Title

State Specific Reactions of Ba({sup 1}S{sub 0}) and Ba({sup 1}D{sub 2}) with Water and Methanol

Journal

Journal of Chemical Physics, 96(12)

Authors

Davis, H.F.
Suits, Arthur G.
Lee, Yuan T.
et al.

Publication Date

1993

LBL-33577
UC-401

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

CHEMICAL SCIENCES DIVISION

Submitted to Journal of Chemical Physics

State Specific Reactions of Ba($^1S_0$) and Ba($^1D_2$) with Water and Methanol

H.F. Davis, A.G. Suits, Y.T. Lee, C. Alcaraz,
and J.-M. Mestdagh

January 1993

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California and shall not be used for advertising or product endorsement purposes.

Lawrence Berkeley Laboratory is an equal opportunity employer.

Printed on recycled paper

This publication has been reproduced from the best available copy

DISCLAIMER

LBL-33577
UC-401

STATE SPECIFIC REACTIONS OF Ba($^1S_0$) AND Ba($^1D_2$) WITH WATER AND METHANOL

H. Floyd Davis,[a] Arthur G. Suits,[b] and Yuan T. Lee

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

and

Christian Alcaraz and Jean-Michael Mestdagh

Service des Photons, Atomes, et Molécules
CE de Saclay
91191 Gif-sur-Yvette, France

January 1993

[a]Current Address: Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482.

[b]Current Address: Department of Chemistry, Cornell University, Ithaca, NY 14853-1301.

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.

ABSTRACT

The reactions of Ba($6s^2$-$^1S_0$) and Ba($6s5d$-$^1D_2$) with water and methanol were studied under single collision conditions using crossed molecular beams. Reaction of ground state Ba(^1S) + H_2O led to dominant formation of BaO + H_2 at all collision energies studied (12-30 kcal/mol). Although the reaction Ba(^1S) + H_2O → BaOH + H could be observed at collision energies above the endoergicity of the reaction (13 kcal/mole), it remained a minor channel even at the highest collision energy. Electronic excitation of the Ba atom reactant to the metastable $^1D_2$ state led to a large enhancement in reactivity, but the products were BaOH + H rather than BaO + H_2. The dominance of BaO + H_2 from ground state Ba(^1S) even at collision energies nearly equal to the Ba(^1D) excitation energy of 11,395cm^{-1} ($\sim$32 kcal/mole) indicates that the observed reaction state specificity results from participation of different potential energy surfaces for reactions of ground and excited state atoms. Collisions of Ba(^1S) and Ba(^1D) with methanol led only to formation of $BaOCH_3$ + H. We observed no BaOH + CH_3 or BaO + CH_4, despite the fact that they are the more thermodynamically favorable channels. Although reactivity with methanol was strongly enhanced by electronic excitation of the incident Ba atom, no reaction was observed from Ba(^1S) or Ba(^1D) + dimethyl ether (CH_3OCH_3). These observations strongly suggest that the reactions leading to radical formation involve H-atom migration.

I. INTRODUCTION

By judicious choice of the electronic state of a reactant, it is possible to affect or perhaps even control the chemical outcome of a bimolecular reaction. Studies using guided ion beams have shown that the chemistry of the various electronic states of a transition metal ion can change markedly due to the participation of different potential energy surfaces.[1] In the case of neutral species, early studies showed that O(^{1}D) is able to insert into covalent bonds, whereas the ground state O(^{3}P) atom is relatively inert under the same conditions.[2] More recently, the use of crossed supersonic atomic and molecular beams combined with laser excitation of the atomic reactant has made it possible to study the reaction dynamics of different electronic states of an atom as a function of collision energy and alignment of the excited orbital under well defined conditions.[3-5]

In many cases, electronic excitation does not simply provide energy to drive endoergic reactions. Instead, the differing topologies of the potential energy surfaces will determine the reactivities of different states. This was demonstrated in the reaction $Na^* + O_2 \rightarrow NaO + O$.[3,4] When excited to the 4d state, sodium was found to react with O_2, whereas the 5s state (at nearly the same electronic energy) was unreactive.

There has been considerable interest in the interactions between water and isolated metal and main group atoms in the ground and electronically excited states.[6-15] In addition to their importance for understanding the mechanisms of hydration, these interactions are intriguing because unlike most small oxygen-containing molecules, water and its methyl derivatives possess only "Rydberg- like" unfilled molecular orbitals.[16,17] Consequently, reactions are not expected to be initiated by long range electron transfer, and the well known "harpoon mechanism"[5a,18-20] is not generally applicable. Instead, a close collision is necessary to initiate a chemical reaction between the atom and molecule. Because Ba is divalent, its chemistry is quite rich with several possible competing channels. In the case of water or methanol, insertion of the Ba atom into a covalent bond may occur, possibly forming HBaOH, $HBaOCH_3$ or $HOBaCH_3$[6,7]. Decomposition of these intermediates would likely lead to formation of radical products BaOH or $BaOCH_3$. Alternatively, concerted oxygen atom abstraction leading to the closed shell molecules BaO + H_2, or BaO + CH_4, is thermodynamically favored.[21](Table 1)

The reactions of alkaline earth and a variety of other atoms (M) with water have been studied extensively by Margrave and coworkers[7,8,14,15] using matrix isolation techniques and infrared spectroscopy. They found that codeposition of the reactants in a low temperature argon matrix led to formation of a $M\text{-}OH_2$ adduct involving a weak interaction (5-10 kcal/mole) between the metal atom and oxygen in water (Table 1). An increased red shift in the adducts' water bending frequency for the heavier alkaline earth atoms has been taken as evidence that the interaction is strongest for barium[7,9]. For alkaline earth and some transition metal atoms, irradiation of the matrix at wavelengths near the metal atomic resonance line led to formation of HMOH and MOH. However, in the case of some transition metal atoms, the oxygen-bonded adduct rearranged spontaneously in the dark to form HMOH. *Ab-Initio* calculations[9,10] for the lighter alkaline earth atoms + water were consistent with these experimental observations. The oxygen bonded adduct was found to represent a small but definite well on the potential energy surface; a substantial potential energy barrier for insertion explained the need for irradiation to promote the reaction. Based on *ab-Initio* calculations[9] and empirical bond energy estimates[7] for alkaline earth atoms, HMOH is expected to be stable, lying about 30 kcal/mole lower in energy than $M+H_2O$.

Very little gas phase work on reactions of water and methanol with neutral atoms using crossed molecular beams has appeared. Due to the absence of long-range electron transfer, the reactions are expected to have small cross sections (<10 Å^2). This factor, together with the possibility of several competing reaction channels makes it difficult to obtain a full picture of the reaction dynamics. This is because many detection techniques[22] do not have comparable sensitivities to all possible channels. However, a number of interesting features have been observed in gas phase reactions to date.

Alcaraz and coworkers[6a] investigated the luminescent channels from the laser-induced reactions of Ba($6s6p^1P_1$) and Ba ($6a5d^1D_2$) with H_2O under single collision conditions. Although no chemiluminescence was observed from reaction of Ba($^1D_2$), the Ba($^1P_1$) reaction led to BaOH($B^2\Sigma^+, A^2\Pi$). No BaO($A^1\Sigma^+$ or $A'^1\Pi$) was observed, even though those channels are more energetically favorable. The lack of the concerted $BaO + H_2$ channel was attributed to a large barrier on the potential energy surface. The spectroscopy of a number of radicals containing alkaline earth metals has been studied by Bernath[23] and coworkers. Electronic excitation of the metal atom led to substantial enhancement of reactivity: most notably, Sr($^1P_1$) + CH_3OH led to formation of $SrOCH_3$. However, the focus was on the spectroscopy of the products rather than on the reaction dynamics.

Although there have been no reports of formation of MO from single collisions of alkaline earth atoms with water or alcohols, such reactions are known to occur for other atomic species. Gole and Pace[11] observed BO chemiluminescence from $B + H_2O \rightarrow BO^* + H_2$. *Ab-initio* calculations[12] indicated a large potential energy barrier for this reaction, which was apparently surmounted by the fast Boltzmann tail of the effusive atomic B beam. Liu and Parson[13] studied the reactions of Y and Sc with water and alcohols under single collision conditions. Only the MO product was observed; either the hydroxide was not formed or it's LIF spectrum was outside the wavelength range studied.

We have performed crossed molecular beams studies of the reactions of ground state ($6s^2$-$^1S_0$) and metastable ($6s5d$-$^1D_2$) barium atoms with water and its alkyl derivatives; methanol (CH_3OH), and dimethyl ether (CH_3OCH_3). In our study, products were detected using an electron bombardment ionizer-quadrupole mass spectrometer.[5a,24] This, together with the measurement of angular and velocity distributions of the products allowed us to identify all reaction channels, including those leading to products in the ground electronic state. Our work complements the chemiluminescence experiments of Alcaraz et al[6]; the combined results allow us to gain considerable insight into the dynamics of the reactions. By changing the kinetic energy of the atomic and molecular beams, we compared the effect of reactant collision energy to reactant electronic energy. We find that the reactions with water are largely state specific: at all collision energies, ground state Ba(^{1}S) reacted to form the molecular products BaO + H_2 by a concerted mechanism. In reactions of metastable Ba(^{1}D), however, the products were BaOH + H. In reactions with CH_3OH, only $BaOCH_3$ + H was observed from Ba(^{1}S) or Ba(^{1}D), despite a much larger exoergicity for formation of BaOH + CH_3 or BaO + CH_4 (Table II). Dimethyl ether (CH_3OCH_3) led to no reactive signal from ground state or electronically excited Ba, even at the highest collision energy, 30 kcal/mole. These observations suggest that the formation of radicals results from hydrogen atom migration, a process strongly enhanced by electronic excitation of the incident barium atom.

II. EXPERIMENTAL

A continuous, seeded supersonic beam of barium atoms was formed in a molybdenum oven source with separately heated barium reservoir and nozzle. The beam was skimmed by a heated (1000° C) molybdenum skimmer and collimated to ~1° half width by a set of defining slits. Details of the apparatus[5a,24] and the atomic beam source[25] are available elsewhere. The molecular beam was formed by bubbling helium or hydrogen carrier gas through the liquid sample held in a refrigerated bath and expanding the mixture through a 0.005" or 0.010" diameter nozzle. A dilute mixture ($<5\%$) and high nozzle temperature (~200°C) was necessary to eliminate dimers and larger clusters. The water was distilled; the methanol, dimethyl ether, t-butyl hydroperoxide, and $H_2{}^{18}O$ were obtained from Aldrich Chemical Company. Both beams were differentially pumped and crossed at 90° in a liquid nitrogen cooled chamber maintained at $\sim 1\times10^{-7}$ Torr.

Reaction products were detected by a triply differentially pumped electron impact ionizer-quadrupole mass spectrometer that could be rotated in the plane of the atomic and molecular beams[5a,24]. An important goal of the experiment was to measure relative yields of BaOH (m/e=155) and BaO (m/e=154). This is inherently difficult due to the close proximity of the mass peaks and fragmentation of BaOH to BaO^+ upon electron bombardment ionization. Considerable effort was made to characterizing the fragmentation patterns of the product molecules as well as their transmission through the quadrupole mass filter. Fortunately, resolving these products is aided by the favorable kinematic relationships which confine BaO and BaOH to a very narrow scattering angle and lead to rather large signal levels. Also, the background count rate in the mass spectrometer detector is nearly zero at these heavy masses. Most importantly, the natural isotopic abundance of Ba is favorable-- the isotopes with masses 138, 137, and 130-136 are 71.70%, 11.23% and 17.07% naturally abundant, respectively.[26] By operating the mass spectrometer at a high resolution setting, it was possible to distinguish between the $^{138}BaOH$ (m/e=155) and ^{138}BaO (m/e=154) parent ion peaks with only a minor contribution at m/e=154 from $^{137}BaOH$. Fragmentation of BaOH to BaO^+ upon 200 eV electron bombardment ionization was a factor to consider in the analysis. This fragmentation ratio is difficult to measure with great accuracy since there appears to be few clean sources of BaOH in the gas phase. The reaction of $Ba(^1D)$+ t-butyl hydroperoxide formed both BaOH + t-butoxy radical and Ba-t-butoxide + OH. Due to the similar exoergicities of the reactions, and the heavier recoil partner for the BaOH product, it was possible to monitor pure BaOH far from the Ba beam outside the angular range for Ba-t-butoxide. This allowed us to measure the fragmentation pattern obtaining a value of $BaOH^+/BaO^+ = 1.0 \pm 0.2$. This ratio compares favorably with that observed from the product of the reaction $Ba(^1D) + H_2O$, which we estimate to be 90-100% BaOH. We have no way to measure the dependence of this pattern on internal excitation of BaOH, but since ionization involves removal of the non-bonding radical electron[26,27], it is expected to be small. Adequate discrimination between m/e=154 and m/e=155 was checked by monitoring the BaO product (m/e=154) known to result from the $Ba + O_2$ crossed beams reaction,[29,30] and increasing the resolution to extinguish signal observed at m/e=155. It has been found in other work that fragmentation of BaO to Ba^+ is relatively insensitive to internal excitation.[5a,31] Product time of flight distributions were obtained using the cross-correlation method, as described previously[5a,32]. The velocity distributions of each beam were measured directly using a 4-slot chopper wheel instead of the cross correlation wheel.[5a]

The metastable barium atomic beam was formed by optically pumping the Ba(^{1}P$\leftarrow$^{1}S) resonance upstream of the interaction region using a Coherent 699-21 ring dye laser operating single frequency near 553nm with Rhodamine 560 dye.[5a] A fraction of the Ba(^{1}P) atoms undergo radiative decay to the metastable ^{1}D state. Based on measurements described elsewhere[5a] and using the published branching ratios[33] for decay of Ba(^{1}P), the ^{138}Ba in the beam consisted of 45% Ba(^{1}D), 15% Ba(^{3}D) and 40% Ba(^{1}S), with all other isotopes in the ground (^{1}S) state. Product angular and velocity distributions were obtained by running parallel experiments at various detector angles with the laser on and off. We have not attempted to study the reactivity of Ba(^{1}P) with water or its alkyl derivatives.

III. RESULTS

A. Reaction of Ba(^{1}S) + H_2O

The reactive and nonreactive scattering of Ba($^1S_0$) + H_2O was studied at several collision energies in the range 12-30 kcal/mole. The Newton diagram for Ba + H_2O at a nominal collision energy of 12 kcal/mole is shown in Fig. 1. The solid circle denotes the maximum calculated BaO velocity from the BaO + H_2 reaction, and the dotted circle shows the maximum velocity of nonreactively scattered Ba atoms. The mean collision energy is just below the 13 kcal/mole endoergicity for Ba(^{1}S) + H_2O → BaOH + H. Assuming that supersonic expansion of 5% H_2O in He at 200°C leads to no vibrational cooling, <2% of the H_2O molecules will have a quantum of symmetric bending excitation (1594 cm^{-1}).[16] At E_{coll}= 12 kcal/mole, only these molecules and the fastest velocity components of each supersonic beam could react to form BaOH + H. However, our experiments indicate that the dominant reaction is actually Ba(^{1}S) + H_2O → BaO($X^1\Sigma$) + H_2. A number of checks were conducted to prove that the BaO signal was in fact due to bimolecular collisions between Ba + H_2O. First, the BaO product intensity peaked at the center of mass laboratory angle (18°) consistent with the known masses and velocities of the Ba + H_2O colliding pair (Fig 1). Contributions from reactions of possible contaminants, such as O_2 or $(H_2O)_n$ were ruled out since the laboratory center-of-mass angles associated with collisions of those species with Ba is considerably larger. A major concern arose from our observation of trace quantities of BaO in the Ba beam itself. Since the vapor pressure of BaO is extremely low[34] at the oven temperature, it must arise from reaction of Ba atoms in the beam with residual gasses (O_2, H_2O) present in the differential pumping region. This BaO impurity remains primarily within the atomic beam. However, we could also detect some BaO outside the beam due to elastic and inelastic collisions between the impurity and water in the molecular beam. In order to eliminate this undesirable signal, a series of experiments were conducted using $H_2{}^{18}O$ in the molecular beam instead of ordinary distilled water. Figure 2 shows the $Ba^{18}O$ time of flight spectra (m/e=156) from reaction of ground state Ba with $H_2{}^{18}O$. The quadrupole mass spectrometer was operated at unit mass resolution--as expected, no signal could be observed at m/e=156 ($Ba^{18}O$) under the same conditions when normal distilled water was used in the molecular beam. Thus, this signal must result from single collisions between Ba + $H_2{}^{18}O$. Figure 3 shows the time of flight spectra recorded at Ba^+ (m/e=138) under the same conditions. At this collision energy, the $Ba^{18}O$ signal level was weak compared to the Ba signal from nonreactive scattering. The observed Ba signal (Fig. 3) primarily resulted from nonreactive elastic and inelastic collisions. The maximum velocity for this nonreactively scattered Ba is shown as a dotted line in the Newton diagram (Fig. 1)-- the fast and slow components of the Newton circle can be clearly seen in the Ba time-of-flight spectra (Fig. 3) at lab angles smaller than 30 degrees.

