33**, 149, (1962).
[23] Y. T. Lee, in: *Atomic and Molecular Beam Methods, Vol. 1*, edited by G. Scoles, Oxford University Press, New York, (1988)
[24] W. B. Miller, S. A. Safron, and D. R. Herschbach, J. Chem. Phys. **56**, 3581, (1972).
[25] M. Covinsky, Ph.D. Thesis, University of California at Berkeley, (1990).
[26] M. Steinberg and K. Schofield, J. Chem. Phys. **94**, 3901, (1991).
[27] R. H. McFarland and J. D. Kinney, Phys. Rev. **137**, A1058, (1965).
[28] P. S. Weiss, Ph. D Thesis, Chapter III, University of California at Berkeley, (1985).
[29] Millard H. Alexander, J. Chem. Phys. **69**, 3502, (1978).
[30] L. Andrews, J. Chem. Phys. **54**, 4935, (1971); R. R. Smardzewski and L. Andrews, J. Phys. Chem. **77**, 801, (1973); L. Andrews, J. T. Hwang, and C. Trindle, *ibid.* **77**, 1065, (1973).
[31] H. Huber and G. A. Ozin, J. Mol. Spectrosc. **41**, 595, (1972).
[32] D. M. Lindsay, D. R. Herschbach and A. L. Kwiram, Chem. Phys. Lett. **25**, 175, (1974).
[33] P. A. G. O'Hareand A. C. Wahl, J. Chem. Phys. **56**, 4516, (1972).
[34] W. S. Struve, J. R. Krenos, D. L. McFadden, and D. R. Herschbach, J. Chem. Phys. **62**, 404, (1975).
[35] L. King and D. R. Herschbach, Faraday Disc. Chem. Soc. **55**, 331, (1973).
[36] A. G .Suits, H. Hou, and Y. T. Lee, J. Phys. Chem. **94**, 5672, (1990).
[37] K. T. Lu, H. Hou, A. G. Suits, and Y. T. Lee, unpublished results.

VII. Figure Captions

Fig. 1 The energy level diagram for $Na_2 + O_2$. Shaded regions indicate the uncertainties in the energetics. Computation is done based on changes in the bond dissociation energies ΔD_0 for each reactions. Values for D_0(Na-O), D_0(O-O) and D_0(Na-Na) are from standard handbooks.[11][12][13] D_0(Na-ONa) is from the results of M. Steinberg and K. Schofield[26]. D_0(Na-O_2) is from the results of H. Figger and coworkers.[14] The energy of Na_2O_2 complex is obtained from our *ab initio* calculation using *Gaussian 92*.[37]

Fig. 2 Newton Diagram for $Na_2 + O_2$ at nominal collision energy E_c = 8 kcal/mol. The Circle indicates the limiting velocity of the ground state NaO_2 products obtained using Equation (1). Θ_{CM} is the Na_2/O_2 center of mass angle. Θ_m indicates the angle of Na/O_2 center of mass, where we observed maximum signal for NaO_2 channel.

Fig. 3 Time-of-flight spectra measured for m/e = 39 (NaO^+) at collision energy 8 kcal/mol. NaO^+ is from the electron impact fragmentation of NaO_2. Open circles are the experimental data. Solid lines indicate the best fit using P(E) and T(θ) shown in Fig. 5.

Fig. 4 Laboratory angular distribution of NaO^+ signal at E_c = 8 kcal/mol. Open circles are experimental data. Solid line is the fit using P(E) and T(θ) shown in Fig. 5.

Fig. 5 Product center of mass translational energy distribution P(E) and angular distribution T(θ) that best fit the experimental data.

Fig. 6 Newton Diagram for $Na_2 + O_2$ at nominal collision energy E_c = 23 kcal/mol. The circles indicate the limiting velocities of the ground state products. Θ_{CM} is the Na_2/O_2 center of mass angle. Θ_m indicates the angle of Na/O_2 center of mass, where we observed maximum signal for NaO_2 channel.

Fig. 7 Time-of-flight spectra measured for m/e = 39 (NaO^+) at collision energy 23 kcal/mol. NaO^+ is from the both NaO_2 and NaO channel. Open circles are the experimental data. Solid lines indicate the total fit. Dotted lines indicate

the contribution from the NaO_2 + Na channel and dash lines indicate the contribution from the NaO + NaO channel.

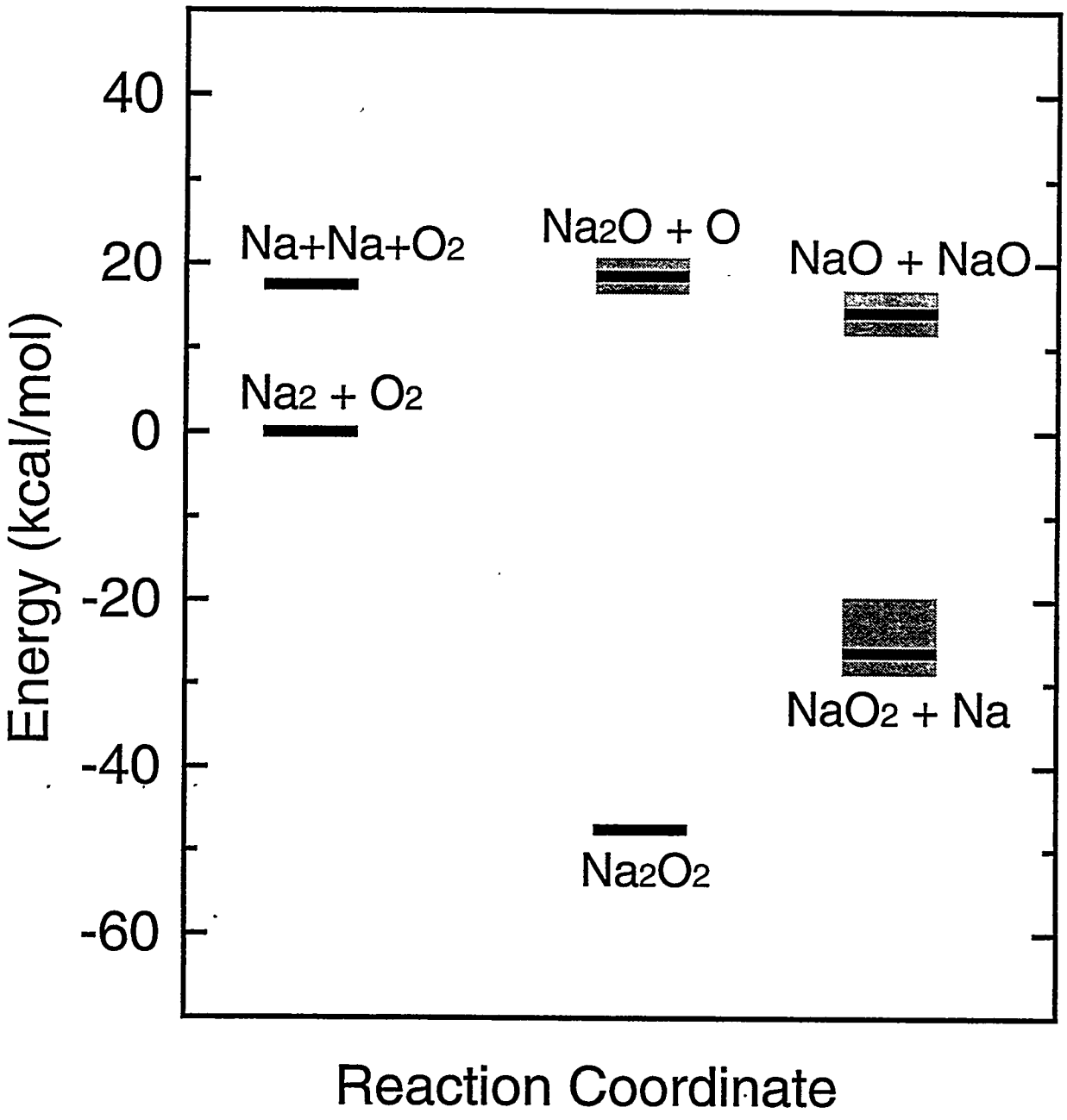
Fig. 8 Laboratory angular distribution of NaO^+ signal at E_c = 23 kcal/mol. Solid line indicates the total fit. The dotted line indicates the contribution from the NaO_2 + Na reaction channel, and the dash line is for the NaO + NaO channel.

