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Submitted to the Journal of Chemical Physics

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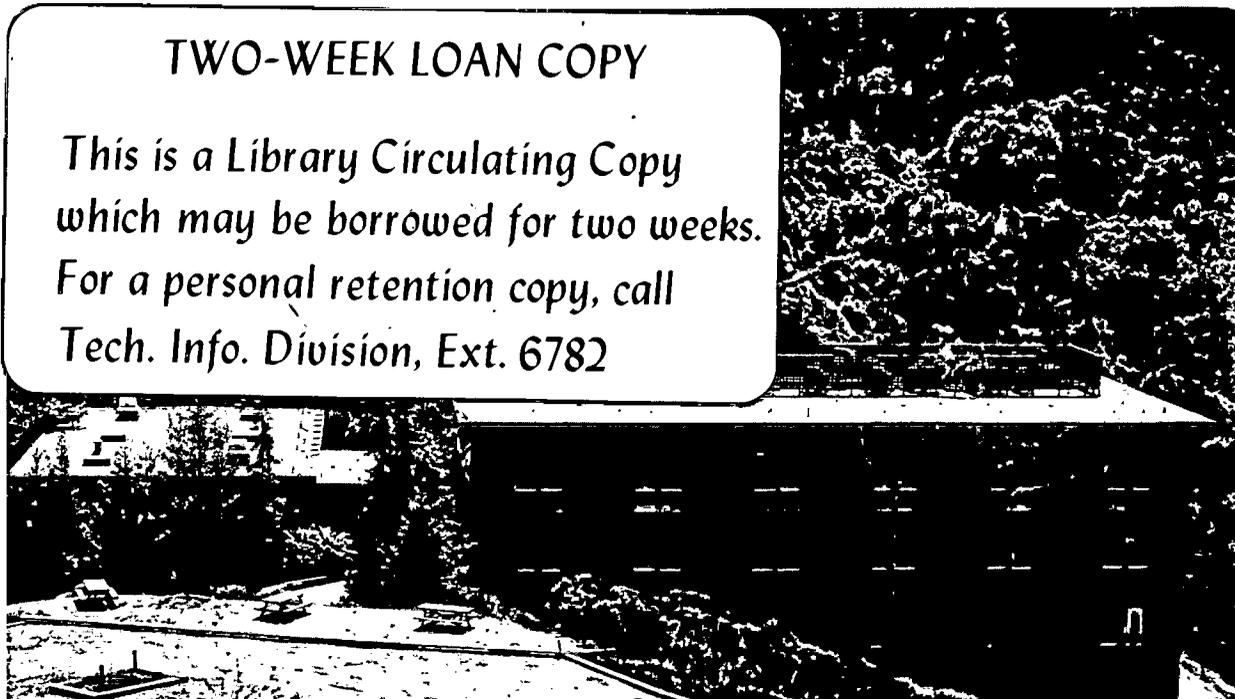
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September 1979

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OBSERVATION OF CH₃O PRODUCT IN THE CROSSED
BEAM STUDY OF THE O(¹D₂) + CH₄ REACTIONP. Casavecchia^a, R. J. Buss, S. J. Sibener^b,
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SEPTEMBER 1979

The reaction of O(¹D₂) with methane has been a matter of considerable interest in the past, primarily for its role in stratospheric chemistry.¹ UV photolysis of N₂O-CH₄ or O₃-CH₄ mixtures has been used to study this reaction in gas phase²⁻⁶ and also in a liquid argon medium.⁷ At the present time the reaction is understood⁶ to proceed along two distinct pathways: a) by insertion of O(¹D₂) into the C-H bond to form "hot" methanol, which fragments in the absence of stabilizing collisions; b) by abstraction of H atoms to form OH and CH₃ radicals. These results seem to be supported by a series of experiments on the reactions of O(¹D₂) with some simple saturated hydrocarbons.⁸ However, contradictory results have been put forth from different groups,²⁻⁷ especially on the fragmentation of "hot" methanol. The main disagreements are the extent of H₂

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elimination from "hot" methanol resulting in the formation of formaldehyde, and whether other precursor radicals, such as CH_3O or CH_2OH , are formed at all. Dimethyl ether has been observed in a low pressure study,³ but there is no direct experimental evidence on the identity of the precursor radicals.