Figure 4 shows the best fit translational energy distribution (P(E)) and center of mass angular distribution ($T(\theta)$) used in the simulation of the data in Figs. 2 and 3 (solid lines). A considerable amount of wide angle nonreactive Ba signal was observed at this collision energy. In figure 3, the minor component (dotted line) in the Ba signal near $180\mu s$ is the contribution from fragmentation of BaO product to Ba^+ in the electron bombardment ionizer. This contribution was calculated using the best fit to the BaO data and the measured BaO fragmentation ratio. From the relative Ba and BaO signal level, we estimate that the cross section for the reaction $Ba(^1S) + H_2O \rightarrow BaO + H_2$ is $< 2Å^2$ at 12 kcal/mole.

Mass scans of the product from the reaction of ground state Ba indicate that formation of $BaO + H_2$ dominates at all collision energies between 12 and 30 kcal/mol. Raising the collision energy above the 13 kcal/mole endoergicity for formation of BaOH + H opened up this channel, but the observed BaOH signal level remained substantially smaller than from $BaO + H_2$ even at 30 kcal/mole, the highest collision energy studied. Figure 5 shows the angular distributions for the BaO and BaOH from reaction of ground state $Ba(^1S) + H_2O$ at a collision energy of 23 kcal/mole. Due to the reaction endoergicity and light H-atom recoil partner, the Newton circle for the BaOH product is very small-- the product is constrained to appear near the center-of-mass angle and a substantial fraction of all reaction products enter the detector. In the case of the dominant $BaO + H_2$ channel however, a smaller fraction of the BaO is collected for a given detector angle since the products are scattered over a much larger Newton circle. By monitoring both channels at the CM angle (25°), our detection sensitivity is strongly biased towards the minor BaOH + H channel. This differing kinematic relationship and the occurrence of both channels is clearly illustrated (Fig. 5). At a collision energy of 23 kcal/mole, the width of the laboratory angular distribution observed at BaO^+ is more than 20 degrees, whereas that for $BaOH^+$ is ~ 10 degrees. Time-of-flight data for the products from $Ba(^1S) + H_2O$ reactions are shown in figures 6 and 7. The optimized P(E) and $T(\theta)$ used to fit the data are shown in figure 8. The small contribution to the BaO time-of-flights from fragmentation of BaOH to BaO^+ in the ionizer is shown in dotted lines in Fig. 7. The laboratory angular distribution for both channels peaked at the center of mass angle (Fig. 5). Based on the fit to the BaO time of flight profiles, (which are considerably broader than those for BaOH) we conclude that there is a substantial release of translational energy in the $BaO + H_2$ products (Fig. 8). The best fit to the BaO lab angular distribution led to a CM angular distribution that was approximately isotropic. It should be pointed out that due to kinematic limitations we would not be able to resolve a slight forward or backscattering. It is even more difficult to make conclusions about the BaOH angular and velocity distribution since the data is more compressed due to the light H atom recoil partner. However, our data does indicate that the CM angular distribution cannot be strongly forward or backscattered.

B. Reaction of Ba(^{1}D) with H_2O and D_2O

Excitation of the incident Ba atom to the metastable 6s5d-^{1}D state led to a dramatic increase in the observed signal level at all collision energies studied. Whereas the dominant product in the ground state reaction was BaO + H_2, reaction of Ba(^{1}D) leads primarily, and possibly exclusively, to formation of BaOH + H. Figure 9 shows the time of flight spectra obtained while monitoring $BaOH^+$. At a collision energy of 12 kcal/mole, the BaOH signal level at the center-of-mass angle (18°) from Ba(^{1}D) was approximately 20 times greater than BaO signal from Ba(^{1}S). The BaOH laboratory angular distribution is shown in the upper panel of Fig. 10. Also shown in Fig. 10 is the product translational energy distribution used to calculate the angular distribution and TOF spectra (Fig. 9). The very large increase in fraction of collisions leading to reaction can be seen in the Ba time-of-flight data (Fig 11). Upon excitation of the Ba atom reactant, the dominant contribution (middle peak) to the Ba signal is from fragmentation of BaOH reaction product to Ba^+ in the ionizer. This contrasts with the ground state behavior where the dominant contribution to the Ba^+ signal was from nonreactive scattering leading to a fast and slow peak (Fig. 3). The Ba time-of-flight data for collisions of ground and electronically excited Ba are plotted on absolute scales in figure 12. The large middle component which becomes dominant with the laser turned on (solid line) results from fragmentation of BaOH in the ionizer (middle peak). The fast component from wide angle nonreactive scattering also increased with electronic excitation.

Based on the observed $BaOH^+$:BaO^+:Ba^+ ratio at several detector angles, and the product angular distributions, we conclude that BaOH + H results from >90% of all reactive encounters between Ba(^{1}D) and H_2O. All of the BaO signal could be attributed to fragmentation of BaOH in the electron bombardment ionizer. Although the Newton circle for BaO recoiling from H_2 is considerably larger than for BaOH recoiling from H (Fig 5.), we were unable to see any additional BaO from Ba(^{1}D) + H_2O which could be attributed to the BaO + H_2 channel. After normalizing for the different Jacobian factors, comparison of BaOH and BaOD signal levels from Ba(^{1}D) + H_2O and Ba(^{1}D) + D_2O under similar beam conditions indicated that D_2O is 2.0 ± 0.4 times less reactive than H_2O.

C. Reactions of Ba(^{1}S), Ba(^{1}D) with CH_3OH and CH_3OD.

Three chemically distinct reaction channels, producing BaOH, $BaOCH_3$, and BaO are possible[21,23] from reaction of Ba atoms with methanol as shown in Table II. Since the reaction Ba(^{1}S) + $CH_3OH \rightarrow BaOCH_3$ + H is endothermic by 16.8 kcal/mole[6b], it can only be formed at a relatively high collision energy or from electronically excited Ba(^{1}D). Newton diagrams for reactions of ground state and electronically excited Ba + CH_3OH are shown in Fig. 13 for a nominal collision energy of 15 kcal/mole. Product angular distributions for reactions of Ba with methanol, shown in Fig. 14, indicate that formation of $BaOCH_3$ + H dominates in reactions of ground state and electronically excited Ba. As with water, large signal enhancement was seen upon electronic excitation, with the greatest increase (~20X) at the lowest collision energy studied (15 kcal/mole). At this collision energy, the ground state reaction was only barely detectable (Fig. 14- squares), and it results from reaction of vibrationally excited CH_3OH molecules or from the fastest velocity tails of the beams. The expected laboratory angular range for the BaOH product is much larger than for $BaOCH_3$ due to its heavier recoil partner (CH_3 instead of H- Fig 13). However, we were unable to detect $BaOH^+$ or BaOH daughter products (BaO^+, Ba^+, OH^+) at angles outside of that seen for formation of $BaOCH_3$ + H, even upon electronic excitation. The observed BaO^+ resulted primarily from fragmentation of

$BaOCH_3$ in the electron bombardment ionizer, and so the angular distribution is very similar to that for $BaOCH_3^+$. The very weak BaO^+ contribution at small laboratory angles ($<20°$) results from elastic scattering of BaO impurity present in the Ba beam, as described in section II. Based on the signal levels, we conclude that the yield of $BaOCH_3 + H$ is $>90\%$ from ground state and electronically excited Ba, in spite of the fact that ΔH is much more favorable for $BaOH + CH_3$ production, and formation of $BaO + CH_4$ is highly exoergic even from the ground state (Table II). The observed Ba^+ signal near 25° (Fig. 14) primarily results from fragmentation of $BaOCH_3$ in the electron bombardment ionizer, and the small angle Ba^+ at $\theta < 15°$ results from nonreactive elastic and inelastic scattering.

At the lowest collision energy studied (15 kcal/mole), ground state Ba atoms were found to react weakly, but only to form $BaOCH_3 + H$ (Fig. 14, Top Figure). Spurred by our earlier observation of $Ba(^1S) + H_2O \rightarrow BaO + H_2$, a search was undertaken for $Ba + CH_3OH \rightarrow BaO + CH_4$, but we failed to see any evidence for this channel from ground state or electronically excited Ba up to a collision energy of 30 kcal/mole. Owing to the reaction exoergicities and heavier recoil partners, some BaO or BaOH should have been observed outside of the angular range for $BaOCH_3$ if their formation accounted for more than 10% of the total reaction cross section. Angular distributions for $BaOCH_3$ from $Ba + CH_3OH$ and $Ba + CH_3OD$ at $E_{coll}=30$ kcal/mole are shown in Fig. 15. A comparison of Figs. 14 and 15 indicates that the reactivity of $Ba(^1S)$ does increase with increasing the collision energy from 15 to 30 kcal/mole. However, electronic excitation is far more effective in enhancing the chemical reaction. The deuterium isotope effect observed in the methanol reactions was similar to that seen for water, with CH_3OH having a reaction cross section approximately twice that of CH_3OD at the same collision energy.

D. Collisions of Ba(^{1}S), (^{1}D) with CH_3OCH_3.

No chemical reaction was observed in collisions of ground state or electronically excited Ba atoms with dimethyl ether (CH_3OCH_3) at collision energies up to 30 kcal/mole despite long averaging for BaO^+, $BaOH^+$, and $BaOCH_3^+$. The observed Ba^+ signal was attributed to elastic and nonreactive inelastic collisions.

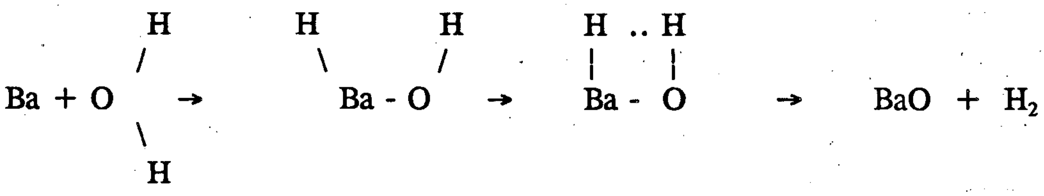
IV. DISCUSSION

A. Reactions with H_2O.

The most striking observation in the Ba + H_2O study was the strong dependence of the product identity on initial electronic state of the reactant Ba atom. At collision energies below the 13 kcal/mole endoergicity for Ba(^{1}S) + H_2O → BaOH + H, the ground state reaction led to formation of BaO + H_2. This channel was weak at 12 kcal/mole, but increased with increasing collision energy. Although the BaOH + H channel did appear at collision energies above its endoergicity, it remained weaker than the BaO + H_2 channel even at 30 kcal/mole, a collision energy approaching the Ba(^{1}D) excitation energy ($\sim$32.6 kcal/mole). Electronically excited Ba(^{1}D), on the other hand, reacted with water to form BaOH + H with a branching ratio of 0.90 - 1.0 at all collision energies.

There are two explanations for the observed product specificity. One possibility is that Ba(^{1}D) + H_2O is correlated to BaOH + H through an excited state surface, whereas ground state Ba(^{1}S) + H_2O correlates to BaO + H_2. Alternatively, the effect might be due to energetics alone: electronic excitation may simply drive the endoergic BaOH + H channel. In this case, the collision of Ba(^{1}D) might be viewed as collisional quenching of electronic excitation during the encounter of the reagents with the vibrationally hot intermediate decaying to form BaOH + H on the ground electronic surface. The large excess energy above the endoergicity provided by the initial electronic excitation would favor simple bond rupture from a reaction intermediate leading to BaOH + H rather than formation of BaO + H_2 through a concerted mechanism having a much smaller pre-exponential factor in the rate constant. However, we believe that this possibility is unlikely in light of the experimental observations. Although BaOH + H was observed weakly from ground state Ba + H_2O at collision energies above its endoergicity, the BaO + H_2 cross section increased and remained dominant with increasing collision energy. If the lack of BaOH + H from the ground state reaction was only due to the endoergicity, then as the collision energy was raised substantially, we should have seen a shift towards the endoergic radical channel. Since the BaOH + H channel remained much weaker than BaO + H_2 even at collision energies near the Ba(^{1}D) excitation energy, arguments based on energetic considerations alone cannot adequately explain the change in product identity upon electronic excitation.

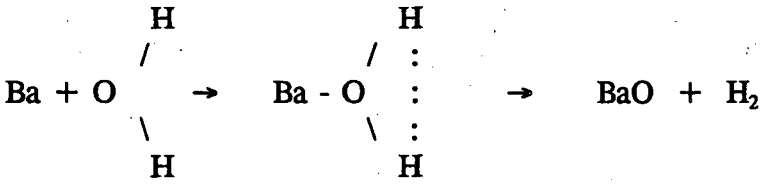
We now return to the possibility that differing intrinsic features of the ground and excited state surfaces lead to strong preference for different chemical products. Two possible mechanisms can be envisioned for the reaction Ba(^{1}S) + H_2O → BaO + H_2. The reaction could be initiated by insertion of Ba(^{1}S) into one of the OH bonds in H_2O. Although HBaOH is expected to be linear or slightly bent, a very low energy bending potential has been calculated for the analogous molecules involving lighter alkaline earth atoms.[7,9] This low energy bending mode could facilitate formation of BaO + H_2 via a four center transition state:



The electron configuration for the ground state Ba(^{1}S) atom is $6s^2$ - the initial repulsion between this "closed shell" atom and water, as well as the need for sp or sd hybridization for formation of two bonds in the insertion intermediate will likely lead to a substantial potential energy barrier in the entrance channel for this mechanism.

Additionally, a substantial potential energy barrier at the 4-center transition state is expected for H_2 elimination from HBaOH since it requires substantial electronic rearrangement. On the other hand, simple rupture of the very weak Ba-H bond in H-Ba-OH should readily lead to BaOH + H with no barrier in excess of the Ba-H bond energy. Consequently, an insertion mechanism will most likely to lead to BaOH + H, rather than BaO + H_2. Since BaO + H_2 was the dominant product, insertion does not seem to play an important role in the ground state Ba(^{1}S) reaction.

Our experimental observations, especially the large exit potential energy barrier leading to a high BaO + H_2 product translational energy release, indicates that a concerted mechanism is involved in the reaction Ba(^{1}S) + H_2O → BaO + H_2 with abstraction of the central O atom from H_2O and simultaneous formation of molecular H_2:



$$\mathrm{Ba} + \mathrm{O}\!\begin{array}{l}/\,\mathrm{H}\\ \backslash\,\mathrm{H}\end{array} \rightarrow \mathrm{Ba - O}\!\begin{array}{l}/\,\mathrm{H}\,:\\ \backslash\,\mathrm{H}\,:\end{array} \rightarrow \mathrm{BaO} + \mathrm{H_2}$$

It is well known that concerted reactions are controlled by symmetry constraints.[35] Symmetry arguments for Ba + H_2O have been discussed previously by Douglas and coworkers.[8] We first consider coplanar trajectories in C_{2v} and C_s symmetry. Approach of Ba(^{1}S) toward H_2O along the C_{2v} (C_s) axis generates a surface of $^1A_1$ ($^1A'$) symmetry. Similarly, the asymptotic molecular product states with atoms in the same geometry as the reactants generate surfaces of $^1A_1$ ($^1A'$) symmetry. However, these states do not correlate diabatically, since the ground state of BaO is best represented as $Ba^{2+}O^{2-}$[36]; this product correlates to very high-lying charge transfer states of the reactants. The neutral reactant surface correlates to high-lying non-ionic product states. The avoided crossing of these two $^1A_1$ ($^1A'$) surfaces generates a substantial potential energy barrier for the concerted reaction-- the presence of this barrier leads to the small reaction cross section and rather large translational energy release observed for the stable closed shell BaO + H_2 products.

The covalent-ionic curve crossing radius (R_x) is often applied to reactions of alkali and alkaline earth atoms with oxygen and halogen containing molecules.[5a,18-20] In units of Angstroms, the crossing point of the ionic and covalent curves is given by:

$$R_x = \frac{14.4}{IP(Ba) - EA(M)}\ (\mathring{A}),$$

where IP(Ba) is the ionization potential of Ba, which is 5.2 eV for Ba(^{1}S) and 4.0 eV for Ba(^{1}D)[18,19]. EA(M) is the 'effective' electron affinity of the molecule (eV), often taken to be somewhere between the vertical and adiabatic electron affinities. All available data indicates that the adiabatic EA(H_2O) $\leq$ -2 eV[37]; electron scattering experiments indicate that the vertical EA is near -6 eV.[38] For Ba(^{1}S), electron transfer requires $R_{coll} \leq 2$ Å. Since this distance is of the same order as a bond length, it is clear that a mechanism involving long range electron transfer (harpooning), followed by decay of an ionic intermediate is inappropriate. However, the reaction products (BaO, BaOH) are highly ionic, and so full electron transfer must ultimately occur in the reaction. Successful formation of BaO + H_2 requires small impact parameter collisions. This is due to: 1) the very small Ba-O approach distance required to initiate transfer of the first valence electron from ground state Ba to water; and 2) the need to overcome the mechanical barrier associated with sufficient symmetric bending of the water molecule to facilitate concerted formation of BaO + H_2. The molecular orbitals for H_2O are:[16]

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2;\ {}^1A_1.$$

The lowest unoccupied orbital is $4a_1$, which is antibonding with respect to the two O-H bonds and bonding with respect to H-H. Small impact parameter collisions can initiate the first electron transfer into the $4a_1$ orbital at a Ba-O distance of approximately 2Å. This is essentially the bond length of BaO.[36] Electron transfer into the $4a_1$ orbital at such close range with the Ba atom near the symmetry axis of H_2O will favor symmetric bending of the water molecule and formation of BaO + H_2. The need for a small impact parameter collision to initiate the first electron transfer is consistent with the rather small reaction cross section seen for the ground state reaction. The second electron transfer required for formation of ground state $Ba^{2+}O^{2-}$ will occur readily as the H_2 departs.