Fig. 9 Translational energy distribution P(E) and angular distribution $T(\theta)$ that best fit NaO_2 channel.

Fig. 10 Translational energy distribution P(E) and angular distribution $T(\theta)$ that best fit NaO channel.

Fig. 11 Na^+ time-of-flight spectra from $Na/Na_2 + O_2$ (Left) and $Na/Na_2 + N_2$ (Right). Open circles are the experimental data. The total fit (solid lines) is composed of four channels including elastic scattering (the fastest, dash-dot-dot), inelastic scattering (the second fastest, long dash), NaO_2 channel (dash-dot) and NaO channel (short dash).

Fig. 12 Schematic drawing that illustrates the relations between the observed signal and various products. σ_i and σ_{iii} are the reaction cross sections for Reaction (i) and Reaction (iii), respectively. $\sigma_{elastic}$ and $\sigma_{inelastic}$ are the cross sections for the elastic scattering and the inelastic scattering of $Na + O_2$. σ_{ion}'s are the ionization cross sections by electron bombardment. The ions so formed undergo further dissociation to give observed signal. ξ is defined as the fraction of NaO^+ among the total Na-containing positive ions produced by electron bombardment of NaO_2. According to the assumption that NaO_2 dissociate completely upon electron bombardment, the fraction of Na^+ from NaO_2 is $(1-\xi)$. η is defined as the fraction of Na^+ among the total Na-containing positive ions from the ionization of NaO.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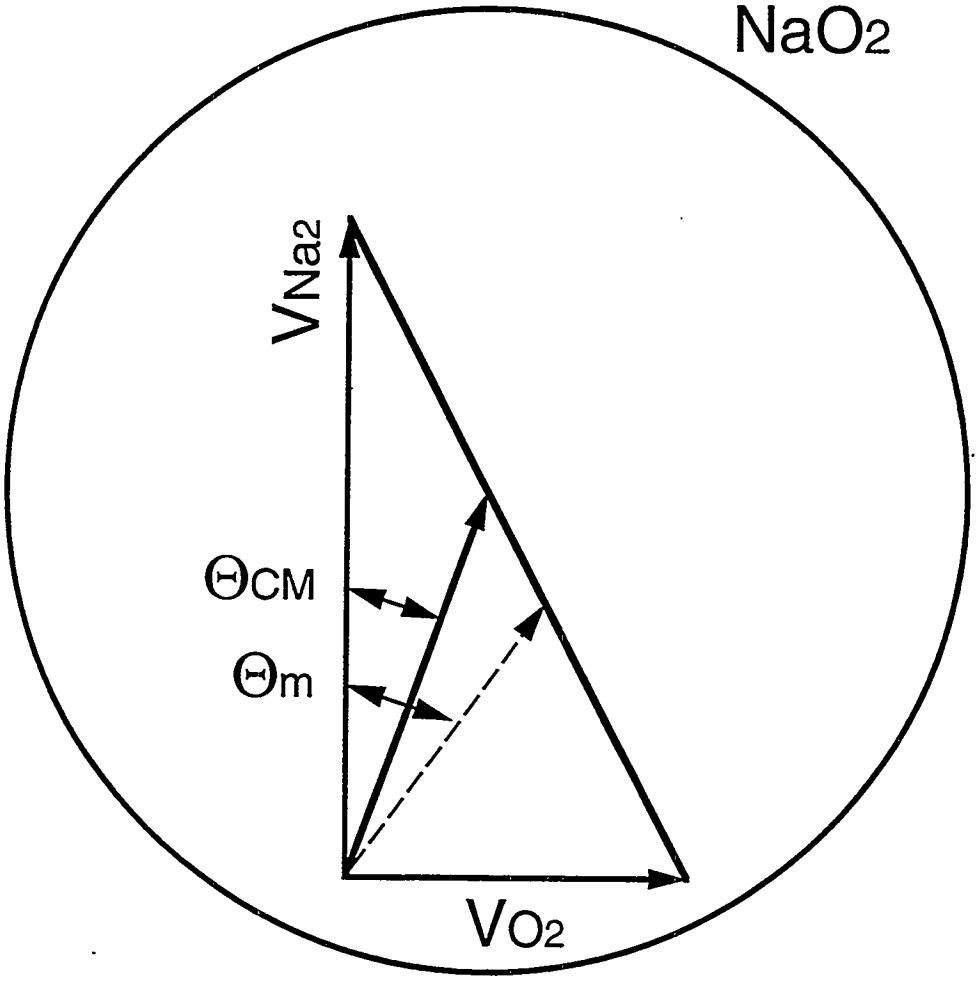
-20
-40
-60
Energy (kcal/mol)
Na+Na+O2
Na2 + O2
Na2O + O
NaO + NaO
NaO2 + Na
Na2O2
Reaction Coordinate

Figure 1.

