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A CROSSED MOLECULAR
BEAM STUDY OF THE $O(^1D_2) + CH_4$ REACTION

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and Y. T. Lee

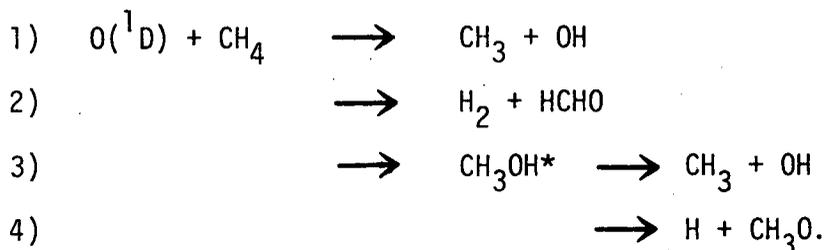
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The reaction of $O(^1D_2)$ with methane has been a matter of considerable interest in the past, primarily for its role in stratospheric chemistry.¹ UV photolysis of N_2O-CH_4 or O_3-CH_4 mixtures has been used to study this reaction in gas phase²⁻⁶ and also in a liquid argon medium.⁷ Lin and DeMore,⁶ in an extensive gas phase study, have identified four primary reactions,



The production of OH, reactions 1 and 3, constitute 90% of the yield, the direct molecular H_2 elimination is about 9%, and reaction 4,

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hydrogen atom loss from the complex is less than 2%. The direct three center elimination of H_2 , reaction 2 warrants more detailed investigation because the dynamics of three center elimination of H_2 have not been studied under single collision conditions. We have performed a crossed molecular beam investigation of this reaction using a supersonic $O(^1D)$ beam source developed recently in our laboratory. Our results shows that in fact, hydrogen atom elimination, reaction 4, greatly exceeds molecular hydrogen elimination which is not observed to occur appreciably.

The seeded $O(^1D_2)$ atomic beam is produced from a high pressure, radio frequency discharge nozzle beam source which has been previously described in detail.⁸ Although the beam also contains $O(^3P)$, undissociated O_2 molecules as well as the He carrier gas, only $O(^1D_2)$ reacts with CH_4 appreciably at low collision energies.⁴ The $O(^1D_2)$ beam was crossed at 90° with a room temperature supersonic beam of pure CH_4 in a collision chamber maintained at $\sim 1 \times 10^{-7}$ torr. Reaction product angular distributions are measured as a function of in-plane scattering angle by a triply differentially pumped rotatable electron bombardment quadrupole mass spectrometer, kept at $\sim 10^{-11}$ torr in the ionization region.⁹ Product velocity distributions at selected angles are determined by a cross correlation time-of-flight (TOF) technique.¹⁰ Product of the reaction was observed at mass 30 and 31. The mass 31 product can be identified with CH_3O (or CH_2OH) radical formation from the chemical reaction. The mass 30 signal cannot be identified solely from the mass spectrometer detection,

because it can arise either from direct production of formaldehyde or from fragmentation of the mass 31 product in the ionizer. In order to identify the mass 30 signal, angular and velocity distributions were obtained. Figure 1 shows the angular distribution of mass 30 product from the reaction of $O(^1D)$ with CH_4 at a collision energy of 6.4 kcal/mole. The product is distributed fairly symmetrically about the center of mass angle. The mass 31 signal (not shown) is contaminated by a small fraction of the O_2 , mass 32, elastically scattered from the oxygen beam by the CH_4 . The elastic contribution can be separated from the reactive mass 31 signal in the time of flight (TOF) distributions. Shown in Fig. 2 is the TOF spectrum for mass 30 and 31 after correcting the latter spectrum by subtracting the mass 32 elastic contribution. The excellent agreement between the distributions is strong evidence that both masses are produced from a single reactive channel. The source of the mass 30 signal, then, is not a dynamically distinct channel, but is the ionizer fragmentation of the CH_3O (or CH_2OH) product. The intensity ratio of the mass 30 to 31 TOF spectra was found to be constant at different angles, verifying that mass 30 and 31 are produced from the same specie. Also consistent with this conclusion is the narrow angular distribution of mass 30 (Fig. 1) which would not be expected from the highly exoergic ($\Delta H = -113$ kcal/mole)¹¹ $HCHO + H_2$ reaction. The most translationally energetic $m/e = 30$ product, if attributed to direct H_2CO formation, would contain less than 15% of the available energy. The H elimination channel can be accompanied by either CH_3O or CH_2OH radical

formation, having slightly different exoergicities¹¹ (33 and 43 kcal/mole, respectively), but the two pathways cannot be distinguished in our experiment.