It is expected that approach of Ba towards the oxygen atom in the plane of the water molecule near the C_{2v} axis will most effectively lead to BaO + H_2 since this geometry will enhance symmetric bending. Since the water molecules are randomly oriented however, most of the collisions involve attack of the Ba atom along trajectories that are not in the plane of the water molecule. In this case, the symmetry is C_1 and all geometries lead to surfaces of A symmetry. However, a substantial barrier is still expected for the same reason as in C_s and C_{2v} symmetries, and small impact parameter collisions will still be required for formation of BaO + H_2.

Although the light H_2 recoil partner results in compression of the BaO angular distribution, it is either forward-backward symmetric or nearly so. Such forward-backward symmetry is often taken to be evidence for the existence of a collision intermediate with a lifetime exceeding one rotational period (1 psec)[5a,39-41]. In most cases, such intermediates are associated with deep chemical wells on the potential energy surface. In the present case, the Ba-H_2O interaction is not much stronger than a typical Van der Waals interaction with a binding energy not greater than 10 kcal/mole[7]. It might thus appear surprising that a large fraction of the colliding partners interact long enough to undergo at least one half of a rotation before product formation. However, a concerted three-center elimination of H_2 requires considerable deformation of water with substantial electronic rearrangement. This necessitates a closely coupled collision with the Ba reaching the repulsive inner wall of the Ba-H_2O interaction potential before the initiation of electron transfer. Although the Ba-H_2O interaction is not very strong, there likely exists entrance and exit potential energy barriers which lead to an effectively deeper well. Also, in the absence of significant steric effects, the CM angular distribution will be broad since non-coplanar trajectories are statistically dominant.

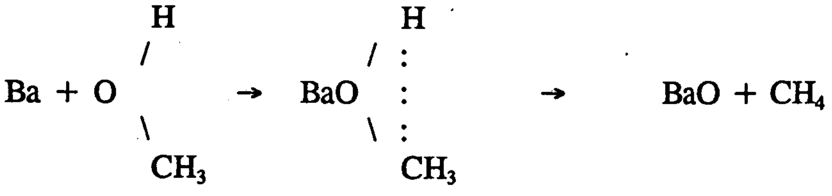
Symmetry arguments may be made for interaction of Ba(^1D) + H_2O. However, the situation is rather more complicated. In C_{2v}, the following surfaces are generated for the reacting pair: $^1A_1$, $^1A_1$, $^1A_2$, $^1B_1$, $^1B_2$. According to Douglas et al[8], the lowest lying states are likely to be $^1A_1$ and $^1A_2$, the former state having the same symmetry as the ground state molecular products BaO + H_2. But again, a substantial barrier is expected to be generated by the crossing of the excited state reactant and ground (or excited) state product surfaces; the existence of a barrier for formation of BaO + H_2 (or BaO* + H_2) on the excited state surface is consistent with the lack of enhancement of BaO formation upon electronic excitation in both our experiment and in that of Alcaraz, et. al.[6]

We now turn to the mechanisms expected for formation of the radical products BaOH + H. Our observation that this channel is promoted by electronic excitation rather than collision energy is good evidence that the reaction occurs much more readily on an excited state surface. This possibility was first suggested by Douglas and Margrave[7] in discussion of the matrix reactions of alkaline earth atoms with water. In their experiment, irradiation of the Ba-OH_2 adduct, resulting from co-condensation of Ba + H_2O in a matrix, near the Ba atomic resonance facilitated "insertion" of the metal atom into the OH bond with subsequent formation of BaOH. The question naturally arises as to whether the gas phase reaction of electronically excited Ba is mediated by an insertion mechanism, and if so, what is the nature of the motion of the atoms during the process? The results of the alcohol experiments are very helpful in our understanding of the radical channel. We turn to those results before returning to a discussion of the $Ba(^1D) + H_2O$ reaction mechanism.

B. Reaction with CH_3OH

The reaction of ground state and electronically excited Ba with CH_3OH shows remarkable preference for formation of $BaOCH_3 + H$. The other product channels $BaOH + CH_3$ and $BaO + CH_4$ either do not exist, or are so weak as to be below the sensitivity of our experiment. We conclude that the hydrogen atom elimination channel accounts for between 90 and 100% of all reactive encounters in the case of ground- and excited state $Ba + CH_3OH$.

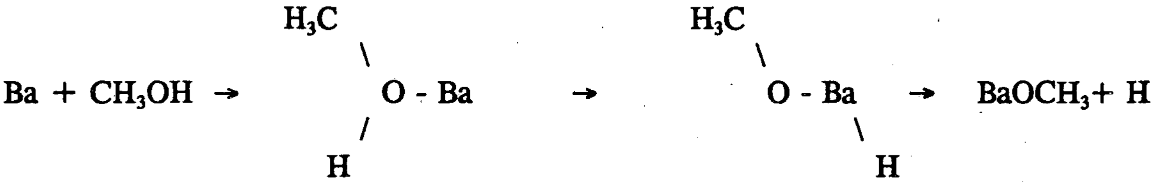
Our finding that the $BaO + CH_4$ channel was negligible from $Ba(^1S$ or $^1D) +$ methanol, whereas $BaO + H_2$ did result from collision of $Ba(^1S)$ with water, is not surprising. Formation of $BaO + CH_4$ would probably have to be of a concerted nature since insertion would likely favor radical production, as outlined earlier for the $Ba + H_2O$ reaction. Such a concerted reaction is less likely in the case for methanol than water, since it requires attack by the H atom from -OH on an sp^3 hybridized carbon atom via a three-center transition state:



$$\mathrm{Ba} + \mathrm{O}\begin{matrix}\mathrm{H}\\ / \\ \\ \backslash \\ \mathrm{CH_3}\end{matrix} \rightarrow \mathrm{BaO}\begin{matrix}\mathrm{H}\\ /\,: \\ : \\ \backslash\,: \\ \mathrm{CH_3}\end{matrix} \rightarrow \mathrm{BaO} + \mathrm{CH_4}$$

The potential energy barrier for this process will be high, since at the transition state the strong $O\text{-}CH_3$ bond has to be nearly broken to facilitate bonding between the tetravalent carbon and the attacking H-atom. However, for trivalent group IIIA elements such as Sc and Y, formation of MO + CH_4 was observed by Liu and Parson[13] under single collision conditions. They were unable to observe formation of the metal hydroxides-- either they were not formed or their LIF spectrum was outside the wavelength range studied.

Upon electronic excitation, the large increase in formation of $BaOCH_3$+ H from methanol is analogous to the increase in BaOH + H from water. The most obvious explanation for the formation of $BaOCH_3$ + H rather than BaOH + CH_3 at all collision energies is that the reaction is dominated by internal migration of the H atom from O to Ba within the Ba-O bonded intermediate:



$$\mathrm{Ba} + \mathrm{CH_3OH} \rightarrow \begin{array}{l} \mathrm{H_3C} \\ \quad\backslash \\ \quad\ \mathrm{O - Ba} \\ \quad / \\ \ \mathrm{H} \end{array} \rightarrow \begin{array}{l} \mathrm{H_3C} \\ \quad\backslash \\ \quad\ \mathrm{O - Ba} \\ \qquad\quad\backslash \\ \qquad\quad\mathrm{H} \end{array} \rightarrow \mathrm{BaOCH_3} + \mathrm{H}$$

It appears that a mechanism involving H-atom migration will involve substantially smaller potential energy barriers than alternative mechanisms leading to $HOBaCH_3$; ie. CH_3 migration or insertion of Ba into the HO-CH_3 bond. This appears to be due to the spherical shape of the H atom 1s orbital: good orbital overlap may be maintained with the O and Ba atoms simultaneously during the H-atom migration process. This situation contrasts the directional nature of the sp^3-hybridized methyl group which necessitates nearly complete rupture of the O-CH_3 bond prior to formation of $HOBaCH_3$. This is somewhat analogous to H_3C-H and H-H bond activation by transition metals such as platinum and palladium.[42,43] In those systems, the potential energy barrier was found to be very small for insertion into H_2. However, a substantial barrier exists for formation of H-M-CH_3 and it was even larger for formation of CH_3-M-CH_3. This behavior was also rationalized in terms of the ability for the spherical H-atom to participate in multicenter bonding.[42,43] Our finding that dimethyl ether is unreactive under single collision conditions also supports our hypothesis that H-atom migration is the dominant mechanism in the radical channels.

This work is the first direct evidence of a metal methoxide in the gas phase under conditions known to involve only a single collision.[44] As far as we know, only one previous M + CH_3OH reaction has been studied in rare gas matrices[14]. Codeposition of Fe + CH_3OH led to formation of an $Fe(CH_3OH)$ adduct with the iron atom bonded to the oxygen atom in methanol. Irradiation of the adduct at $400nm < \lambda < 500nm$ resulted in formation of $HFeOCH_3$ whereas irradiation at $280nm < \lambda < 360nm$ led to $HOFeCH_3$. In other words, a higher photon energy was required for 'insertion' into the C-O bond. Although the original authors did not draw any conclusions about the reaction mechanism, we suggest that H-atom migration is likely to be the lowest energy process in the iron system. It would not be surprising if this was a general feature in reactions of metal and main group atoms with H-atom containing compounds.

C. The effect of deuterium substitution and collision energy on $Ba(^1D)$ reactions.

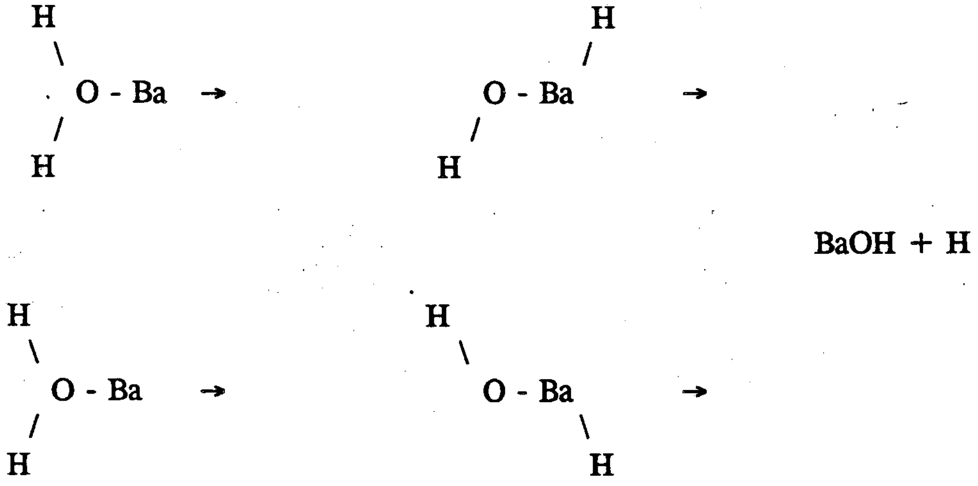
Comparison of BaOH to BaOD signal levels indicated that $Ba(^1D) + D_2O$ was 2.0 ± 0.4 times less reactive than the H_2O reaction. This ratio was found to remain constant to within the stated uncertainty as the collision energy was varied from 12-30 kcal/mole. The ratio between reactive and nonreactive scattering of $Ba(^1D)$ also remained constant to within the experimental uncertainties over this range.

The observed isotope effect observed here is not large by comparison to low temperature experiments where the "semiclassical effect" (i.e. without the occurrence of tunneling) is commonly in the range of 3 to 5.[45,46] Experimental observations[15] and theoretical calculations[47] on the Si + H_2O system have indicated that reaction in rare gas matrices occurs with H-atom migration by quantum mechanical tunneling. Co-

condensation of Si + H_2O led to rapid formation of HSiOH, whereas visible irradiation of Si + D_2O was required for formation of DSiOD. If the barrier for the rate limiting step in the reaction of Ba(^{1}D) + water was large, it might be possible to observe a substantially increased isotope effect with decreasing collision energy if tunneling were important. We have found that the isotope effect remains approximately constant over our experimentally obtainable collision energies. Thus, at these collision energies, quantum mechanical tunneling is not a dominant factor in the deuterium isotope effect that we observe.

D) Product Angular Distributions for the Radical Channels

Although the BaOH and $BaOCH_3$ angular distributions are rather compressed due to their light H or D atom recoil partner, the best fit of the angular and TOF data was found to have a forward backward symmetric center-of-mass angular distribution (to within the sensitivity of the fit). The usual explanation for this angular distribution is the existence of an intermediate HBaOR species with a lifetime exceeding one rotational period. It should be noted, however, that for Ba + H_2O the symmetric product angular distribution might also be attributable to the migration process, which by its very nature is likely to reflect the symmetry of the water molecule:



Since both H atoms are equally likely to migrate within the Ba-O bonded complex, a forward-backward symmetric angular distribution will result even if HBaOH has a lifetime of less than one rotational period.

E. The role of the excited state in H-atom migration.

As was pointed out by Douglas and coworkers[7], HBaOH can be treated by analogy with the HAB molecule, with B = OH. We discuss the particular case of water here; a parallel argument should apply to the reaction of methanol since substitution of H by CH_3 should have little effect on the electronic structure of the Ba core. For HBaOH, the ground state configuration is $^1A'$ $(1a'')^2(6a')^2$, with an excited state $(1a'')^2(6a')(7a')$, also of $^1A'$ symmetry. In the case of the heavier alkaline earth atoms, the ground state 6s-a' orbital of the metal atom probably lies higher than the unoccupied $4a_1$-a' orbital of water.[7] The ground state configuration of Ba+ H_2O in C_s symmetry correlates diabatically with an excited state of HBaOH, whereas the ionic state $Ba^+H_2O^-$ (or possibly $Ba^{2+}H_2O^{2-}$) correlates to the HBaOH ground state. An avoided crossing of these two curves generates a substantial potential energy barrier for the ground state insertion process. We observed the onset of $Ba(^1S) + H_2O \rightarrow BaOH + H$ at collision energies above 13 kcal/mole. This might indicate that the barrier for H atom migration on the ground state surface does not lie much above the reaction endoergicity. Alternatively, the ground state reaction $Ba(^1S) + H_2O \rightarrow BaOH + H$ might result from a direct abstraction mechanism rather than from H-atom migration. In any case, it is clear that in the $Ba(^1S) + H_2O$ reaction, the potential energy barrier for formation of BaOH + H is higher than that for formation of BaO + H_2, which was observed to occur even at the lowest collision energy (12 kcal/mole).

Our observation that electronic excitation is much more effective than collision energy in enhancing the formation of BaOH + H is good evidence that the barrier for formation of H-Ba-OH by H-atom migration is low on the excited state potential energy surface. There has been considerable theoretical work on the activation of covalent bonds by transition metals.[42,43] The reaction M + H-R → H-M-R (R=alkyl) is most favorable for those metal atoms with ground state electronic configurations favorable to sd hybridization, since this readily facilitates formation of two covalent bonds. Bond activation is also favored by electronic configurations which minimize long-range electronic repulsion. In the present case, the 6s5d(^{1}D) configuration has the "singlet diradical" character favorable for formation of H-Ba-OR. This is clearly not the case for Ba 6s^2(^{1}S)-- the closed shell configuration will lead to a weak interaction with H_2O, and the Ba 6s^2(^{1}S) promotion energy is substantial.

The main difference between Ba + H-OR → H-Ba-OR and transition metal reactions such as M + H-R → H-M-R (R=H,CH_3) is that the Ba intermediate has substantial ionic character, whereas the transition metal intermediate is primarily covalently bonded. Since the Ba-water collision timescale is long compared with the vibrational frequency of water, some additional insight into the reaction dynamics may be gained by considering how the transition from the covalent to ionic surface (which must ultimately occur for formation of Ba^+OR^-+H) is affected by vibrational motion. Vertical electron transfer to H_2O (especially from Ba(^{1}S)) is thermodynamically unfavorable, with the lowest vertical electron attachment resonance at 6.4 eV.[38] Interestingly, the literature reveals one experimental observation[37] of H_2O^- in ion cyclotron resonance experiments. It has been determined that this molecule, probably best described[37] as OH^-...H, is stable and lies about 2.1 eV above $H_2O + e^-$. This is below the energy of separated OH^-+H (3.28 eV)[21]. This suggests that electron transfer from Ba to H_2O will be most favorable for collision geometries resulting in asymmetric stretching of the water molecule. For those molecules, the "effective electron affinity" will be near -2.1 eV, and the curve crossing radius for Ba(^{1}D) is ~2.5 Å. Note that the crossing radius based on eq. 1 for Ba(^{1}S) will still be below 2 Å even with this "most favorable" value of -2.1 eV for the EA of H_2O. This difference between the curve crossing radii in these two cases will play a role in determining the identity of the final product. In the case of electronically excited Ba(^{1}D), transfer of the more easily ionized d-electron to the symmetry-allowed orbitals in H_2O will preferentially occur at $\sim$2.5 Å in those collisions leading to asymmetric stretching of the water molecule. The weakly bound H atom in the newly formed $Ba^+H_2O^-$ molecule will readily migrate away from the oxygen *before* the Ba can approach to within the close range required for 3-center H_2 elimination and second electron transfer required for formation of BaO. In the case of ground state Ba(^{1}S) + H_2O, however, chemical interaction and electron transfer is only possible in the case of small impact parameter collisions. This favors formation of BaO + H_2 by a concerted 3 center mechanism.