In order to understand the reaction mechanism and to elucidate the dynamics and energetics of the $\text{O}(^1\text{D}_2) + \text{CH}_4$ reaction, we have performed a crossed molecular beam investigation of this reaction using a novel supersonic $\text{O}(^1\text{D}_2)$ beam source developed recently in our laboratory. The seeded $\text{O}(^1\text{D}_2)$ atomic beam is produced from a high pressure, radio frequency discharge nozzle beam source which has been previously described in detail.⁹ Although the beam also contains $\text{O}(^3\text{P})$, undissociated O_2 molecules as well as the He carrier gas, only $\text{O}(^1\text{D}_2)$ reacts with CH_4 appreciably at low collision energies.⁴ The $\text{O}(^1\text{D}_2)$ 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.¹⁰ Product velocity distributions at selected angles are determined by a cross correlation time-of-flight (TOF) technique.¹¹ Although C^{13}H_4 impurity prevents our studying the hydrogen abstraction channel, we observed scattered signal at $m/e = 30, 31, \text{ and } 32$. Possible origins of $m/e =$

32 are either $\text{CH}_3\text{OH}^\ddagger$ or O_2 , but since the lifetime of $\text{CH}_3\text{OH}^\ddagger$ is expected to be too short ($\leq \times 10^{-12}$ sec)⁶ for it to reach the detector, the m/e 32 signal is believed to be entirely due to elastic scattering of O_2 from CH_4 , as demonstrated by TOF analysis. m/e 31 product was identified with CH_3O (or CH_2OH) radical formation from the chemical reaction. m/e 30 product cannot be identified directly from a mass spectrometric detection, since it can be either formaldehyde (H_2CO) or a fragment of m/e 31 product. But in a crossed molecular beam experiment it is possible to positively identify the origin of m/e 30 from precise measurement of angular and velocity distributions. Figure 1 shows the angular distribution of m/e 30 product at a collision energy E of 6.4 kcal/mole. The m/e 30 angular distribution is rather narrow and is peaked at the center of mass and will be shown to come from the fragmentation of mass 31 product (CH_3O or CH_2OH) in the ionizer. Since the m/e 31 signal is strongly contaminated, especially at small angles, by the low mass tail of the intense m/e 32 elastic signal, a reliable angular distribution of m/e 31 is difficult to obtain. However, in the TOF data the reactive m/e 31 signal is separated from that due to elastic contamination. Figure 2 shows the TOF spectra of m/e 30, 31 and 32 at the center-of-mass angle. The m/e 30 and 31 spectra appear similar and peak at the same velocity, with the strong elastic contribution of m/e 32 appearing as a shoulder on the high velocity side of m/e 31 spectrum. By subtracting the m/e 32

contribution from the m/e 31 distribution we obtain a spectrum (solid line in Fig. 2b) which is identical to the m/e 30 spectrum (Fig. 2a). This strongly suggests that m/e 31 and m/e 30 have the same origin. Moreover, the intensity ratio of the m/e 30 and 31 TOF spectra is constant at different angles, giving further support that m/e 30 detected is a fragment of CH₃O (or CH₂OH), the primary reaction product, in the ionizer of the mass spectrometer. The narrow angular distribution of m/e 30 product also supports our contention that the primary reaction is not the highly exoergic ($\Delta H = -113$ kcal/mole)¹² H₂CO + H₂ reaction. The most translationally energetic m/e 30 product, if attributed to direct H₂CO formation, would contain less than 15% of the available energy. The H elimination channel can be accompanied by either CH₃O or CH₂OH radical formation, having slightly different exoergicities¹² (33 and 43 kcal/mole, respectively), but the two pathways cannot be distinguished in our experiment. The observation of CH₃O (or CH₂OH) formation when an H atom is eliminated after the insertion of O(¹D₂) into the C-H bond also explains the (CH₃)₂O observed by Bradley et al.³ and the CH₃OH product observed by DeMore.⁶ The fact that we do not observe formaldehyde as a product suggests that the H₂ elimination channel from CH₃OH[‡] is not present at all, or plays a very minor role. Although the formation of formaldehyde was inferred in the past, it is interesting to note that the formation of H₂CO has never been detected in the gas phase experiments²⁻⁶ and

in some case even H_2 has not been observed.⁴ The identification of the CH_3O (or CH_2OH) radical as one of the primary reaction products from the single bimolecular reactive collision of $O(^1D_2)$ with CH_4 is unambiguous in our experiment. This certainty is not possible using mass spectrometric identification alone. Common problems of fragmentation associated with mass spectrometric identification of internally excited molecules and radicals can be overcome with additional measurements of their angular and velocity distributions in a crossed molecular beam experiment. The dynamical and energetic constraints of the system provide additional handles for positive product identification.