E_c = 8 kcal/mol



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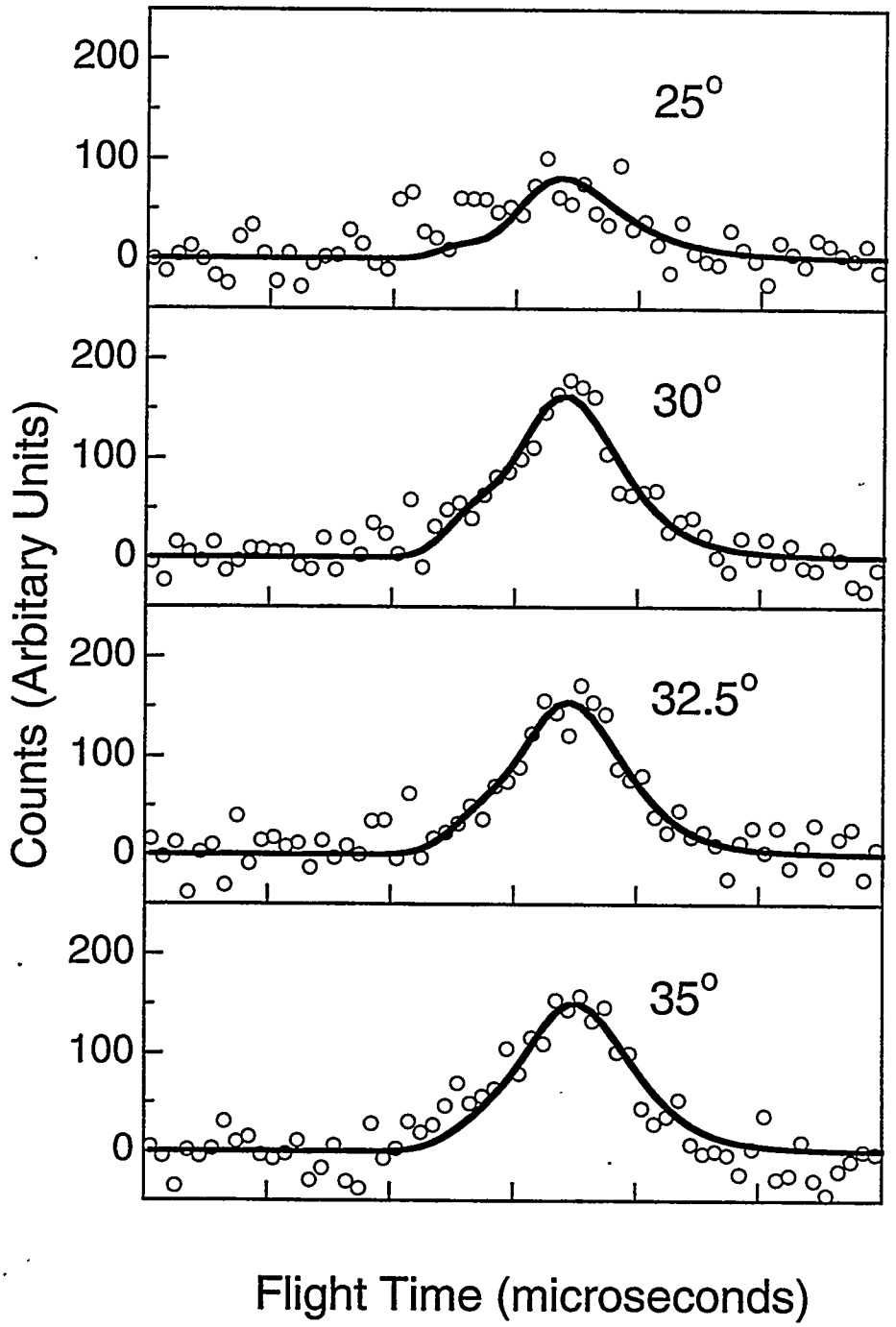
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0
25°
200
100
0
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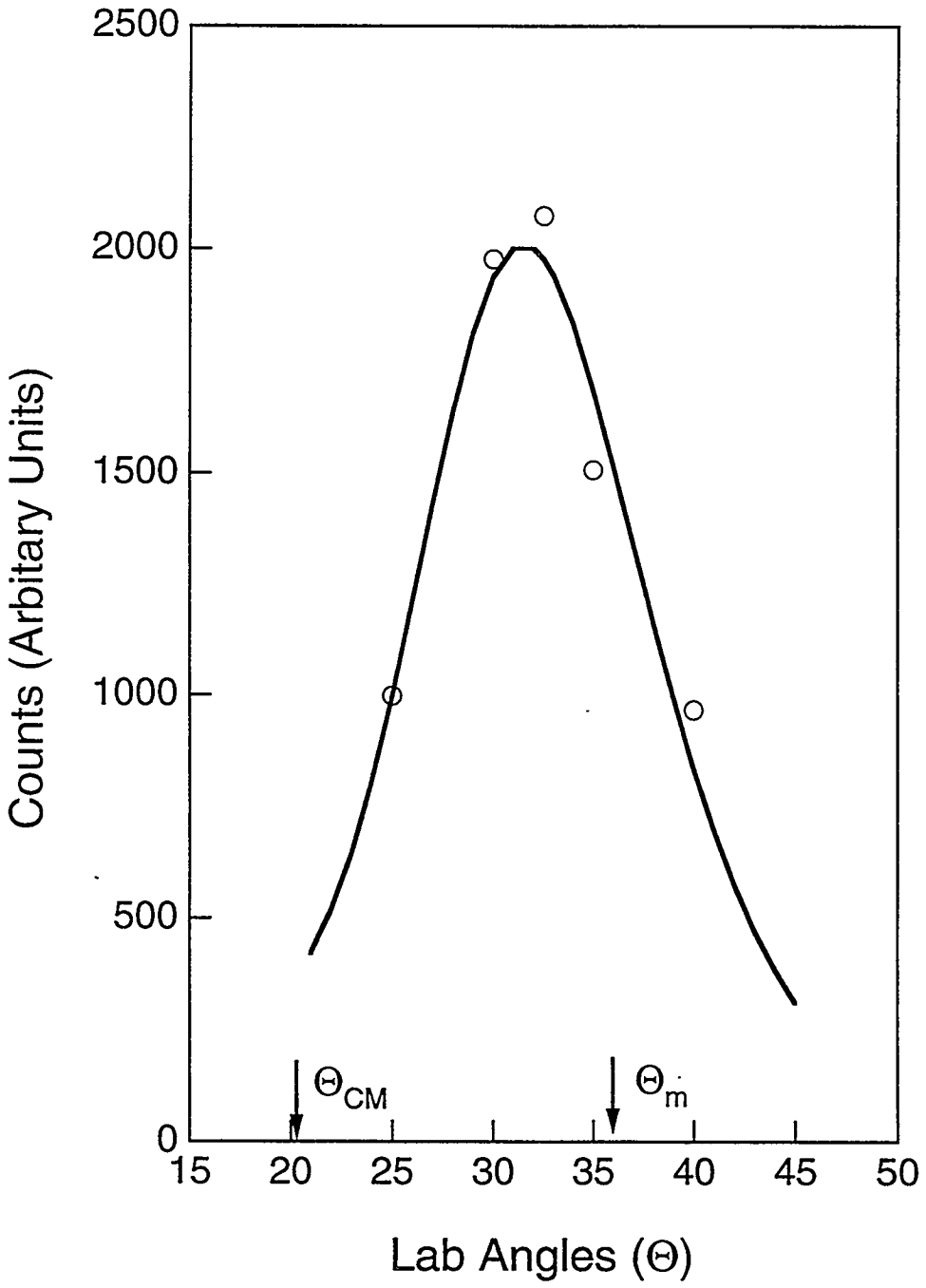
Counts (Arbitary Units)
Flight Time (microseconds)