V. CONCLUSIONS

The reaction of Ba with water illustrates that under appropriate conditions, it is indeed possible to alter the chemical outcome of a neutral reaction by proper selection of the initial electronic state of a reactant. The observation that reaction of ground state Ba(^{1}S) results in BaO + H_2, whereas excited Ba(^{1}D) leads to BaOH + H, is a consequence of the different features on the ground and excited state potential energy surfaces. Due to the existence of a large mechanical barrier and the need for close approach of the reactants, the BaO + H_2 molecular products are favored by ground state barium atoms. For only in the ground state can Ba approach to within $\sim$2 Å before the reaction is initiated. Concerted molecular rearrangement with second electron transfer results in production of BaO + H_2. Formation of radical products, on the other hand, results from H- atom migration. Initial excitation of one valence electron to the 5d-orbital strongly promotes this process. Two main factors seem to be responsible. The "singlet diradical" character of the 6s5d configuration favors the formation of two bonds in H-Ba-OR. Electronic excitation also leads to electron transfer at slightly longer distance, leading to H-atom migration and formation of HBaOR. The rapid escape of one H atom precludes three-center H_2 elimination. The observation of only $BaOCH_3$ from reaction with methanol, and lack of reaction of dimethyl ether has provided additional evidence for the importance of H-atom migration in the radical channels.

VI. ACKNOWLEDGEMENTS

The authors thank Dr. M.H. Covinsky for useful discussions. HFD acknowledges NSERC (Canada) for a 1967 Science and Engineering Fellowship, and AGS thanks the NSF for a Graduate Fellowship. 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.

VII. REFERENCES

1. (a) P.B. Armentrout, Science 251, 175, (1991)., (b) P.B. Armentrout, Ann. Rev. Phys. Chem., 41, 313 (1990). (c) J.L. Elkind and P.B. Armentrout, J. Chem. Phys., 86(4), 1868 (1987). (d) R. Georgiadis and P.B. Armentrout, J. Phys. Chem. 92, 7067 (1988).
2. (a) H. Yamazaki and R.J. Cvetanovic, J. Chem. Phys., 41, 3703 (1964). (b) G. Paraskevopoulos and R.J. Cvetanovic, J. Chem. Phys., 50, 590 (1969); 52, 5821 (1970). c) C.L. Lin and W.B. DeMore, J. Phys. Chem. 76, 1375 (1972). d) R.J. Buss, P. Casavecchia, T.Hirooka, S.J. Sibener, and Y.T. Lee, J. Chem. Phys., 73, 6351 (1980).
3. (a) P.S. Weiss, J.M. Mestdagh, M.H. Covinsky, B.A. Balko, and Y.T. Lee, Chem. Phys., 126, 93, (1988); (b) M.F. Vernon, H. Schmidt, P.S. Weiss, M.H. Covinsky, and Y.T. Lee, J. Chem. Phys., 84(10) 5580, 1986; (c) H. Schmidt, P.S. Weiss, J.M. Mestdagh, M.H. Covinsky, and Y.T. Lee, Chem. Phys. Lett.

118, 6, 539 (1985); (d) J.M. Mestdagh, B.A. Balko, M.H. Covinsky, P.S. Weiss, M.F. Vernon, H. Schmidt, and Y.T. Lee, Faraday Disc., 84, 145 (1987). e) P.S. Weiss, M.H. Covinsky, H. Schmidt, B.A. Balko, Y.T. Lee, and J. M. Mestdagh, Z. Phys. D., 10, 227, (1988).

4. a) Y.T. Lee, Science 236, 793 (1987). b) Y.T. Lee, in *Atomic and Molecular Beam Methods, Vol. 1*, G. Scoles, ed. Oxford University Press, New York, 1988.

5. (a) H.F. Davis, A.G. Suits, and Y.T. Lee, J. Chem. Phys., 96(9), 6710, (1992). (b) H.F. Davis, A.G. Suits, H. Hou, and Y.T. Lee, Ber. Bunsenges. Phys. Chem., 94, 1193 (1990). (c) H.F. Davis, A.G. Suits, and Y.T. Lee, in *Gas Phase Metal Reactions,* A. Fontijn, ed., Elsevier, Amsterdam, 1992. (d) A.G. Suits, H. Hou, H.F. Davis, and Y.T. Lee, J. Chem. Phys., 95, 8207 (1992). (e) A.G. Suits, H. Hou, H.F. Davis, and Y.T. Lee, J. M. Mestdagh, J. Chem. Phys., 95, 8178 (1991). (f) A.G. Suits, H. Hou, H.F. Davis, and Y.T. Lee, J. Chem. Phys., 96, 2777 (1992). (g) A.G. Suits, H. Hou, and Y.T. Lee, J. Phys. Chem., 94, 5672, (1990).

6. a) C. Alcaraz, J.M. Mestdagh, P. Meyadier, P. de Pujo, J.P. Visticot, A. Binet, and J. Cuvellier, Chem. Phys. Lett. 156, 191 (1989) . (b) P. de Pujo, O. Sublemontier, J.P. Visticot, J. Berlande, J. Cuvellier, C. Alcaraz, J.-M. Mestdagh, P. Meynadier, J. Chem. Phys., submitted for publication.

7. a) M.A. Douglas, R.H. Hauge and J.L. Margrave, High Temp. Sci., 17, 201 (1984). b) J.W. Kauffman, R.H. Hauge, J.L. Margrave, High Temp. Sci., 18, 97, (1984). c) R.H. Hauge, J.W. Kauffman, and J.L. Margrave, J. Am. Chem. Soc., 102, 6005 (1980), d) P.F. Meier, R. H. Hauge, and J.L. Margrave, J. Am. Chem. Soc., 100, 2108 (1978).

8. J. W. Kauffman, R.H. Hauge, and J.L. Margrave, (a) J. Phys. Chem, 89, 3541,(1985)., (b) J. Phys., Chem, 89, 3547 (1985).

9. L. A. Curtiss, D.J. Frurip, Chem. Phys. Lett., 75,1,69(1980).

10. S. Sakai, K.D. Jordan, Chem. Phys. Lett., 130, 1,2, 103 (1986).

11. J.L. Gole, S.A. Pace, J. Phys. Chem, 85, 2651 (1981).

12. S. Sakai, K.D. Jordan, J. Phys. Chem, 87, 2293 (1983).

13. K. Liu, J.M. Parson, J. Chem. Phys., 68(4) 1794 (1978)

14. M. Park, R. H. Hauge, Z.H. Kafafi, and J. L. Margrave, J. Chem. Soc. Chem. Comm., 1570 (1985).

15. Z.K. Ismail, R.H. Hauge, L. Fredin, J.W. Kauffman, and J.L. Margrave, J. Chem. Phys., 77(4), 1617, (1982).

16. G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. III, Electronic Spectra and Electronic Structure of Polyatomic Molecules.* Van Nostrand Reinhold, Princeton, New Jersey, 1966.

17. M.B. Robin, *Higer Excited States of Polyatomic Molecules, Vol III.*, Academic Press, New York, 1985, pg. 165.

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

19. Magee, J. Chem. Phys., 8, 687, (1940).

20. a) Ronald R. Herm, in: *Alkali Halide Vapors,* edited by. P. Davidovits and D.L. McFadden (Academic Press, 1979) p. 189.

    b) R.D. Levine and R.B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity,* (Oxford University, New York, 1987).

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

22. For a discussion of various detection methods, see G. Scoles, ed. *Atomic and Molecular Beam Methods, Vol. 1* Oxford University Press, New York, 1988.

23. a) C.R.Brazier, L.C. Ellingboe, S. Kinsey-Nielsen, and P.F. Bernath, J. Am. Chem. Soc., 108, 2126 (1986). b) C. R.Brazier, L.C. Ellingboe, S. Kinsey-Nielsen, and P.F. Bernath, J. Am. Chem. Soc., 108, 2126 (1986). c) C.R. Brazier, P.F. Bernath, S. Kinsey-Nielsen, L.C. Ellingboe, J. Chem. Phys., 82, 1043 (1985). d) S. Kinsey-Nielsen, C.R. Brazier, P.F. Bernath, J. Chem. Phys., 84, 698 (1986). e) P.F. Bernath, S. Kinsey-Nielsen, Chem. Phys. Lett., 105,

663, (1984).

24. Y.T. Lee, J.D. McDonald, P.R. LeBreton, and D.R. Herschbach, Rev. Sci. Instrum., 40, 1402 (1969).
25. H.F. Davis, A.G. Suits, M.H. Covinsky, and Y.T. Lee, in preparation.
26. R.C. Weast, editor, *CRC Handbook of Chemistry and Physics*, CRC, Boca Raton, Florida, 1987.
27. The electronic structures of BaOH and $BaOCH_3$ are analogous to the alkaline earth halides: For a discussion of the insensitivity of fragmentation of the alkaline earth halides with internal excitation upon electron impact see Ref. 28.
28. C.A. Mims, S-M Lin, R.R. Herm, J. Chem. Phys. 58(5), 1983 (1973).
29. T.P. Parr, A. Freedman, R.Behrens, Jr., R.R. Herm, J. Chem. Phys, 72(9), 5163 (1980).
30. R.R. Herm, S.M. Lin, C.A. Mims, J. Phys. Chem. 77(25),2931 (1973).
31. C. Batalli-Cosmovici and K.W. Michel, Chem. Phys. Lett, 11, 245 (1971).
32. G. Comsa, R. David, B.J. Schumacher, Rev. Sci. Instrum., 52(6) 789 (1981).
33. (a) S. Niggli and M.C.E. Huber, Phys. Rev. A, 35, 7, 2908, (1987); (b) A.F. Bernhardt, Appl. Phys., 9,19 (1976).
34. R.S. Newbury, G.W. Barton, A.W. Searcy, J. Chem. Phys., 48(2), 793 (1968).
35. R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Academic Press, New York (1969)
36. J.G. Pruett, R.N. Zare, J. Chem. Phys. 62, 2050,(1975)
37. L.J. deKoning, N.M.M. Nibbering, J. Am. Chem. Soc., 106, 7971, (1984).
38. C.E. Melton, J. Chem. Phys., 57,(10),4218,(1972).
39. Miller, S.A. Safron, and D.R. Herschbach, Discuss. Faraday Soc. 44, 108 (1967).
40. W.B. Miller, Thesis, Harvard University, (1969).
41. a) D.O. Ham, J.L. Kinsey and F.S. Klein, Disc. Faraday. Soc. 44, 174 (1967). b) D.O. Ham, J.L. Kinsey, J. Chem. Phys., 48(2), 939 (1968). c) D.O. Ham and

J.L. Kinsey, J. Chem. Phys., 53(1), 285 (1970).

42. (a) J.J. Low, W.A. Goddard III, J. Am. Chem. Soc., 106, 8321, (1984). (b) J.J. Low, W.A. Goddard III, J. Am. Chem. Soc., 106, 6928, (1984) c) J.J. Low, W.A. Goddard, Organmometallics, 5, 609 (1986). d) J.J. Low, W.A. Goddard III, J. Am. Chem. Soc., 108, 6115 (1986).

43. a) M. Blomberg, U. Brandemark, P. Siegbahn, J. Am. Chem.Soc., 105, 5557 (1983). b) M. Blomberg, U. Brandemark, L. Pettersson, P. Siegbahn, P. Int. J. Quantum Chem., 23, 855 (1983). c) M.R.A. Blomberg, P.E.M. Siegbahn and M. Svensson, J. Phys. Chem., 95, 4313 (1991).

44. Bernath and coworkers (Ref 23) postulated that the large increase in signal with electronic excitation resulted from the onset of a direct mechanism.

45. W.D. Forst, *Theory of Unimolecular Reactions* , Academic, New York, 1973.

46. S.E. Barlow, J.M. Van Doren, C.H. DePuy, V.M. BierBaum, I. Dotan, E.E. Ferguson, N.G. Adams, D. Smith, B.R. Rowe, J.B. Marquette, G.Depeyrat, M. Durup-Ferguson, J. Chem. Phys, 85(7) 3851,(1986).

47. A. Tachibana, M. Koizumi, H. Teramae, and T. Yamabe, J. Am. Chem. Soc., 109, 1383,(1987).

Table I. **Thermodynamics of the Ba + H_2O System**[6,7,18]

Reaction		ΔH(kcal/mole)
Ba(^1S) + H_2O	$\rightarrow$ Ba-OH_2	~ -5
	$\rightarrow$ HBaOH	~-30
	$\rightarrow$ BaOH(X) + H	+13
	$\rightarrow$ BaO(X) + H_2	-14.9
Ba(^1D) + H_2O	$\rightarrow$ BaOH(X) + H	-19.8
	$\rightarrow$ BaO(X) + H_2	-47.3
	$\rightarrow$ BaO(A,A') + H_2	~ 0

Table II. **Thermodynamics of the Ba + CH_3OH System**[6,7,18]

Reaction		ΔH(kcal/mole)
Ba(^1S) + CH_3OH	$\rightarrow$ Ba-OH(CH_3)	~ -5
	$\rightarrow$ $HBaOCH_3$	~ -30
	$\rightarrow$ $HOBaCH_3$	~ -30
	$\rightarrow$ BaOH(X) + CH_3	-15.0
	$\rightarrow$ BaO(X) + CH_4	-42.7
	$\rightarrow$ $BaOCH_3$(X) + H	+16.8
Ba(^1D) + CH_3OH	$\rightarrow$ BaOH(X) + CH_3	-47.6
	$\rightarrow$ BaO(X) + CH_4	-75.3
	$\rightarrow$ $BaOCH_3$(X) + H	-15.8

Table III. Thermodynamics of the Ba + CH_3OCH_3 System[6,7,18]

Reaction		ΔH(kcal/mole)
$Ba(^1S) + CH_3OCH_3$	$\rightarrow BaOCH_3(X) + CH_3$	-6.6
	$\rightarrow BaO(X) + C_2H_6$	-49.2

VIII. LIST OF FIGURES

Fig 1. Newton Diagram for Ba(^{1}S) + H_2O at E_{coll}=12 kcal/mole. Inner circle shows maximum center of mass velocities for BaO from Ba + H_2O → BaO + H_2. Larger circle shows Ba velocity from elastic scattering from H_2O.

Fig 2. Ba^{18}O time-of-flight spectra from Ba(^{1}S) + $H_2{}^{18}O$ → Ba^{18}O + H_2 at E_{coll}= 12kcal/mole. ooooo- experimental data. —— Fit to data using P(E) and T(θ) from figure 4.

Fig 3. Ba time-of-flight spectra from Ba(^{1}S) + H_2O collisions at a collision energy of 12 kcal/mole. The fastest and slowest peaks are due to the forward and backward components of the Newton circle. The small component near 180μs is the contribution from fragmentation of BaO to Ba$^+$ in the electron impact ionizer.

Fig 4. Best fit product translational energy distribution (P(E)) and center of mass angular distribution (T(θ)) for BaO + H_2 reaction channel (solid line) and nonreactive inelastic Ba + H_2O channel (dotted line).

Fig 5 BaO and BaOH angular distributions from reaction of Ba(^{1}S) + H_2O at a collision energy of 23 kcal/mole showing relative signal intensities for both channels. Nominal Newton diagram for two reaction channels is also shown.

Fig 6. Ba^{18}OH time-of-flight spectra from Ba(^{1}S) + $H_2{}^{18}O$ at E_{coll} =23 kcal/mole.

Fig 7. Same as Fig. 6 but mass spectrometer set at Ba^{18}O. Small dotted line near 180μs denotes contribution from Ba^{18}OH fragmentation in electron bombardment ionizer.

Fig 8. Product translational energy distribution P(E) for BaO and BaOH from reaction of Ba(^{1}S) + $H_2{}^{18}O$ at E_{coll}= 23 kcal/mole. Shaded area denotes uncertainty in derived P(E) for BaOH + H channel.

Fig 9. BaOH time-of-flight spectra from Ba(^{1}D) + H_2O collisions at E_{coll} = 12 kcal/mole. Solid line shows best fit to data.

Fig10 Upper Figure: BaOH Angular Distribution from Ba(^{1}D) + H_2O at E_{coll}=12 kcal/mole. Lower Figure: Translational energy distribution for BaOH from

$Ba(^1D) + H_2O$ at E_{coll}= 12kcal/mole.

Fig11 Ba time-of-flight spectra from $Ba(^1D) + H_2O$ colisions at E_{coll} = 12 kcal/mole. The fastest and slowest peaks are due to the forward and backward components of the Newton circle. The large middle component is calculated contribution from fragmentation of BaOH to Ba^+ in the ionizer.

Fig12 Ba time-of-flight spectra at 12kcal/mole showing effect of electronic excitation on reactive component (middle peak) and nonreactive component (fast and slow components).

Fig13 Newton Diagram for possible product channels from reaction with CH_3OH. Upper figure: $Ba(^1S) + CH_3OH$. Lower figure: $Ba(^1D) + CH_3OH$. Circles denote maximum center of mass recoil velocities for Ba-containing products.