ACKNOWLEDGEMENT

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract No. W-7405-Eng-48 and the Office of Naval Research. P.C. acknowledges a fellowship from the Italian Ministry of Education and travel support from NATO grant No. 1444. S.J.S. acknowledges partial fellowship support from the Gulf Oil Research Foundation.

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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. a) Experimental TOF distribution of m/e 30 product in time space. The dark line is drawn through the data for clarity. b) Experimental TOF distributions of m/e 31 (o) and m/e (Δ) in time space. The dark line represents m/e 31 TOF distribution corrected for m/e 32 contribution (see text). Other dotted or dashed lines are drawn through the data for clarity. Error bars ($\pm 2\sigma$) are of the size of the data points for m/e 32 TOF distribution.

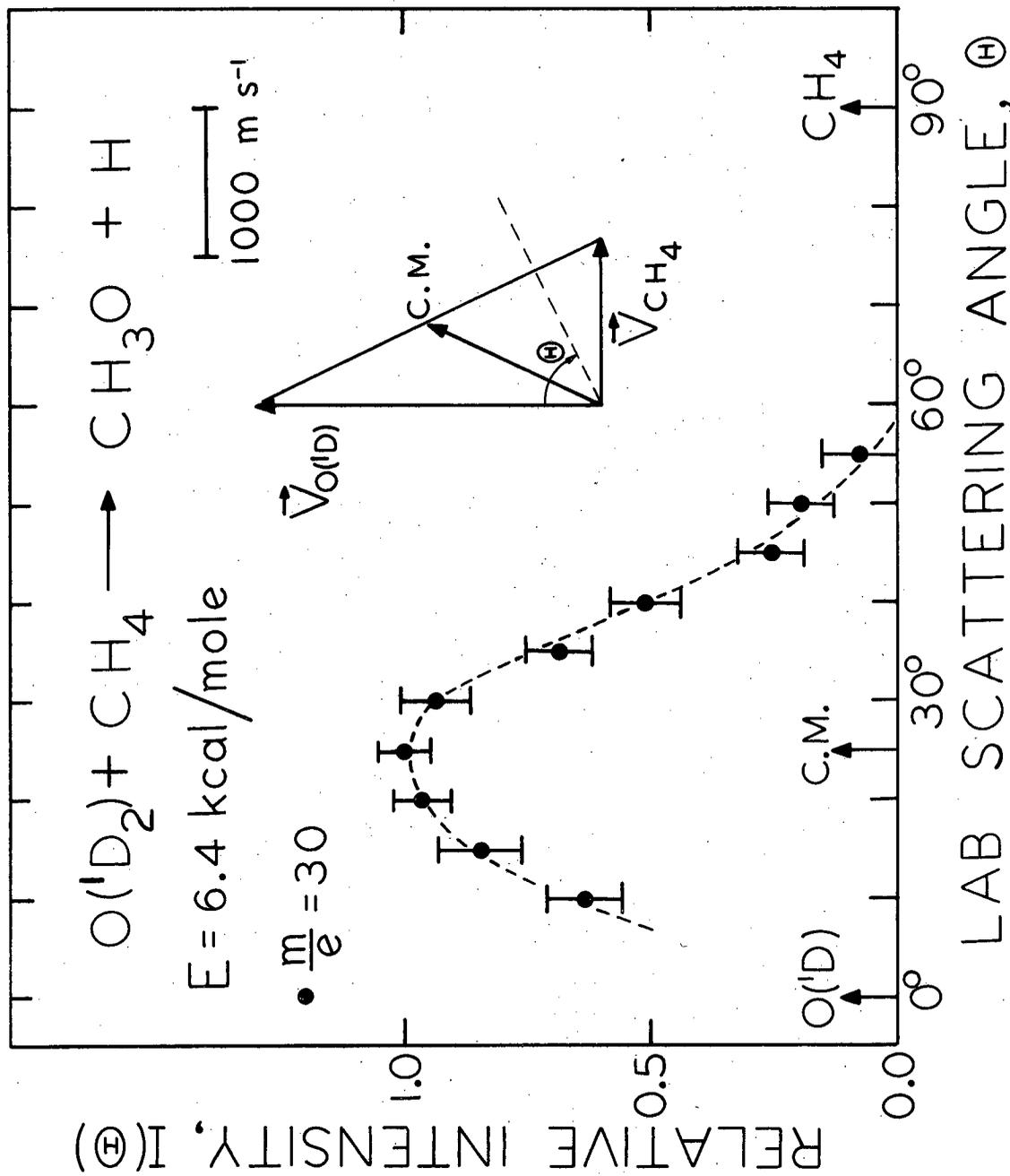


Fig. 1

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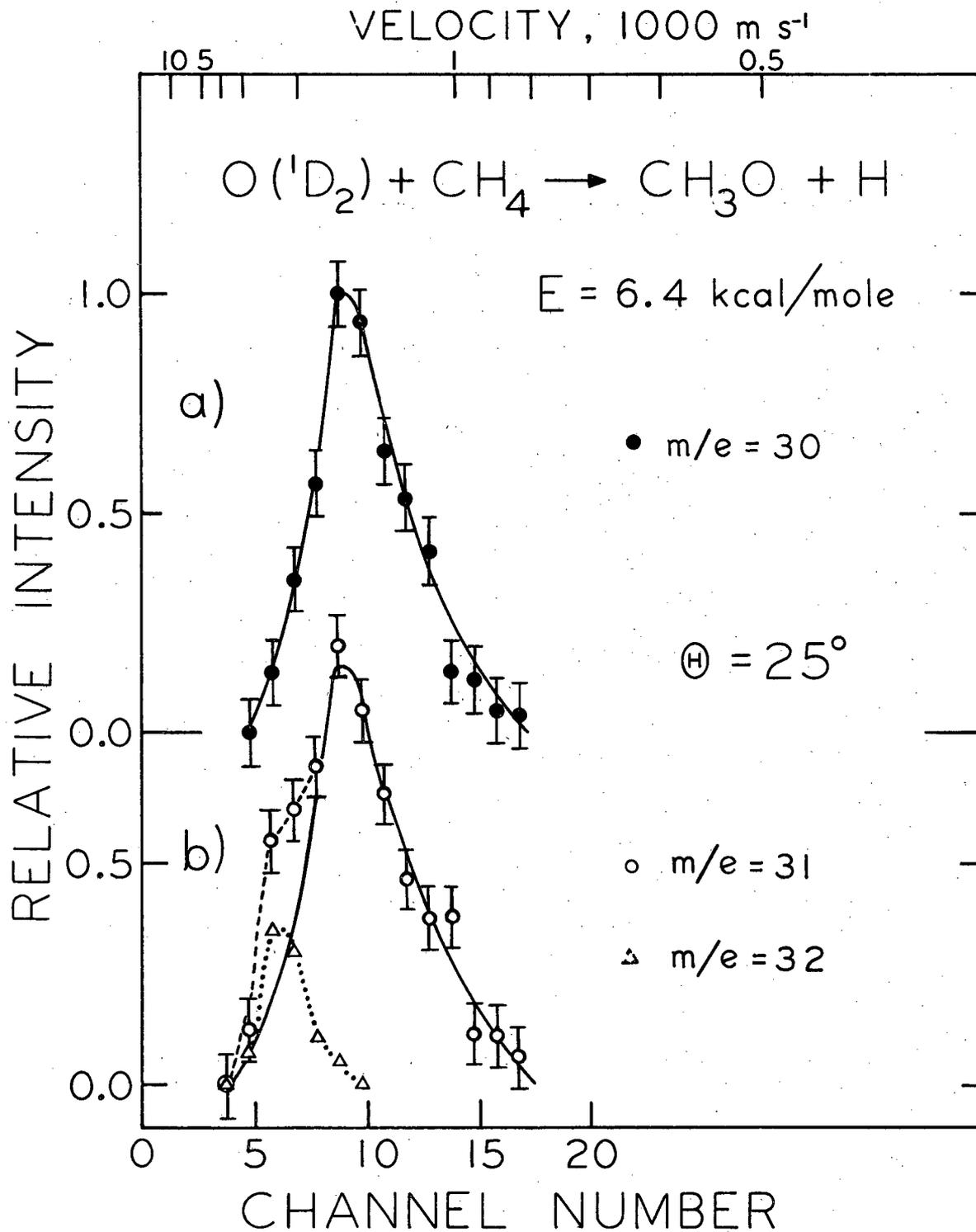


Fig. 2

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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