From the breadth of the product angular and velocity distributions, we estimate that the mean product translational energy is 15 kcal/mole. In the gas phase experiments, the translationally hot hydrogen atoms will react with CH_4 with very high cross section, producing H_2 at a much higher rate than would be expected assuming thermalized H atoms.

We have estimated our detection sensitivity for H_2 elimination by assuming a statistical product energy distributions for this channel and calculating the product distributions expected. From our failure to detect any evidence of molecular H_2 elimination we conclude that reaction 2 is less than 25% of the H atom elimination under our reaction conditions.

This study has shown that the H atom substitution process greatly exceeds H_2 elimination in the reaction $\text{O}(^1\text{D}) + \text{CH}_4$. This result is in agreement with our rate calculations based on a recent ab initio study of the H_4CO potential energy surface¹² which found the barriers to H_2 loss from methanol producing hydroxymethylene, 94 kcal/mole and formaldehyde, 100 kcal/mole. With these barriers to H_2 molecular elimination, the simple CH bond cleavage was calculated to be the dominant process.

ACKNOWLEDGEMENT

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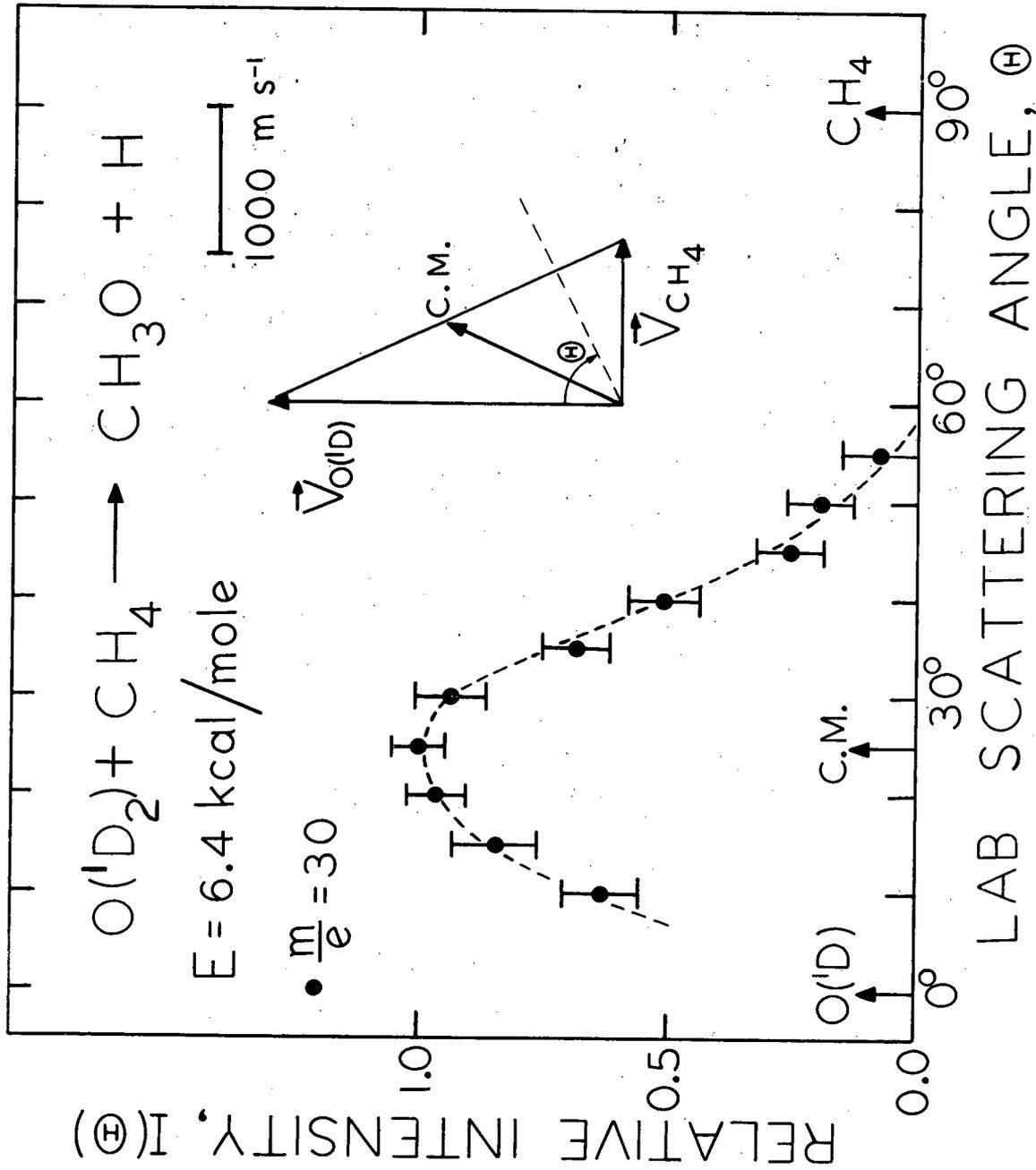
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FOOTNOTES AND REFERENCES