Figure 3.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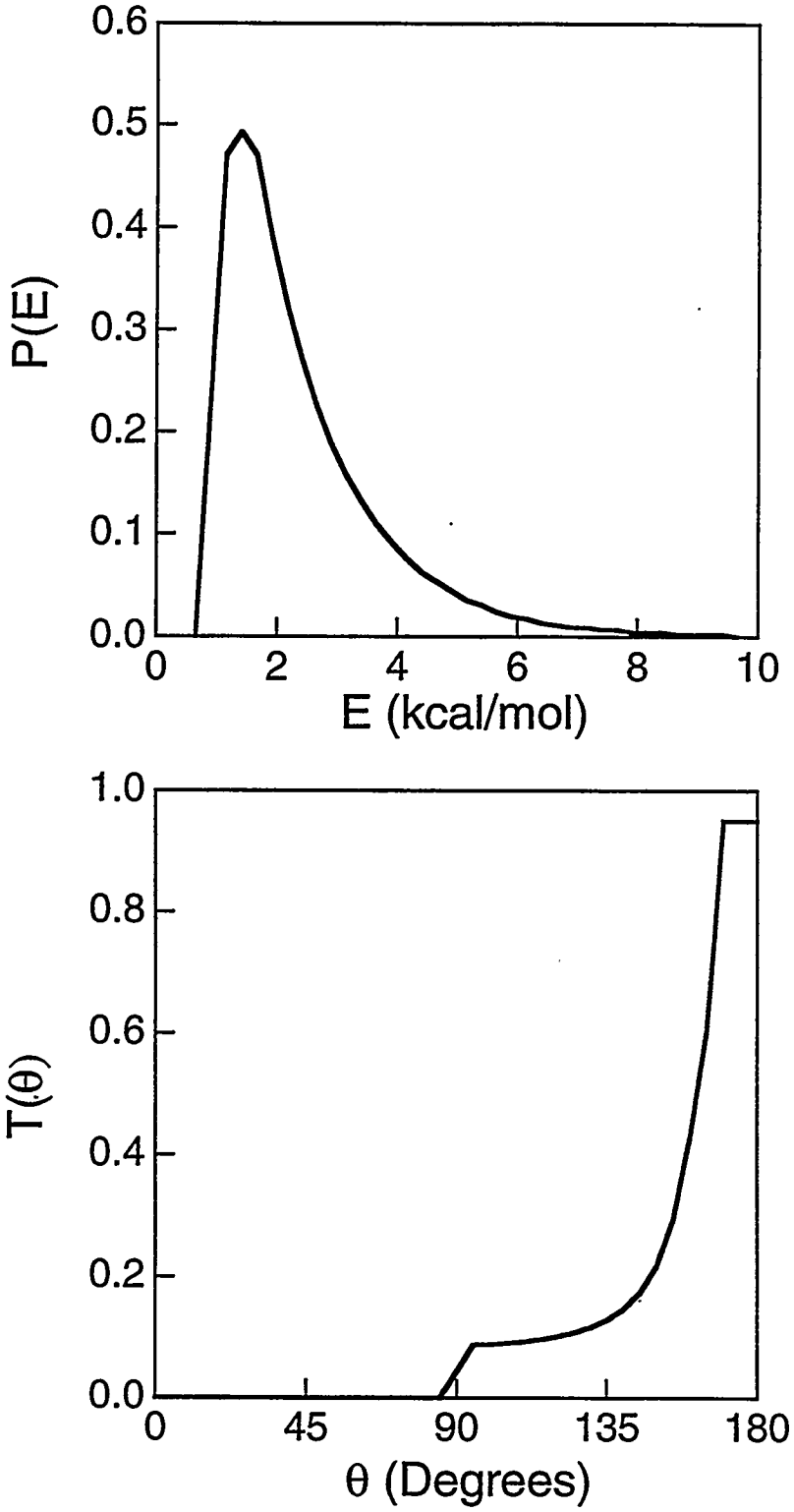
Lab Angles (Θ)
Θ_CM
Θ_m