Fig14 Angular distributions for $BaOCH_3$, BaO, and Ba resulting from Ba + CH_3OH at 15 kcal/mole, showing effect of laser excitation on the incident Ba atom. BaO and Ba signal at wide angle (>15°) results from fragmentation of $BaOCH_3$ product in the electron bombardment ionizer.

Fig15 $BaOCH_3$ angular distributions from Ba + CH_3OH (upper figure) and Ba + CH_3OD (lower figure) at collision energy of 30kcal/mole, showing effect of laser excitation of Ba atom. Although $BaOCH_3$ signal increased with collision energy, electronic excitation was far more effective in promoting reaction.

Fig16 Energy level diagram for Ba + H_2O. The energy levels indicate the known or most probable values. Shaded regions indicate maximum uncertainties in energies of reaction intermediates or transition states. Reaction paths observed in this study are indicated by lines connecting reactants to products. Solid lines indicate primary reaction channels; dotted line indicates minor channels. Products and intermediates not connected to lines were not observed in this work or in chemiluminescence experiments described in Ref 6.

Fig17 Same as Fig. 16, but reaction is Ba + CH_3OH.

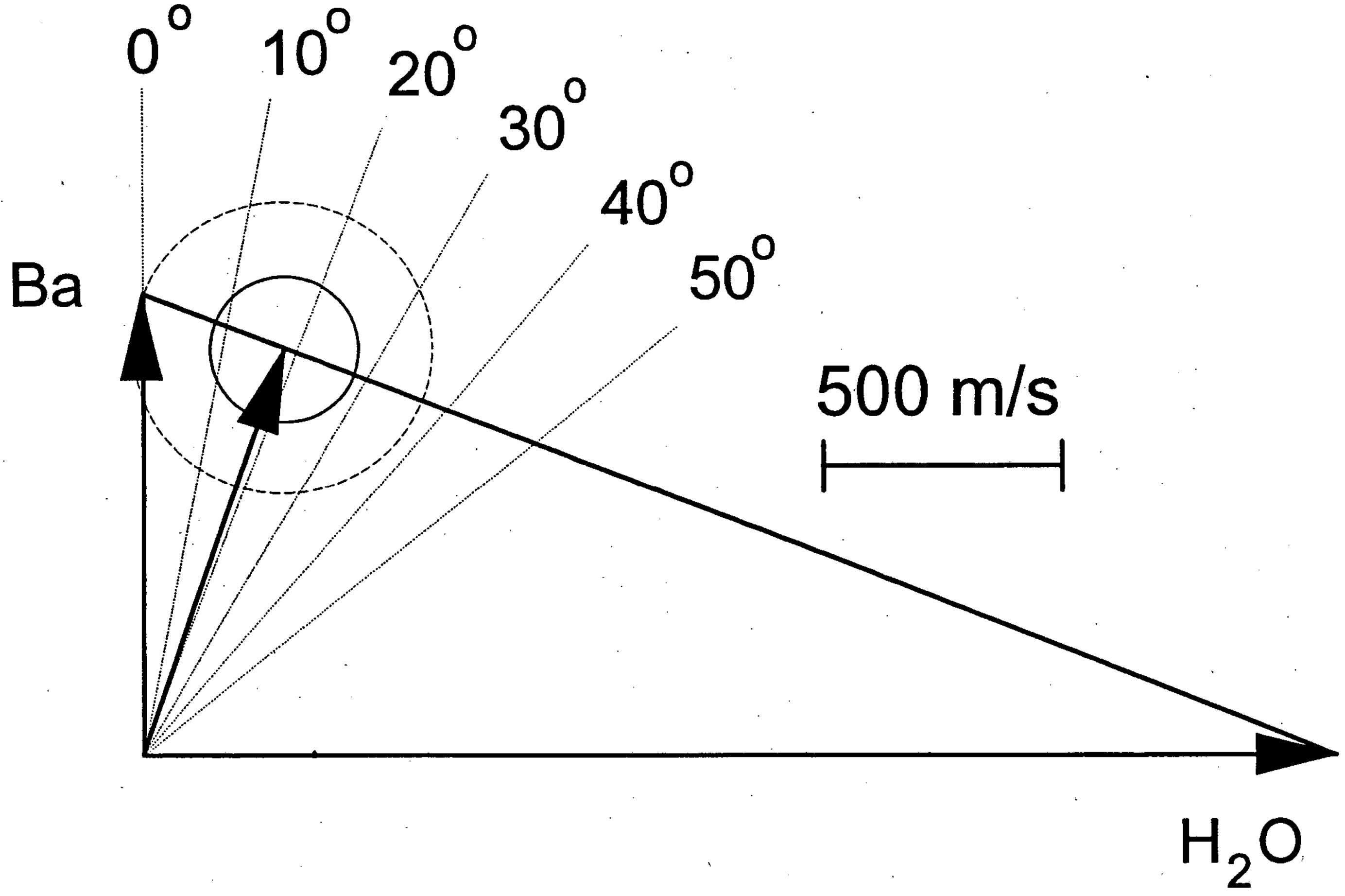


Fig. 1

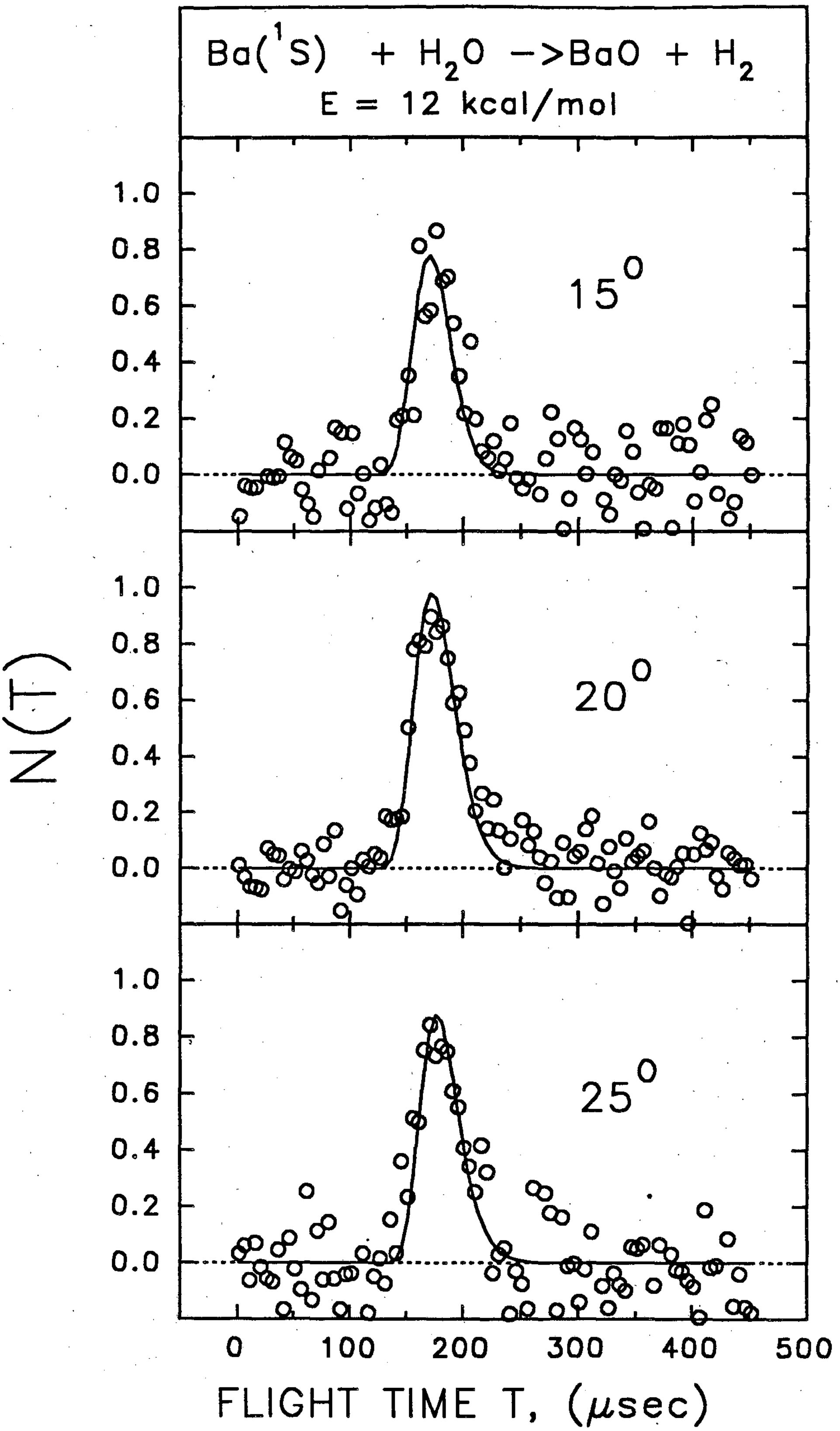

Ba(^{1}S) + H$_2$O ->BaO + H$_2$
E = 12 kcal/mol
1.0
0.8
0.6
0.4
0.2
0.0
15^0
20^0
25^0
N(T)
0
100
200
300
400
500
FLIGHT TIME T, (μsec)

Fig. 2

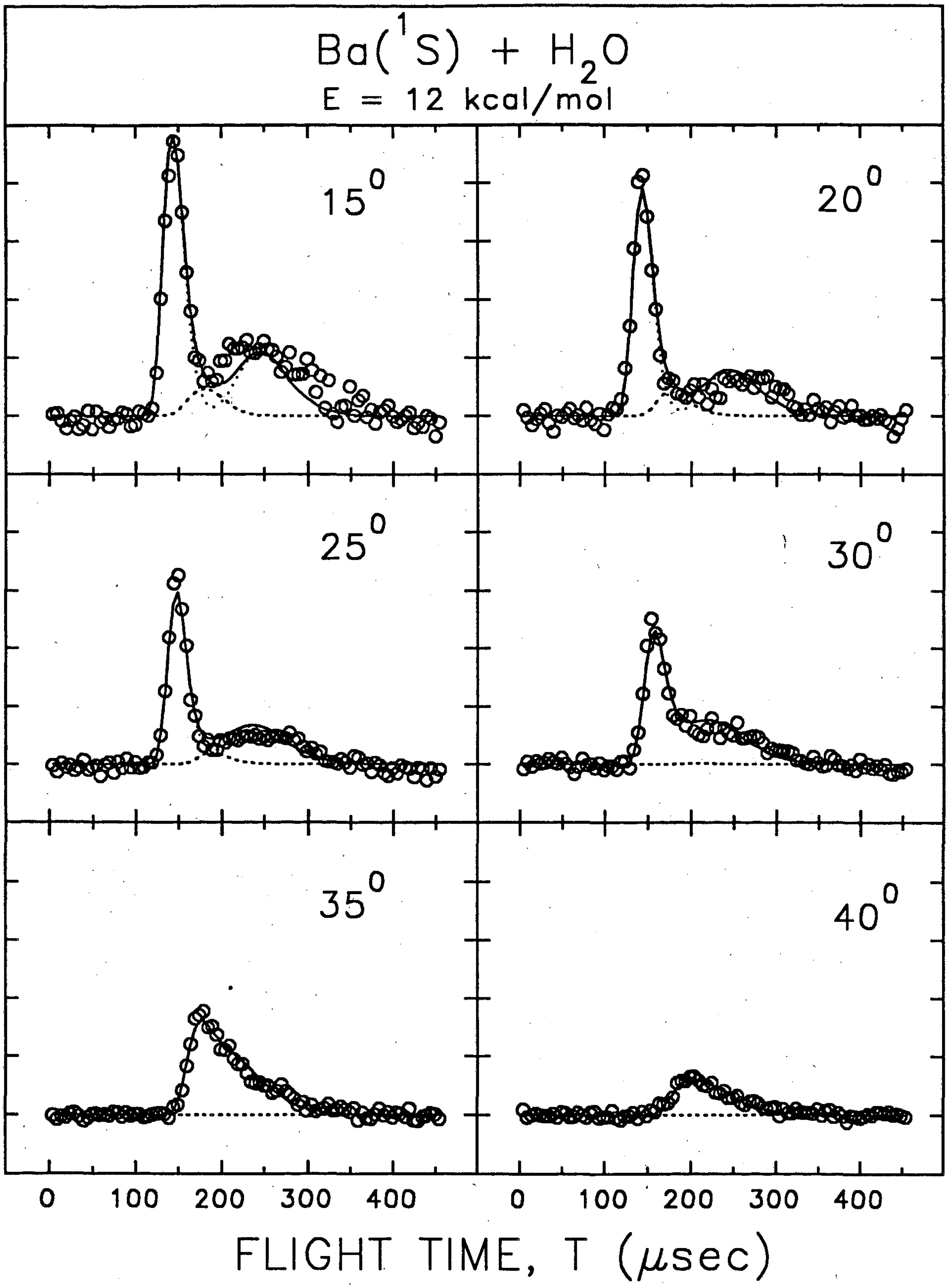

$Ba(^1S) + H_2O$
E = 12 kcal/mol
15°
20°
25°
30°
35°
40°
N(T)
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
FLIGHT TIME, T (μsec)

Fig. 3

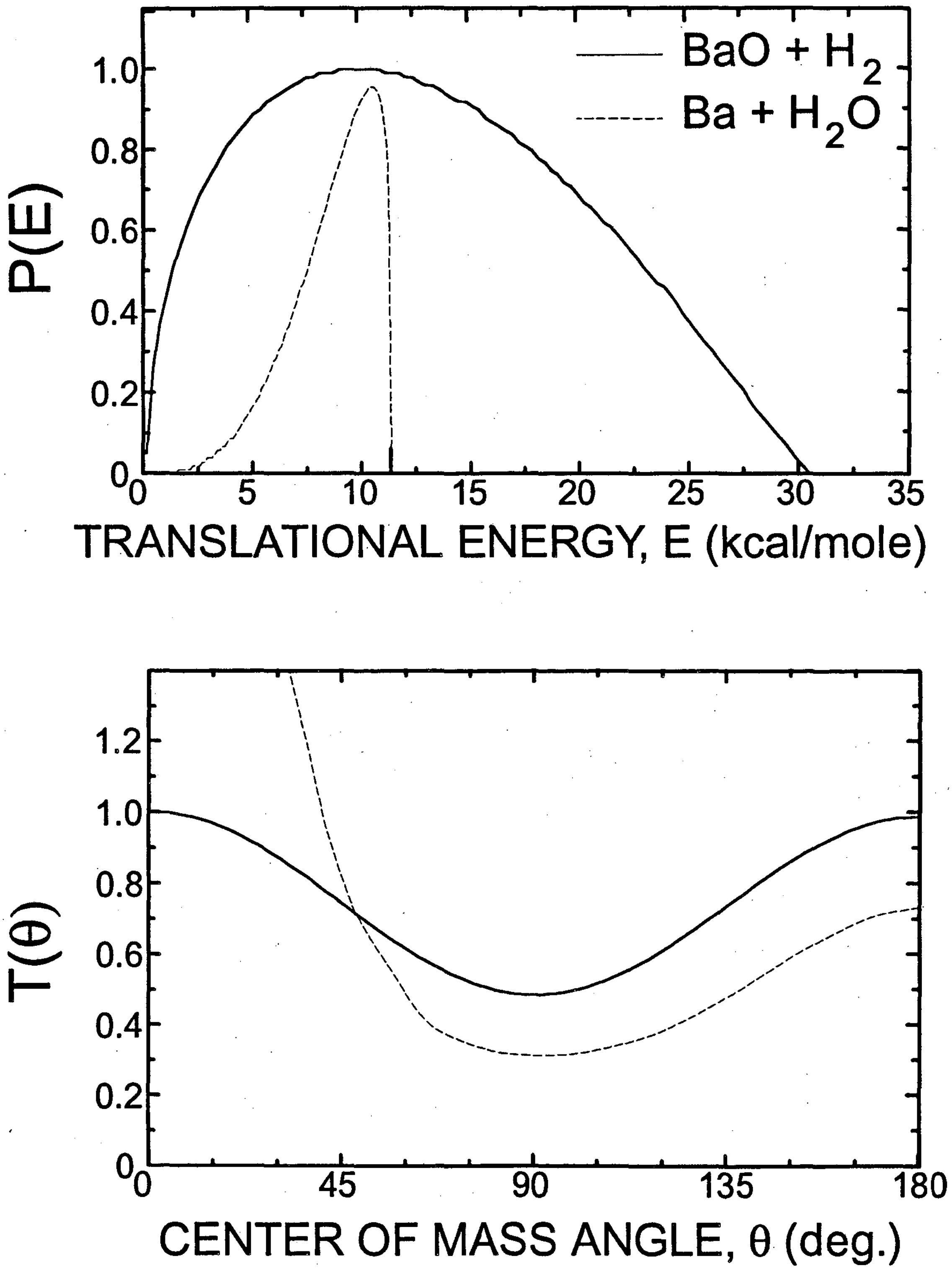

BaO + H2
Ba + H2O
P(E)
1.0
0.8
0.6
0.4
0.2
0
0
5
10
15
20
25
30
35
TRANSLATIONAL ENERGY, E (kcal/mole)
T(θ)
1.2
1.0
0.8
0.6
0.4
0.2
0
0
45
90
135
180
CENTER OF MASS ANGLE, θ (deg.)