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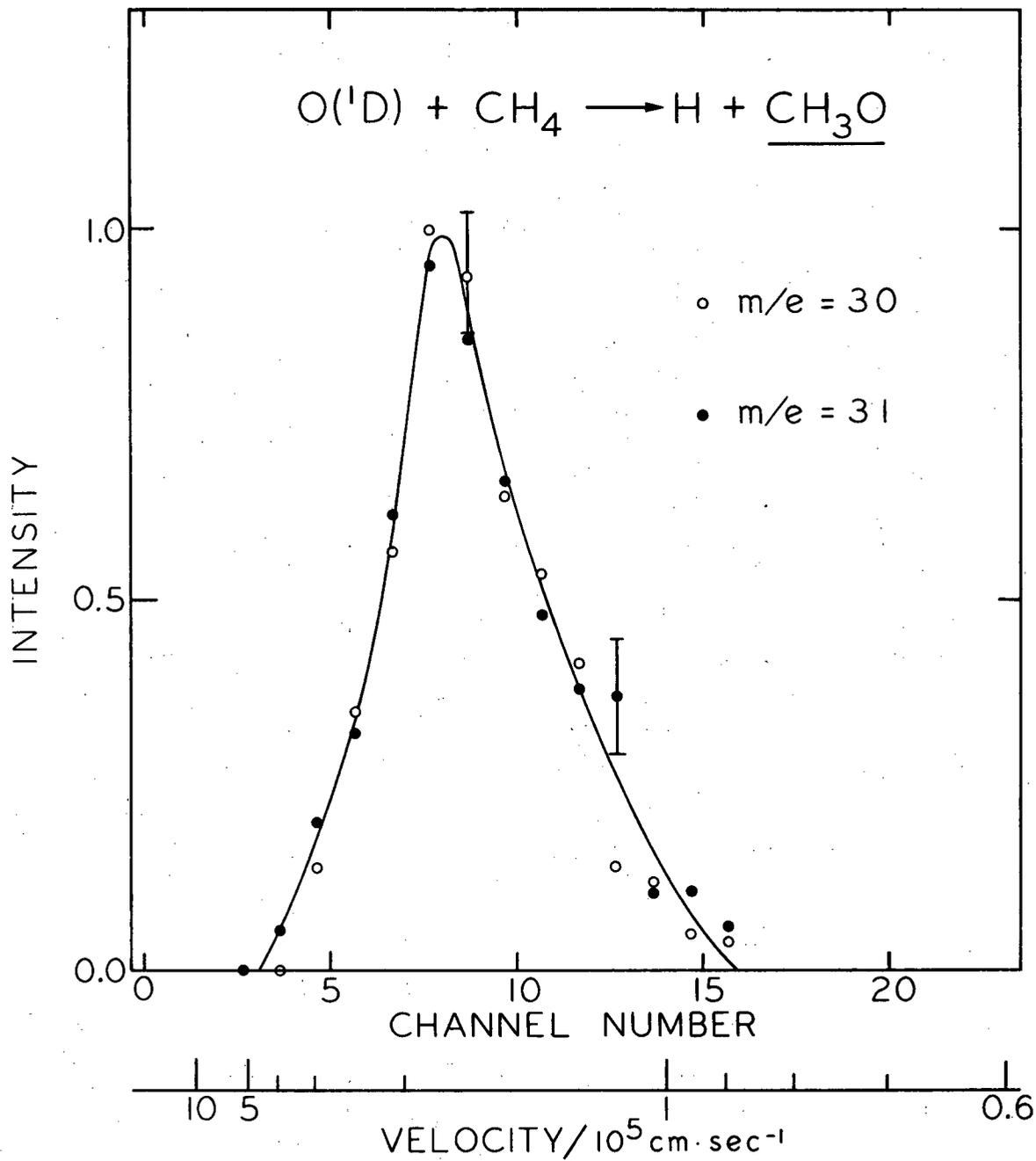
FIGURE CAPTIONS

- Fig. 1. Laboratory angular distribution from the $O(^1D_2) + CH_4$ reaction. The primary reaction product found was CH_3O (or CH_2OH), which subsequently fragmented in the ionizer. The dashed line is drawn through the data for clarity.
- Fig. 2. Experimental TOF of mass 30 (\circ) and mass 31 (\bullet). A line is drawn through the points for clarity. Error bars are typical of all points and represent 95% confidence limits.



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Fig. 1



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Fig. 2

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