Figure 4.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P(E)
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2
4
6
8
10
E (kcal/mol)
1.0
0.8
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0.4
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0.0
T(θ)
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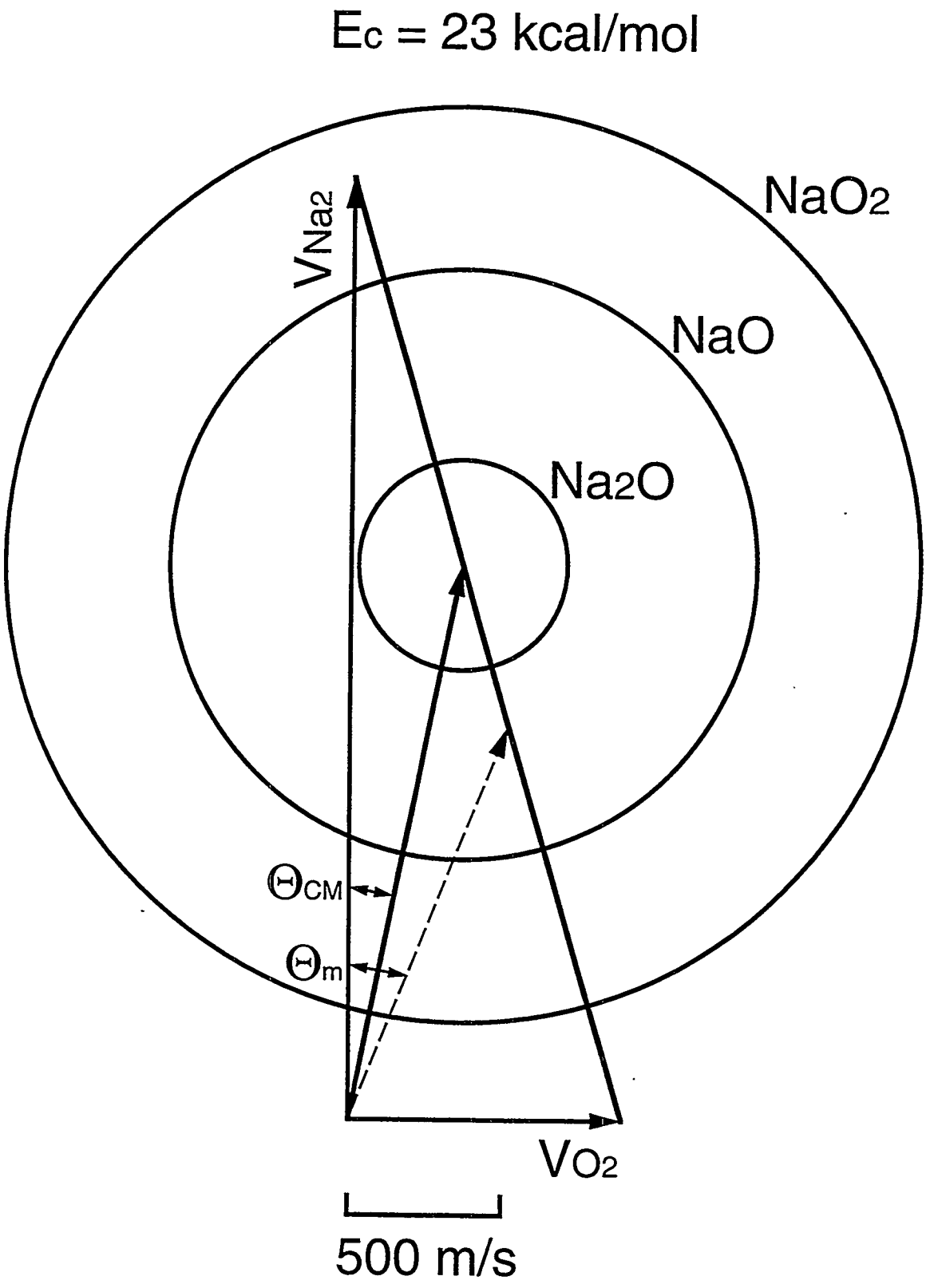
45
90
135
180
θ (Degrees)

Figure 5



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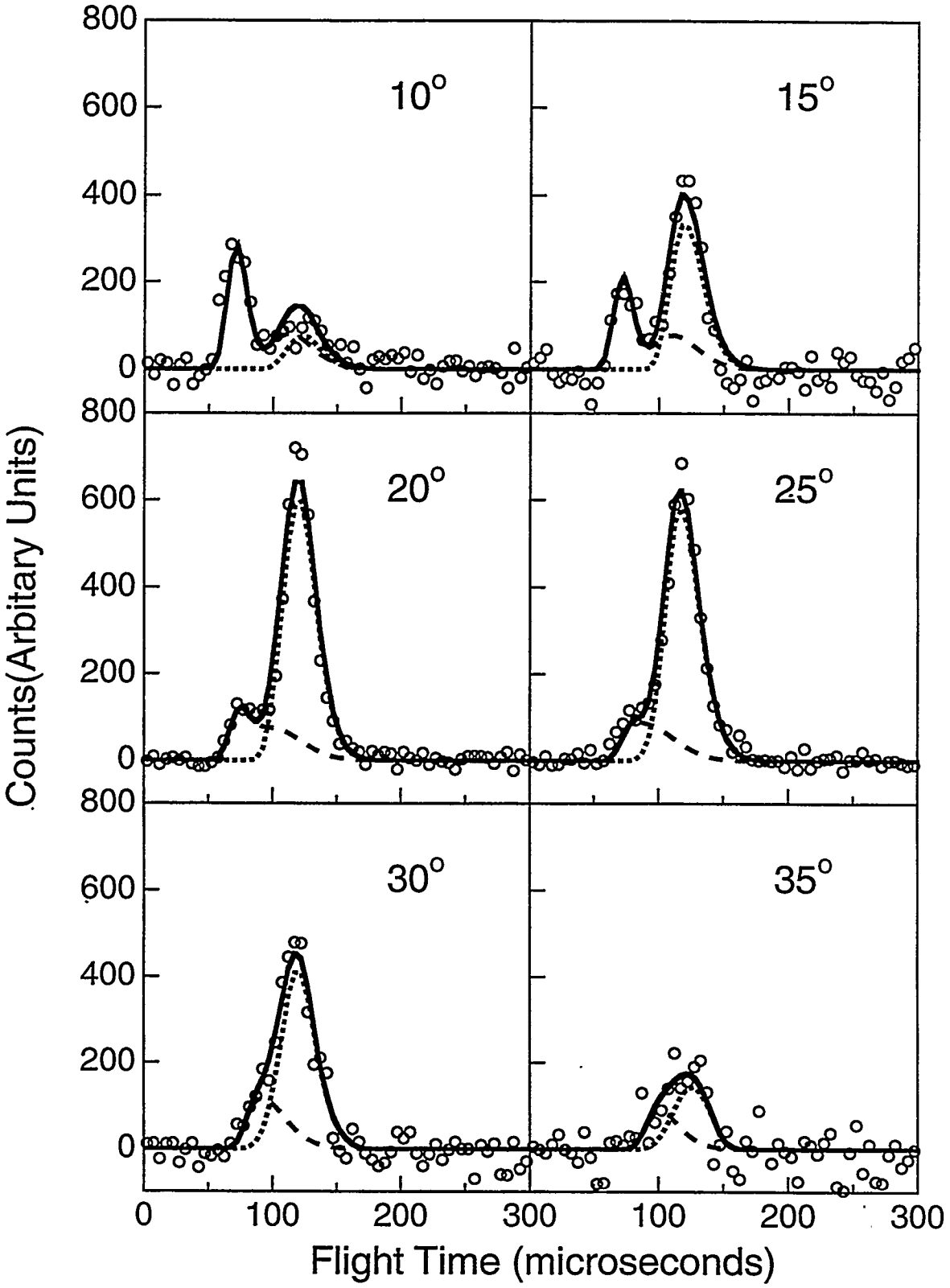
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Counts(Arbitary Units)
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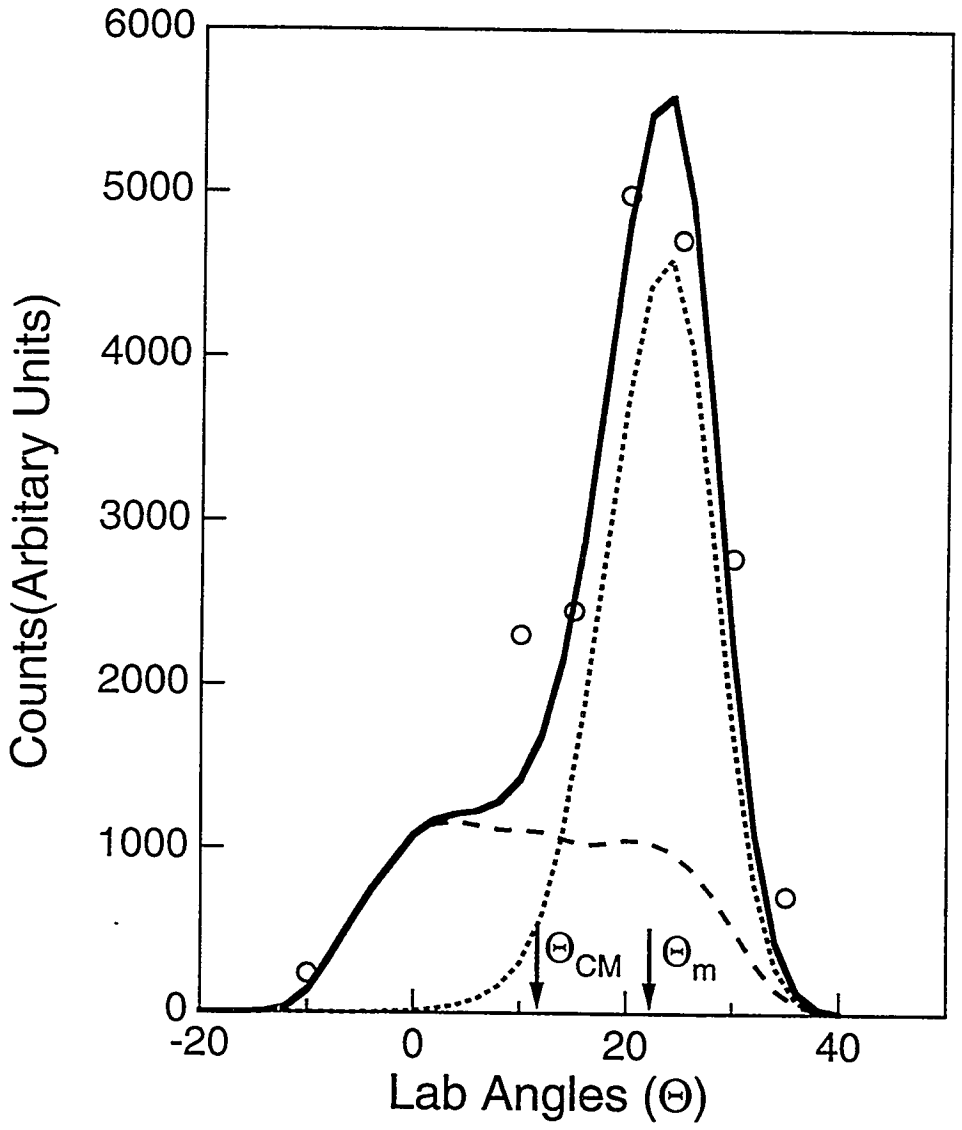
200
300
Flight Time (microseconds)