Fig. 4

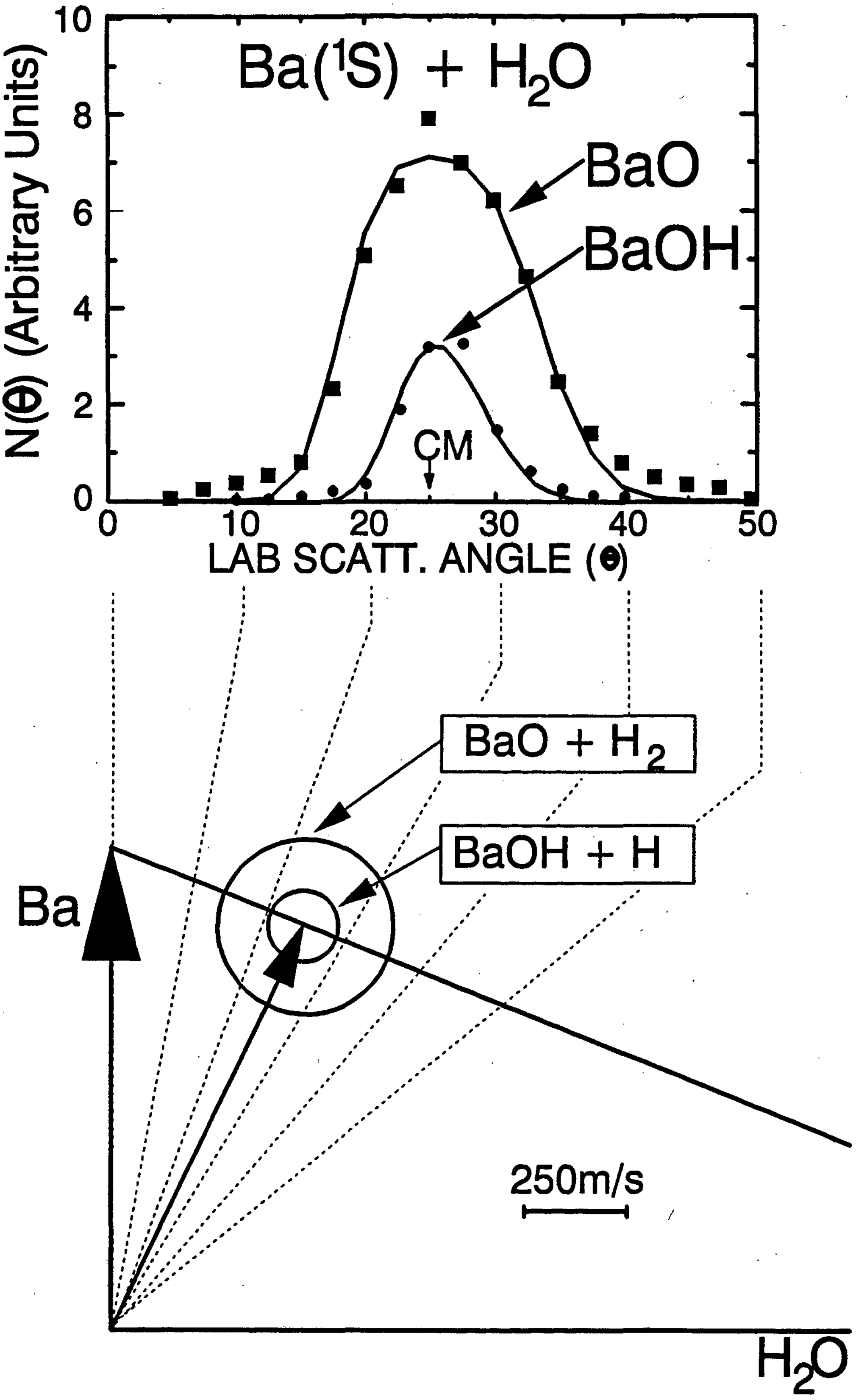

Ba(¹S) + H₂O
N(Θ) (Arbitrary Units)
0
2
4
6
8
10
BaO
BaOH
CM
0
10
20
30
40
50
LAB SCATT. ANGLE (Θ)
BaO + H₂
BaOH + H
Ba
250m/s
H₂O

Fig. 5

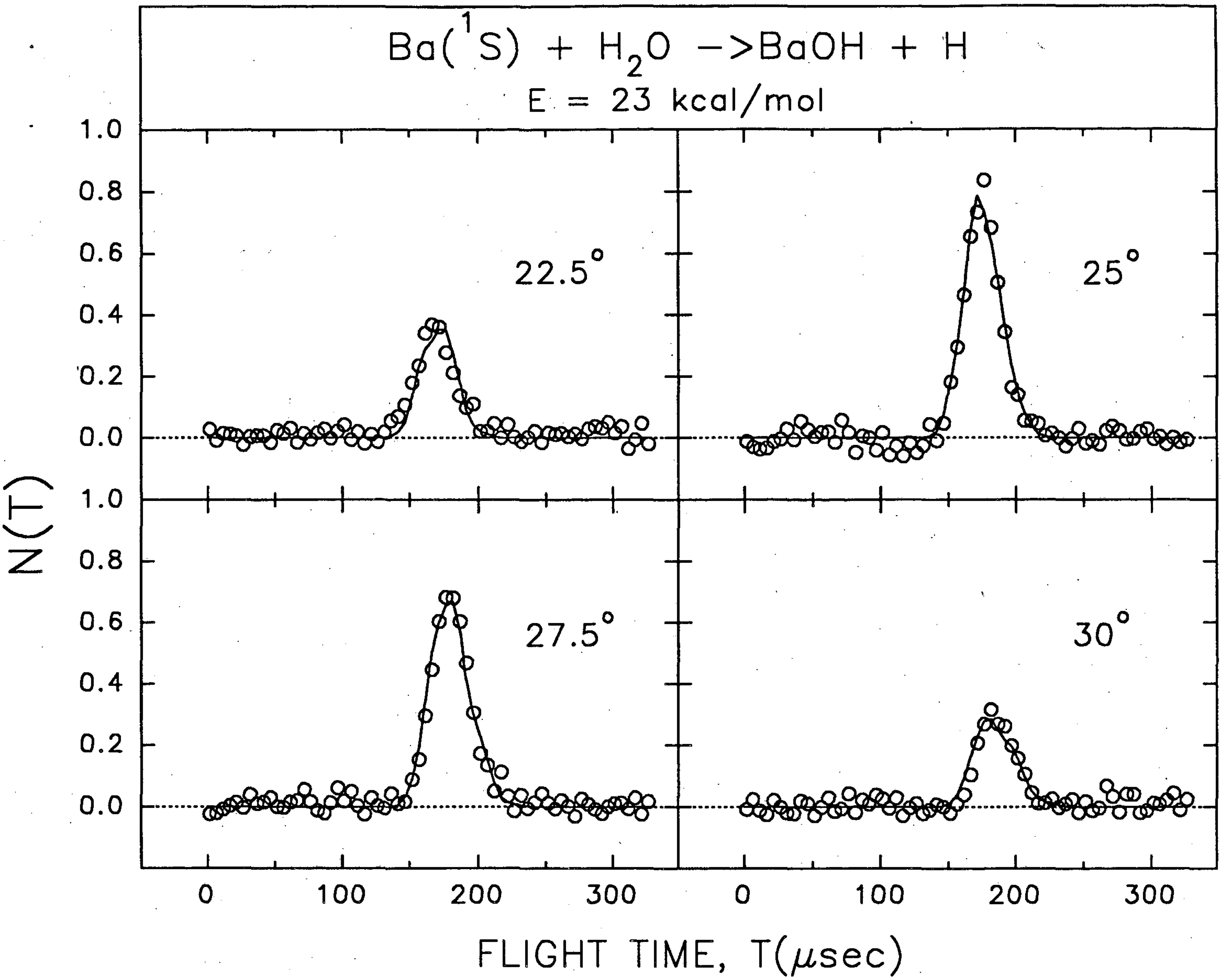

$Ba(^1S) + H_2O \rightarrow BaOH + H$
E = 23 kcal/mol
22.5°
25°
27.5°
30°
N(T)
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
FLIGHT TIME, T(μsec)

Fig. 6

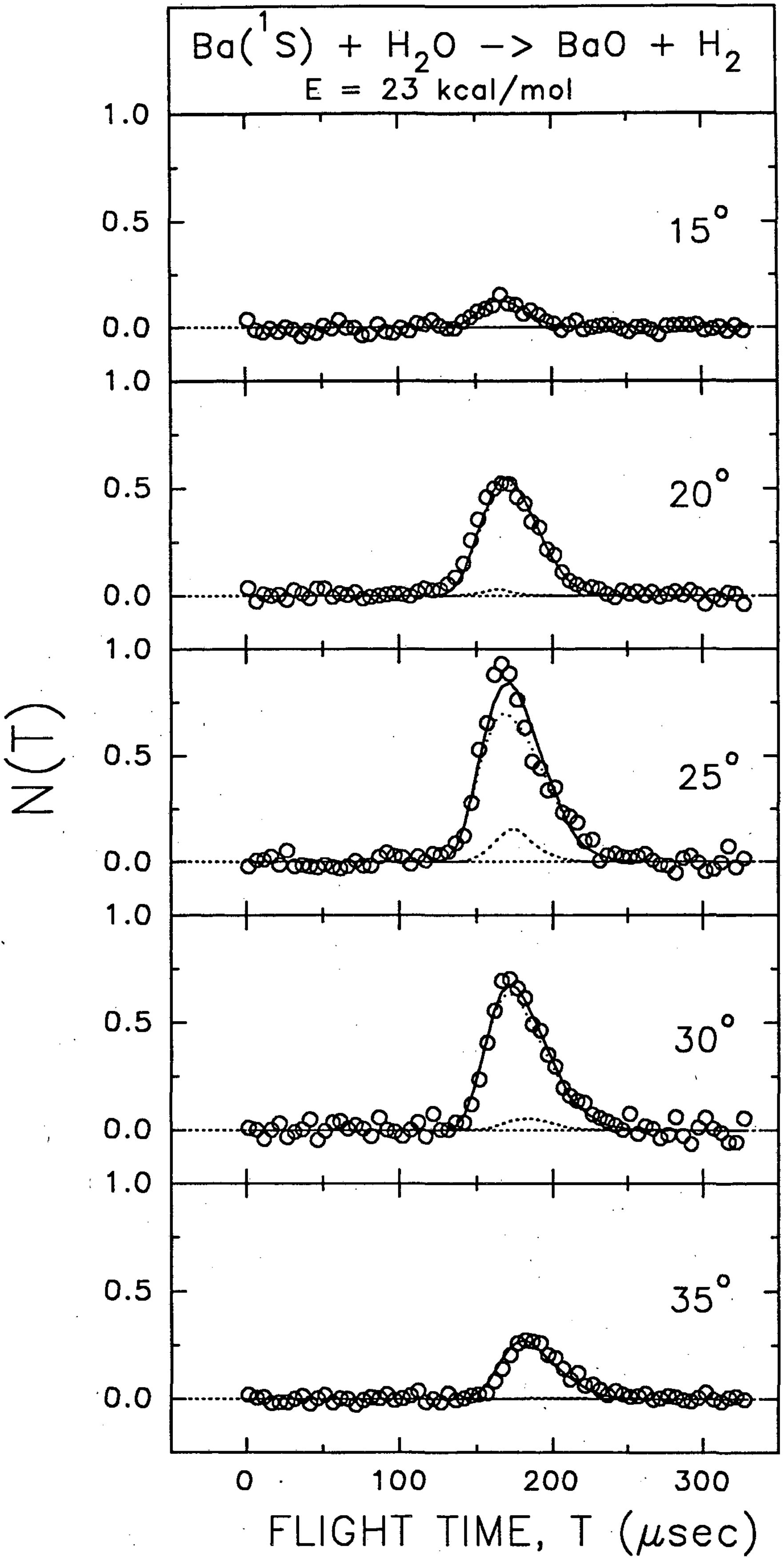

$Ba(^1S) + H_2O \rightarrow BaO + H_2$
E = 23 kcal/mol
1.0
0.5
0.0
15°
20°
25°
30°
35°
N(T)
0
100
200
300
FLIGHT TIME, T (μsec)

Fig. 7

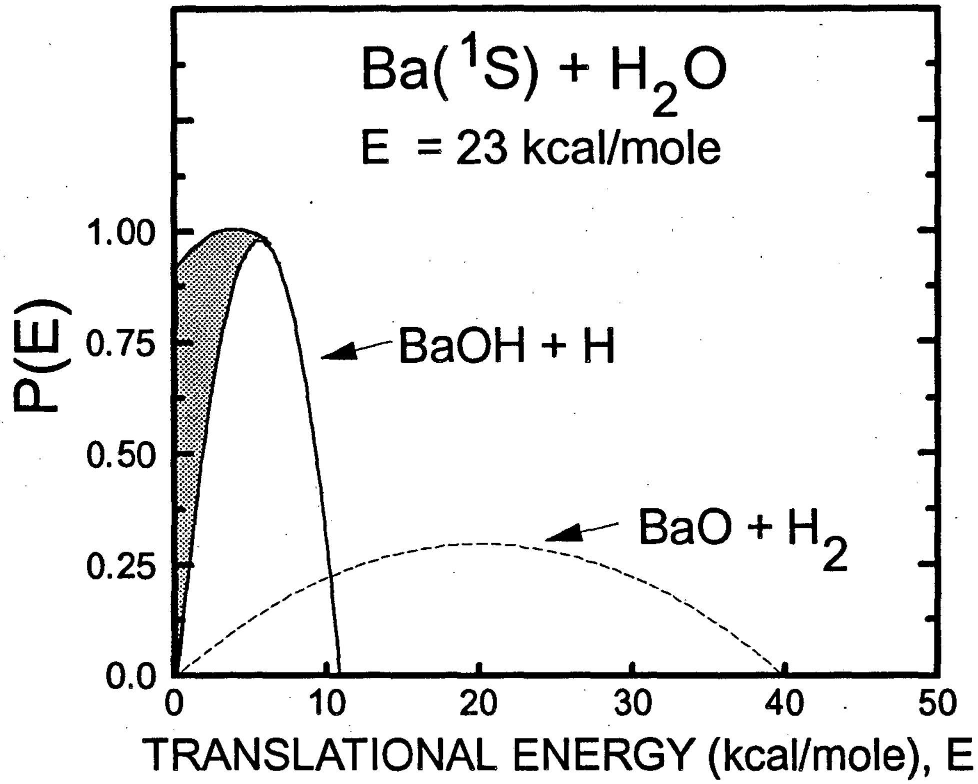

Ba(1S) + H2O
E = 23 kcal/mole
1.00
0.75
0.50
0.25
0.0
P(E)
BaOH + H
BaO + H2
0
10
20
30
40
50
TRANSLATIONAL ENERGY (kcal/mole), E

Fig. 8

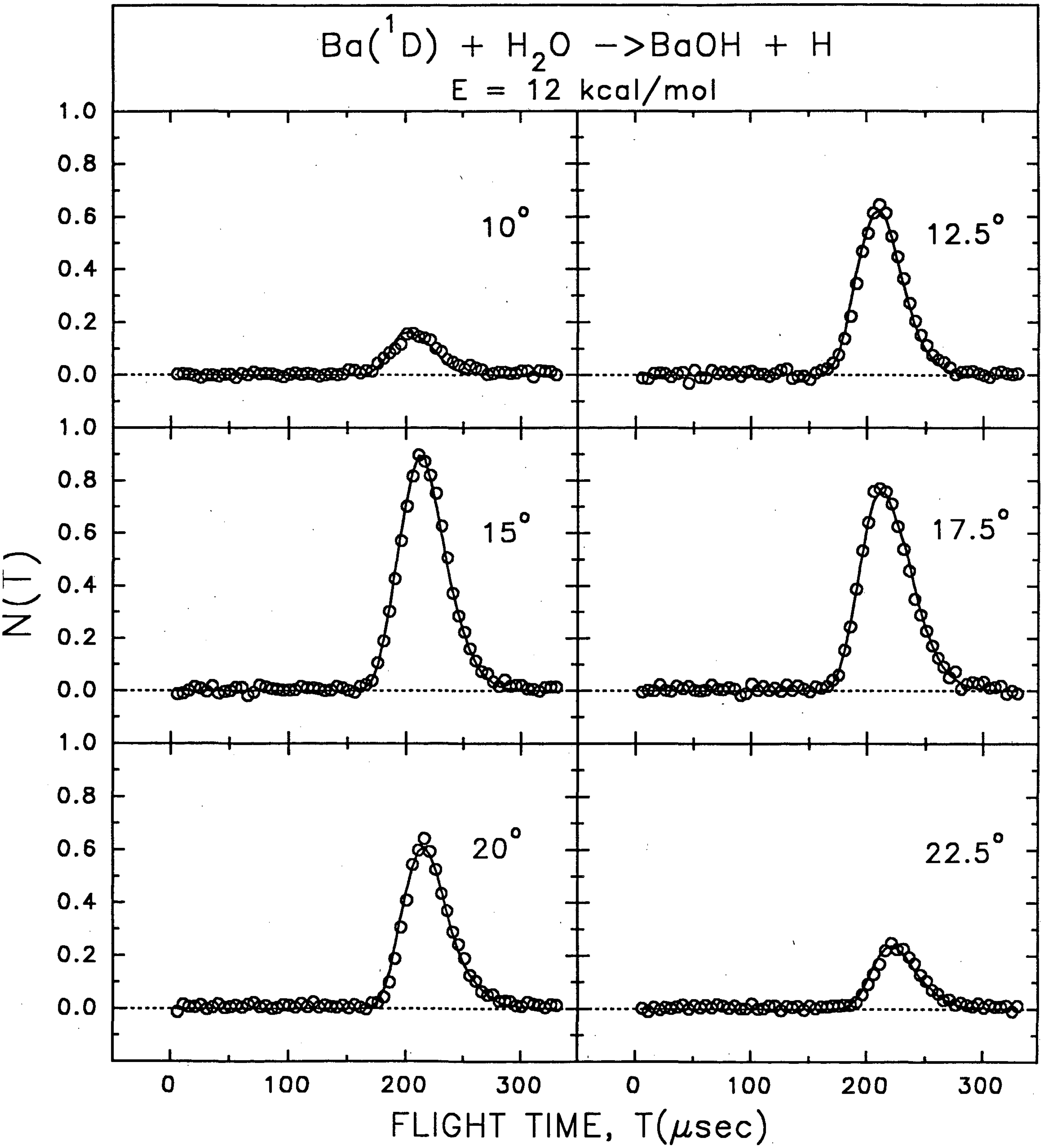

$Ba(^1D) + H_2O \rightarrow BaOH + H$
E = 12 kcal/mol
10°
12.5°
15°
17.5°
20°
22.5°
N(T)
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
FLIGHT TIME, T(μsec)