Figure 7.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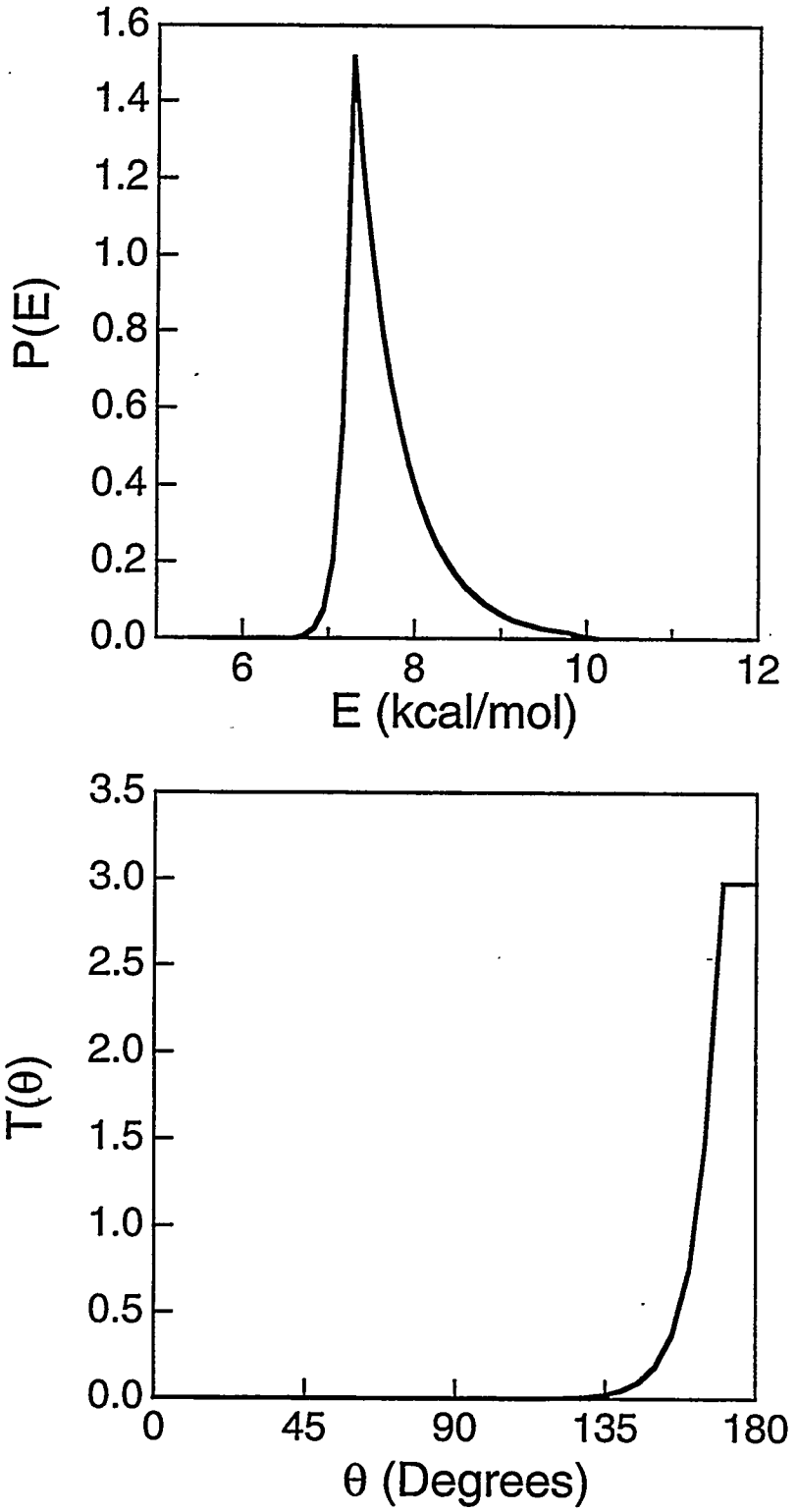
Lab Angles (Θ)
Θ_CM
Θ_m

Figure 8.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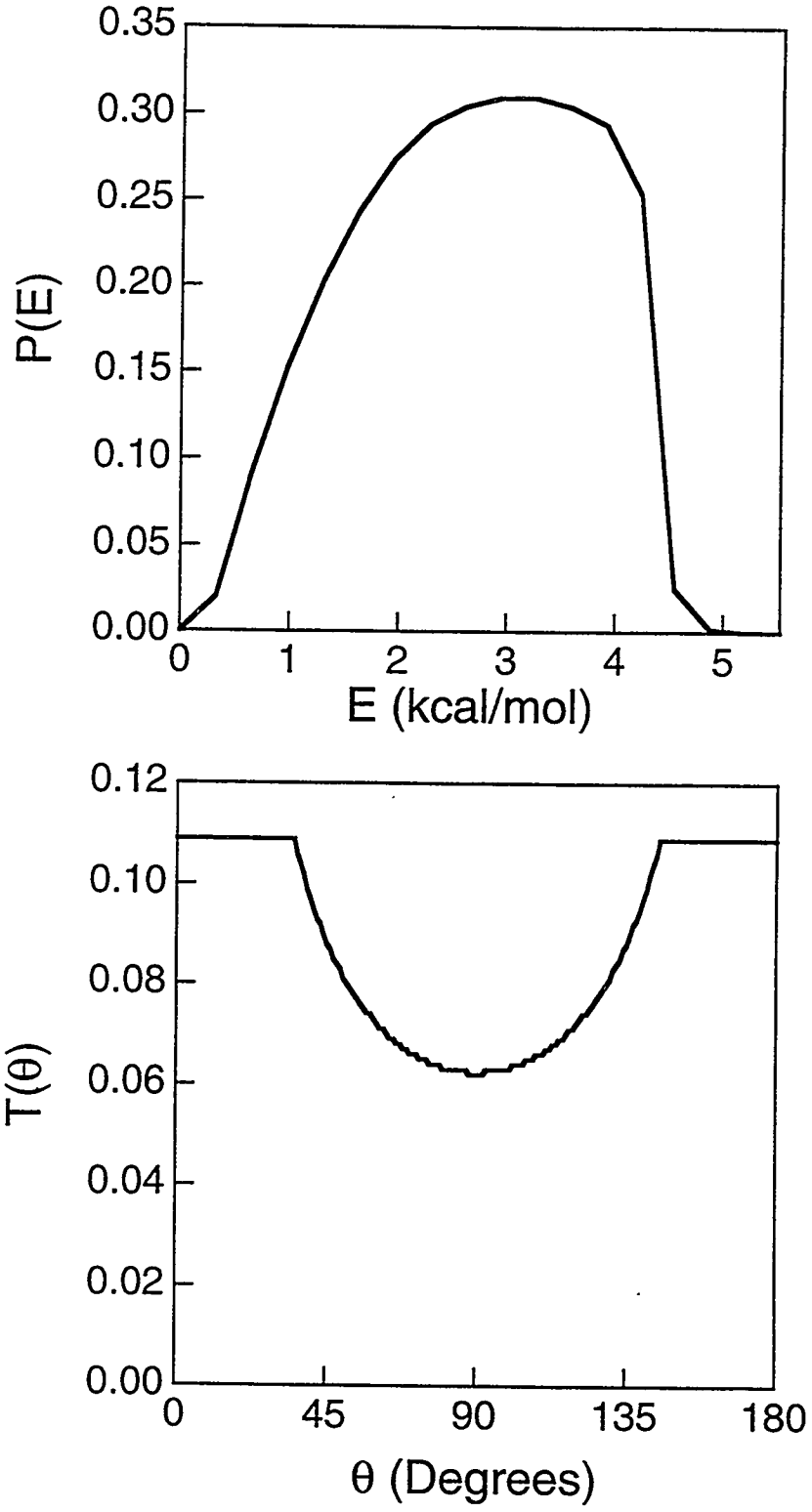
1.0
0.8
0.6
0.4
0.2
0.0
6
8
10
12
E (kcal/mol)
T(θ)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
45
90
135
180
θ (Degrees)