Fig. 9

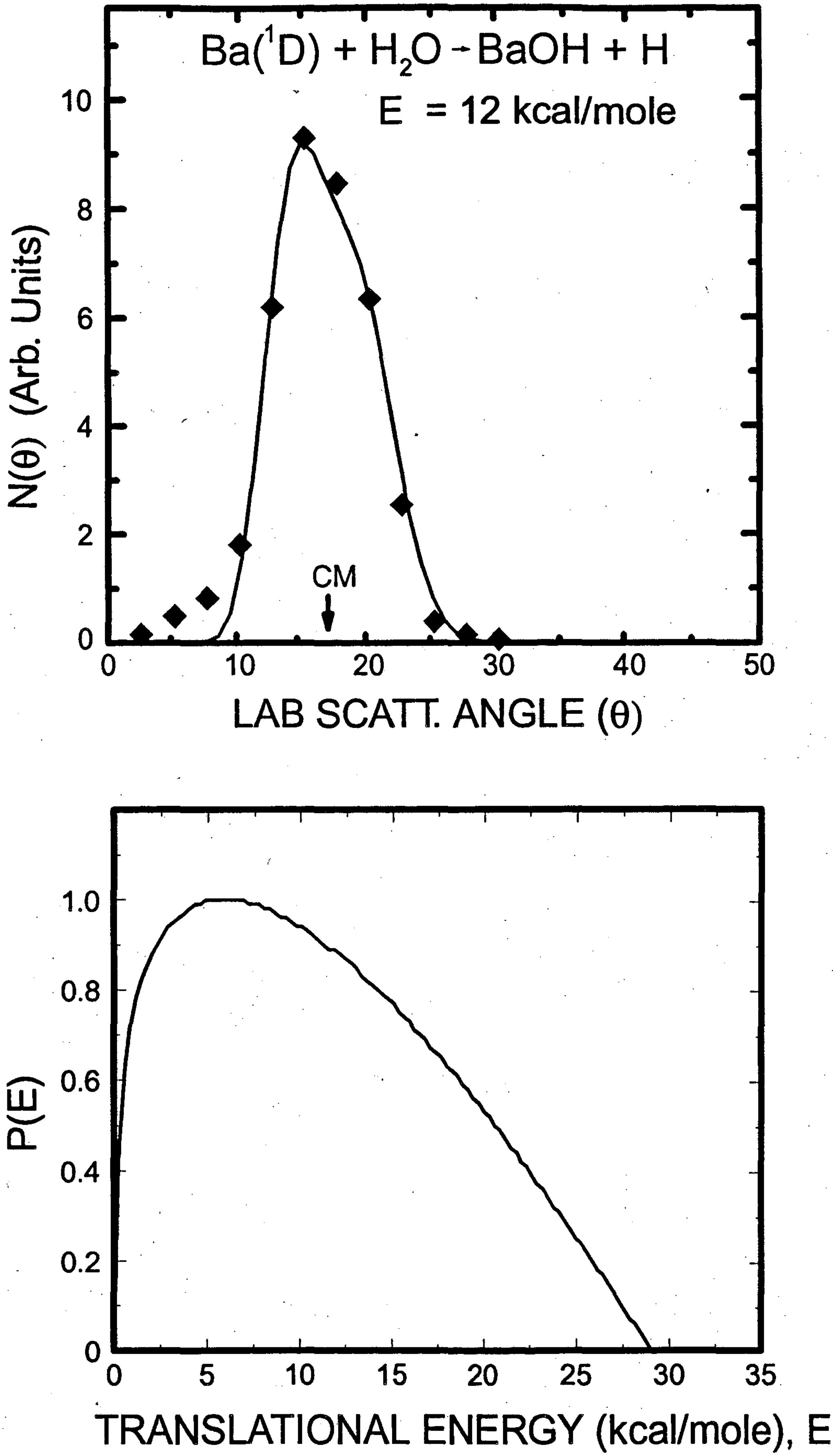

Ba(¹D) + H₂O → BaOH + H
E = 12 kcal/mole
N(θ) (Arb. Units)
0
2
4
6
8
10
CM
0
10
20
30
40
50
LAB SCATT. ANGLE (θ)
P(E)
0
0.2
0.4
0.6
0.8
1.0
0
5
10
15
20
25
30
35
TRANSLATIONAL ENERGY (kcal/mole), E

Fig. 10

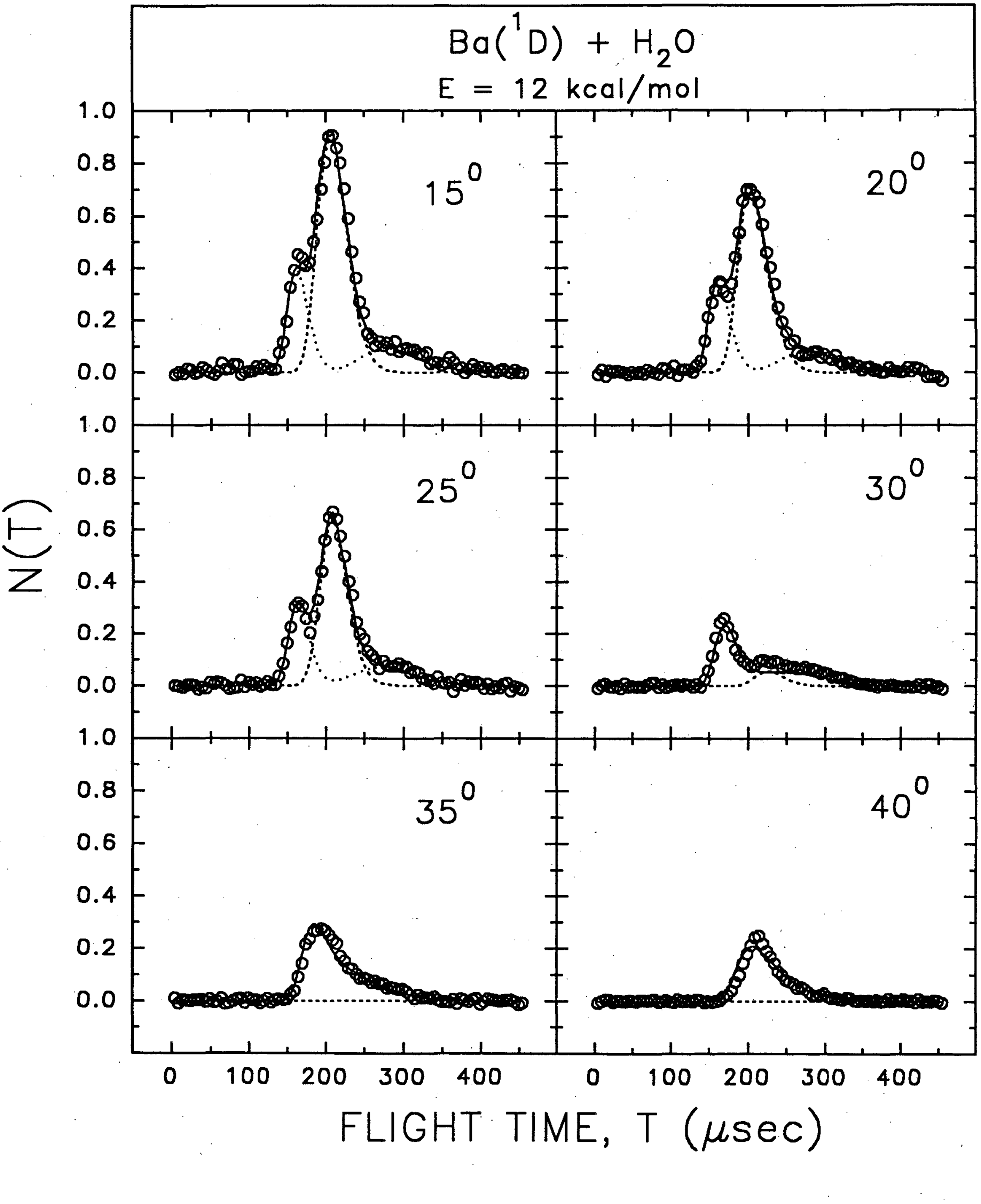

Ba(^{1}D) + H$_2$O
E = 12 kcal/mol
N(T)
1.0
0.8
0.6
0.4
0.2
0.0
15^0
20^0
25^0
30^0
35^0
40^0
0
100
200
300
400
FLIGHT TIME, T (μsec)

Fig. 11

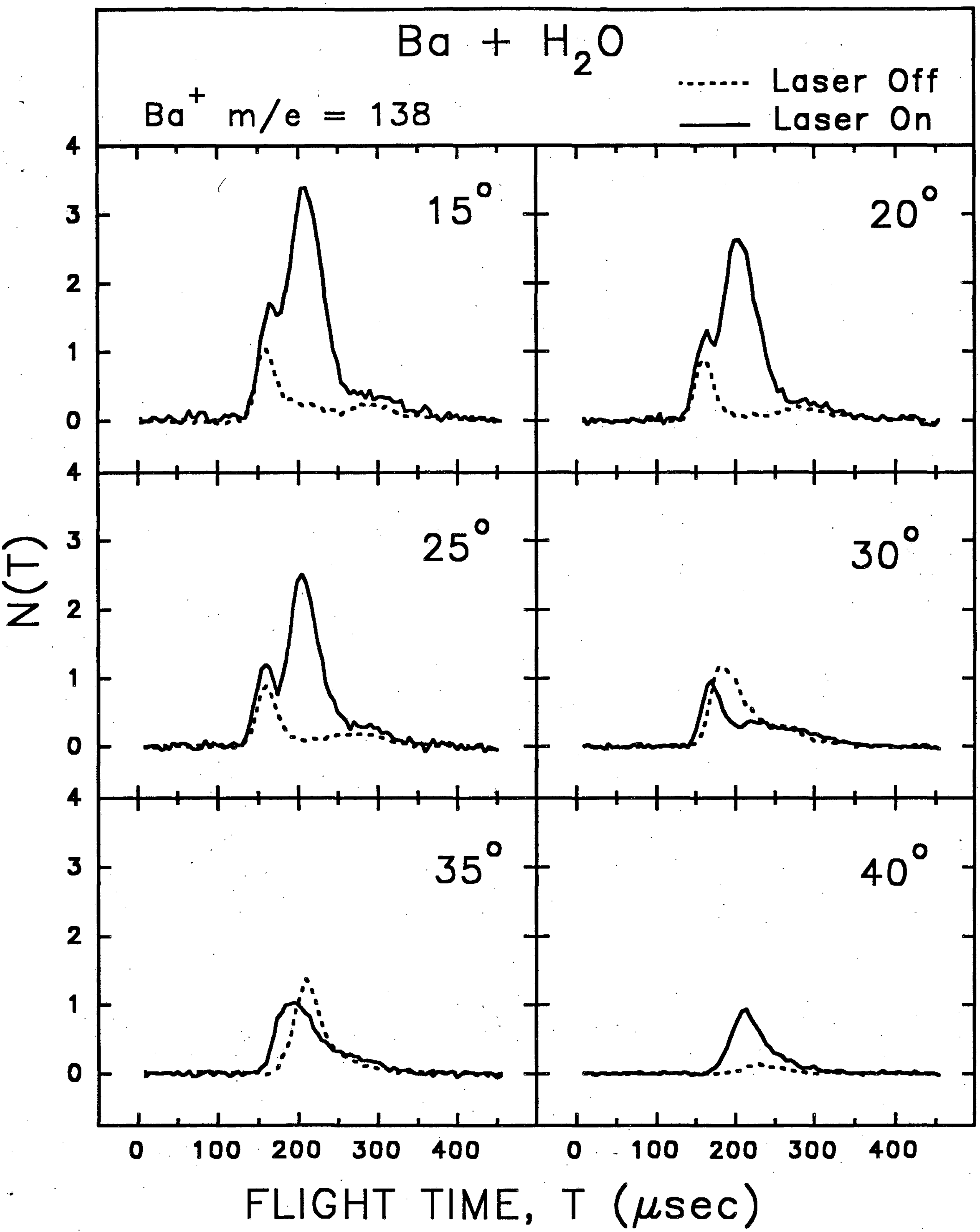
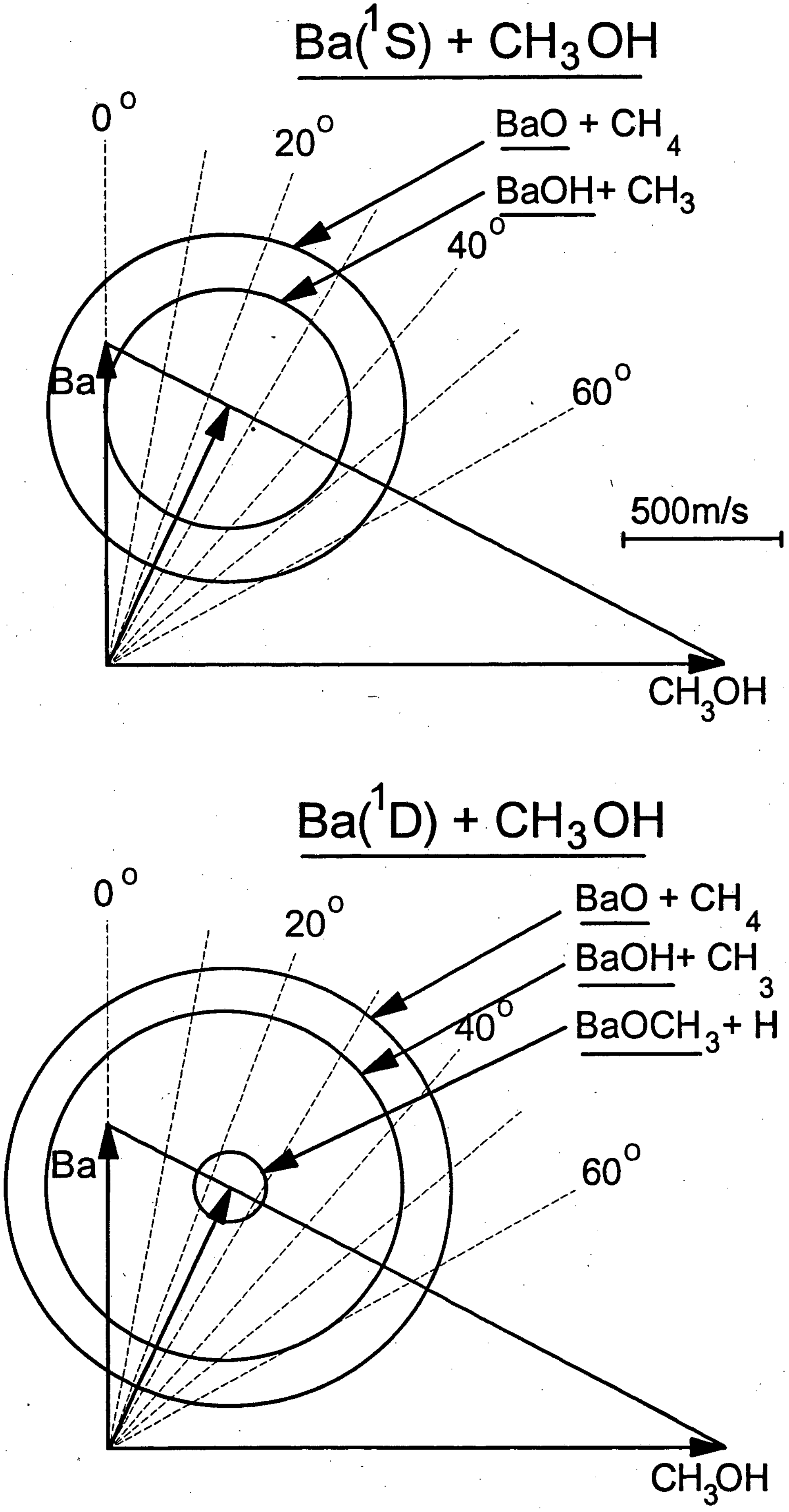