Figure 9.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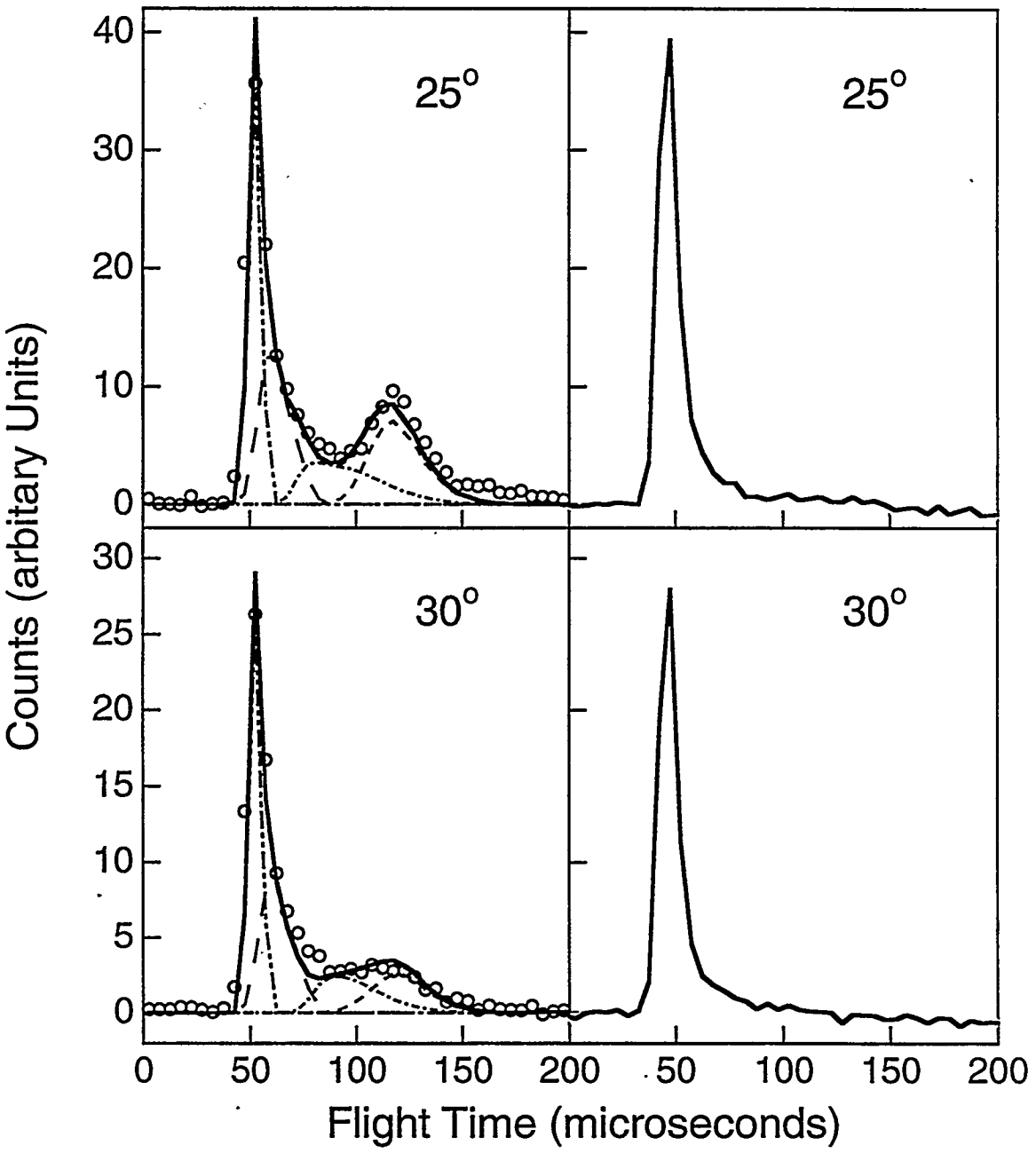
0.10
0.05
0.00
P(E)
0
1
2
3
4
5
E (kcal/mol)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
T(θ)
0
45
90
135
180
θ (Degrees)

Figure 10.


25°
25°
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30°
Counts (arbitary Units)
Flight Time (microseconds)
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150
200
50
100
150
200

Figure 11.

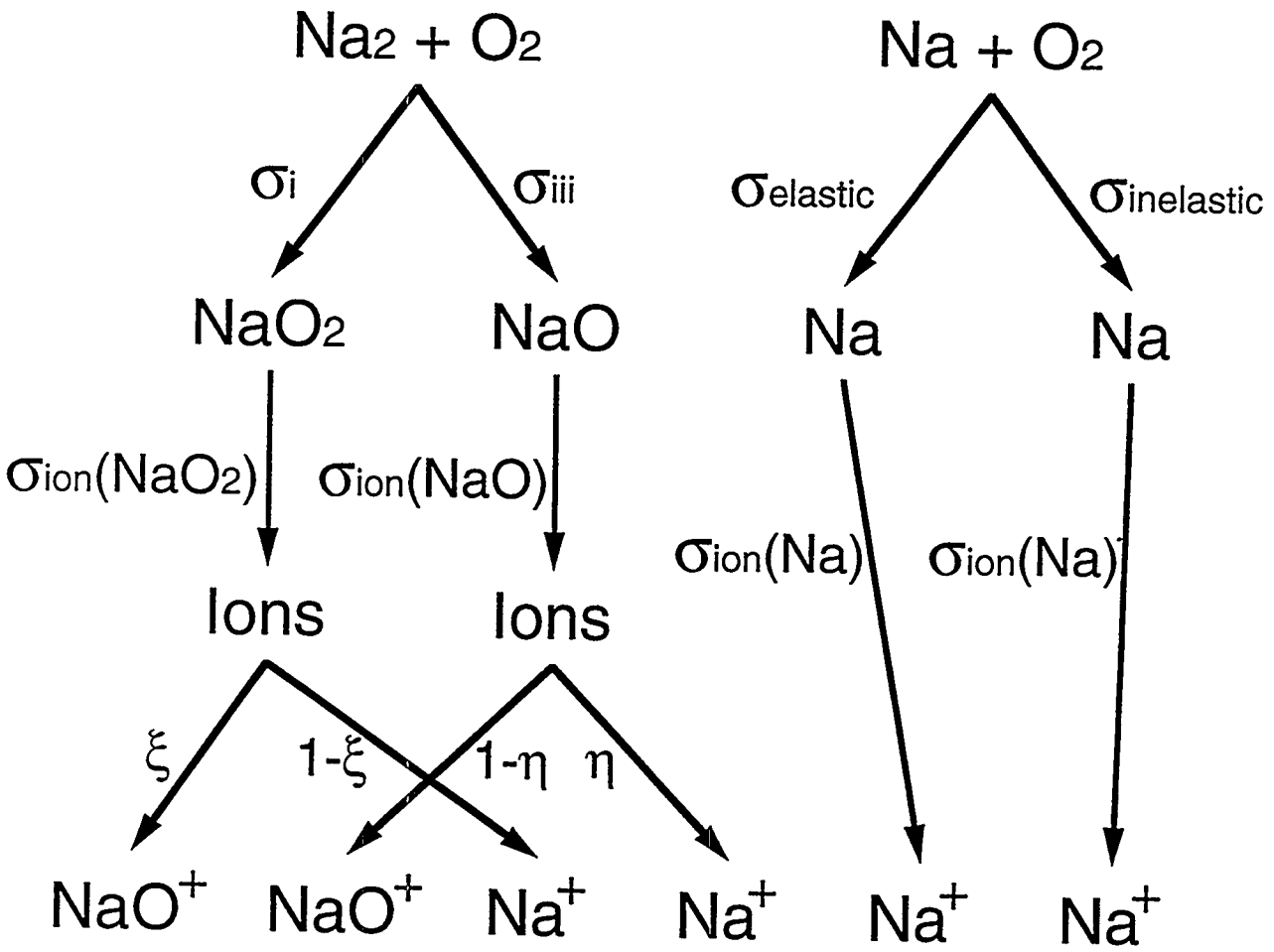
Na2 + O2
σi
σiii
NaO2
NaO
σion(NaO2)
σion(NaO)
Ions
Ions
ξ
1-ξ
1-η
η
NaO+
NaO+
Na+
Na+
Na + O2
σelastic
σinelastic
Na
Na
σion(Na)
σion(Na)
Na+
Na+

Figure 12