Ba + H_2O
Ba$^+$ m/e = 138
Laser Off
Laser On
15°
20°
25°
30°
35°
40°
N(T)
0
1
2
3
4
0
100
200
300
400
FLIGHT TIME, T (μsec)

Fig. 12



Ba(^{1}S) + CH$_3$OH

Ba(^{1}D) + CH$_3$OH

Fig. 13

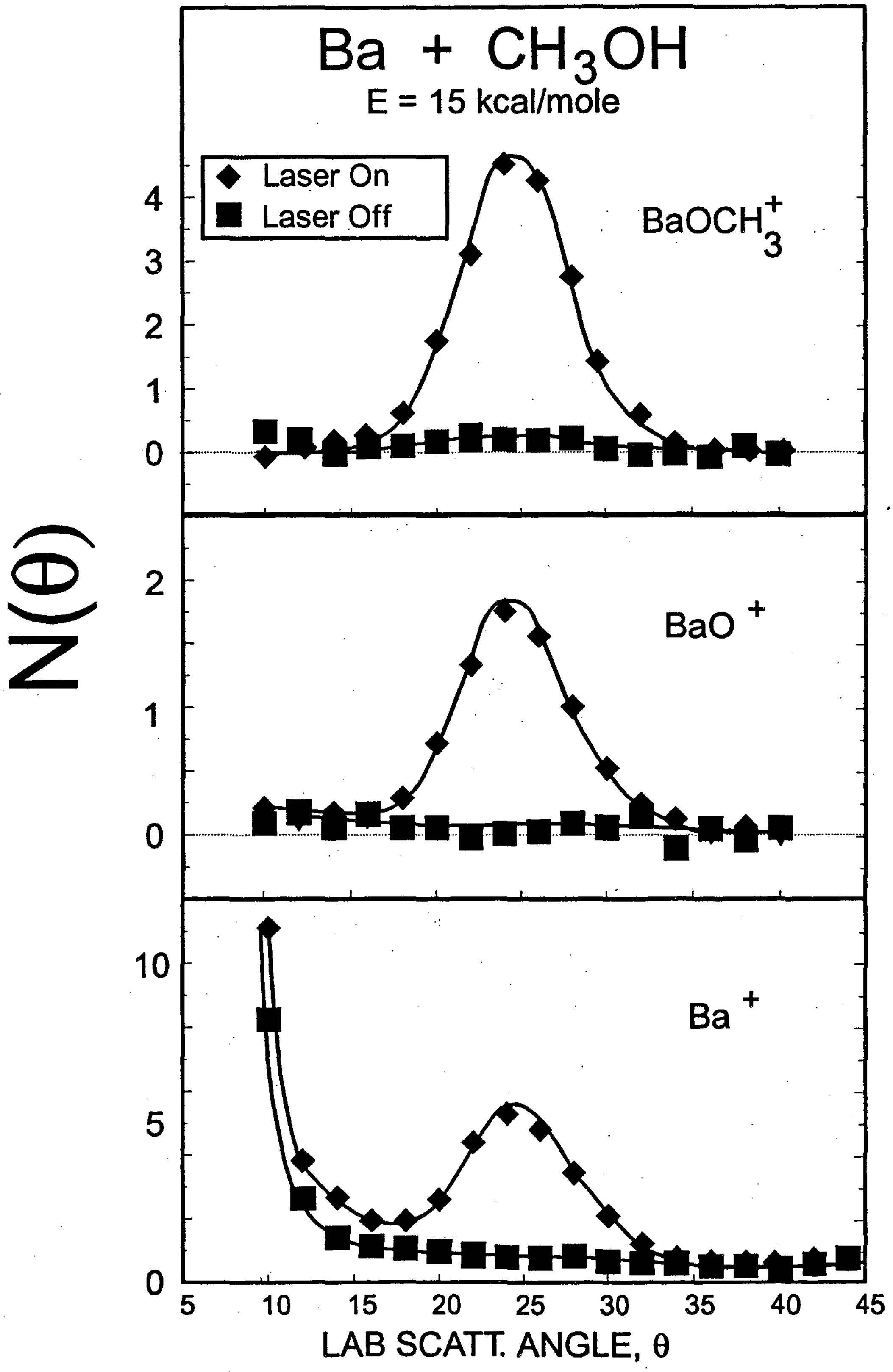

Ba + CH_3OH
E = 15 kcal/mole
◆ Laser On
■ Laser Off
$BaOCH_3^+$
BaO^+
Ba^+
N(θ)
0
1
2
3
4
0
1
2
0
5
10
5
10
15
20
25
30
35
40
45
LAB SCATT. ANGLE, θ

Fig. 14

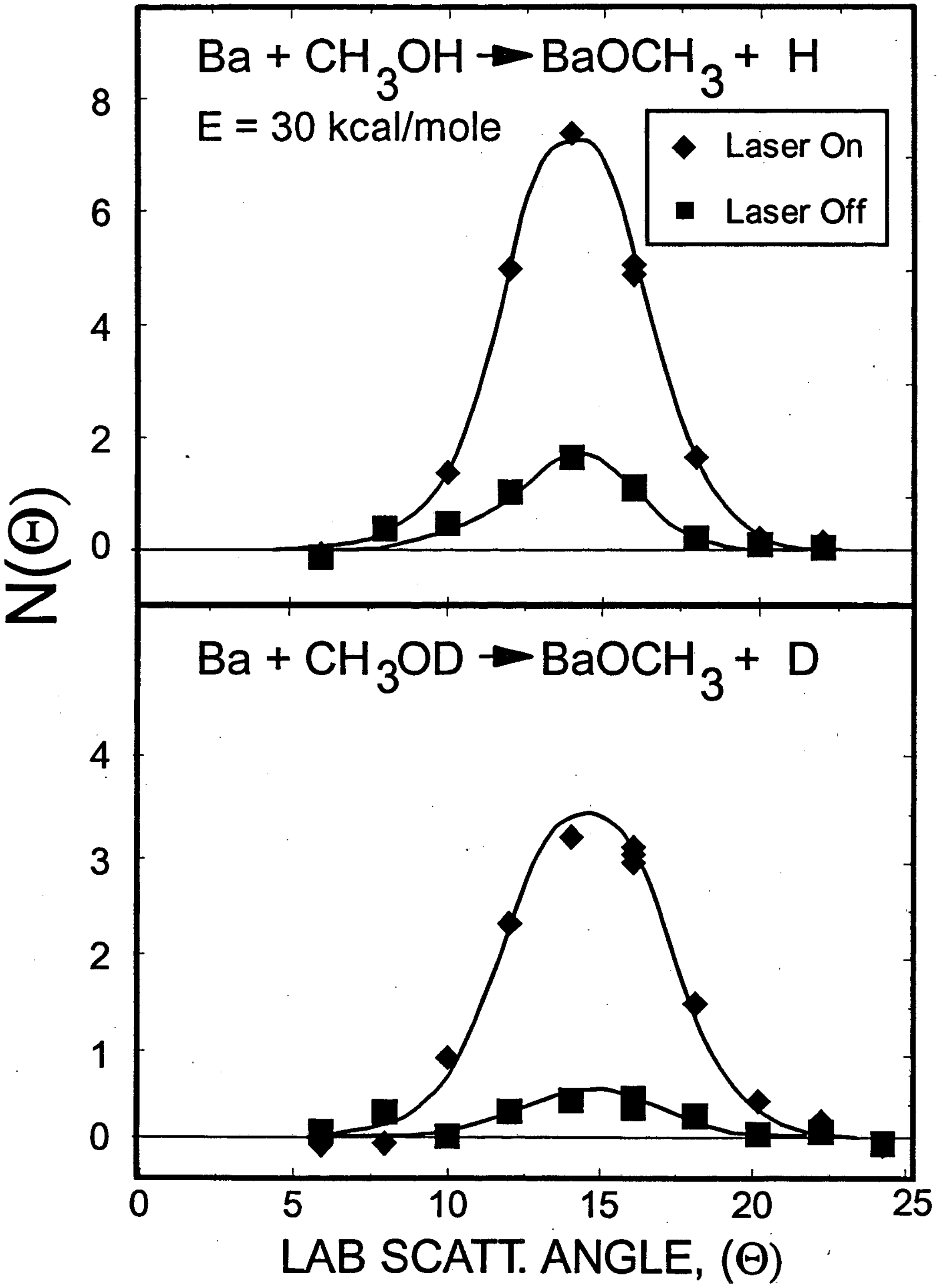

Ba + CH$_3$OH → BaOCH$_3$ + H
E = 30 kcal/mole
◆ Laser On
■ Laser Off
8
6
4
2
0
N(Θ)
Ba + CH$_3$OD → BaOCH$_3$ + D
4
3
2
1
0
0
5
10
15
20
25
LAB SCATT. ANGLE, (Θ)

Fig. 15

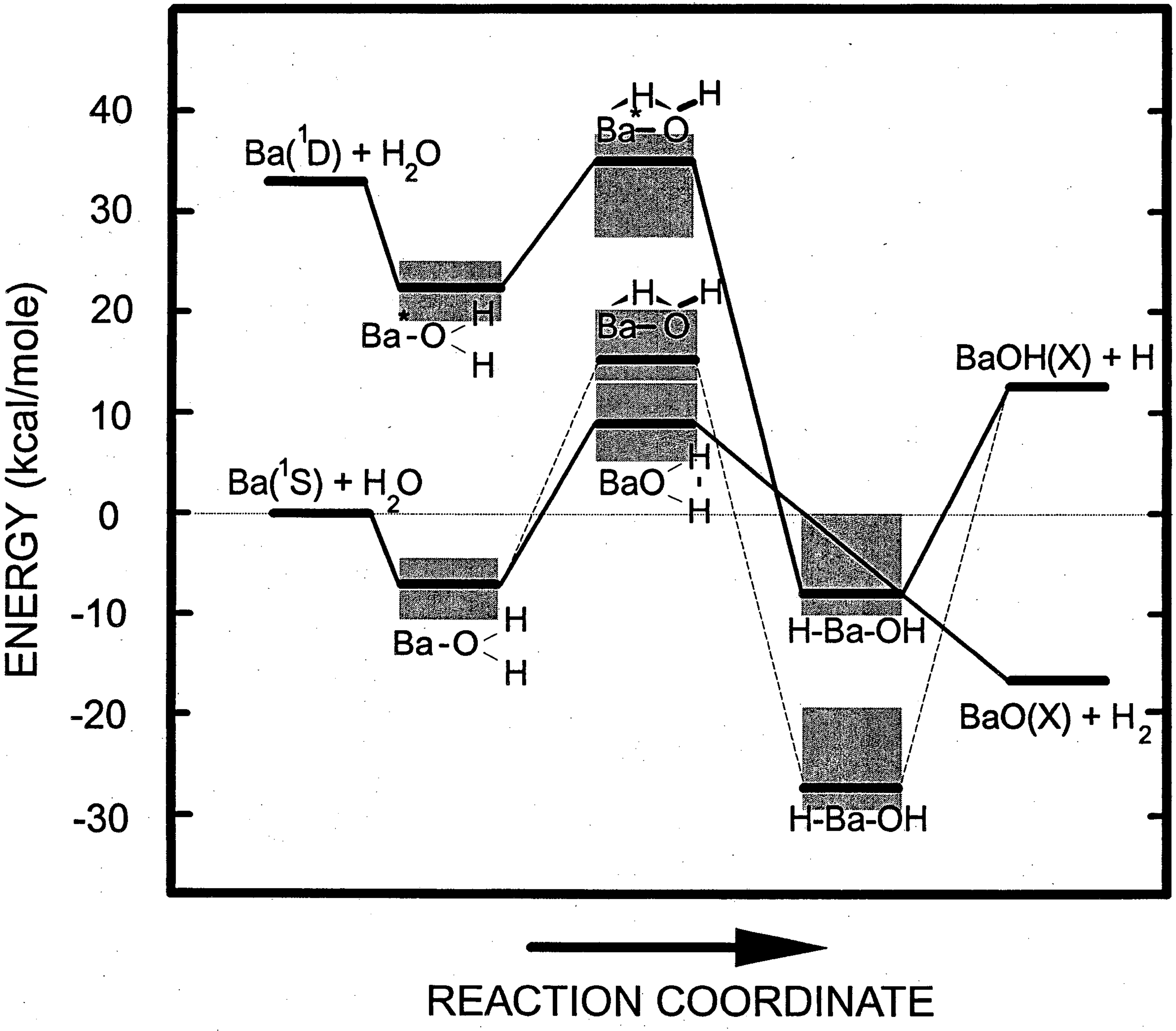

40
30
20
10
0
-10
-20
-30
ENERGY (kcal/mole)
Ba(1D) + H2O
Ba*-O-H-H
Ba*-O with H-H
Ba-O with H-H
BaO with H-H
Ba(1S) + H2O
Ba-O-H-H
H-Ba-OH
H-Ba-OH
BaOH(X) + H
BaO(X) + H2
REACTION COORDINATE

Fig. 16

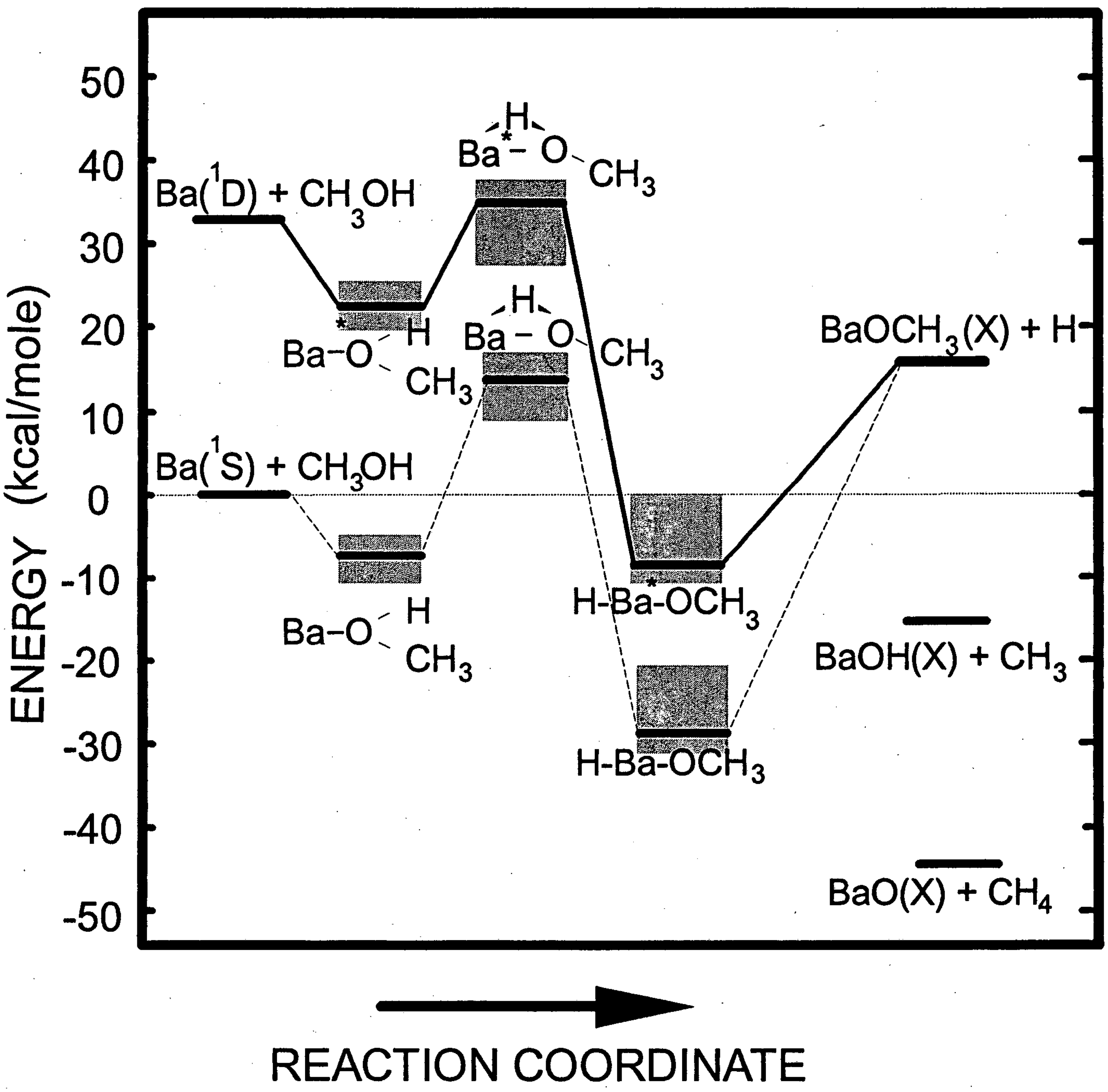

50
40
30
20
10
0
-10
-20
-30
-40
-50
ENERGY (kcal/mole)
REACTION COORDINATE
Ba(¹D) + CH₃OH
Ba(¹S) + CH₃OH
Ba*–O–H, CH₃
Ba–O–H, CH₃
H, Ba*– O – CH₃
H, Ba – O – CH₃
H-Ba*-OCH₃
H-Ba-OCH₃
BaOCH₃(X) + H
BaOH(X) + CH₃
BaO(X) + CH₄

Fig 17