

## ENHANCEMENT OF DEUTERATED ETHANE ON JUPITER

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### ABSTRACT

We report laboratory measurements of cross sections of  $\text{CH}_3\text{D}$  and  $\text{C}_2\text{H}_5\text{D}$  in the extreme ultraviolet. The results are incorporated in a photochemical model for the deuterated hydrocarbons up to C2 in the upper atmosphere of Jupiter, taking into account the fast reactions for exchanging H and D atoms between  $\text{H}_2$  and  $\text{CH}_4$ ,  $\text{H} + \text{HD} \leftrightarrow \text{D} + \text{H}_2$ ,  $\text{CH}_3 + \text{D} \leftrightarrow \text{CH}_2\text{D} + \text{H}$ . Since there is no reliable kinetics measurement for the reaction,  $\text{CH}_2\text{D} + \text{H} \rightarrow \text{CH}_3 + \text{D}$ , we use Yung et al.'s estimate for its rate constant. The strong temperature dependence for this reaction leads to large isotopic fractionation for  $\text{CH}_3\text{D}$  and  $\text{C}_2\text{H}_5\text{D}$  in the upper atmosphere of Jupiter, where their production rates depend on the abundance of deuterated methyl radical. The model predicts that the D/H ratio in deuterated ethane is about 15 times that of the bulk atmosphere. A confirmation of this result would provide a sensitive test of the photochemistry of hydrocarbons in the atmosphere of Jupiter.

*Subject heading:* planets and satellites: individual (Jupiter)

### 1. INTRODUCTION

Extensive observations of D/H ratios of  $\text{H}_2$  and  $\text{CH}_4$  in the atmosphere of Jupiter have been carried out in recent years. The  $(\text{D}/\text{H})_{\text{H}_2}$  ratio ranges from  $2.2 \times 10^{-5}$  to  $2.6 \times 10^{-5}$  (Encrenaz et al. 1996; Mahaffy et al. 1998). The  $(\text{D}/\text{H})_{\text{CH}_4}$  ratio ranges from  $1.8 \times 10^{-5}$  to  $2.9 \times 10^{-5}$  (Feuchtgruber et al. 1999; Encrenaz et al. 1999). However, the D/H ratios for other hydrocarbons, especially  $\text{C}_2\text{H}_6$ , are unknown. The deuterated compounds in the upper atmospheres of giant planets have not been modeled, except for HD and  $\text{CH}_3\text{D}$  (e.g., Parkinson et al. 1999). The main reasons are the lack of photochemical and kinetics data related to the deuterated compounds.

In this Letter, we present measurements of absorption cross sections of the most important deuterated hydrocarbons,  $\text{CH}_3\text{D}$  and  $\text{C}_2\text{H}_5\text{D}$ , in the extreme ultraviolet (EUV) and preliminary results of a photochemical model of deuterated hydrocarbons in the stratosphere of Jupiter. There are three major mechanisms for deuterium-hydrogen fractionation: (1) the difference in photolysis rates between  $\text{CH}_4$  and  $\text{CH}_3\text{D}$  and between  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_5\text{D}$ ; (2) the difference in molecular diffusion rates in the upper atmosphere between hydrogen and deuterium species; and (3) the different exchange rates between deuterated and nondeuterated species; e.g., the rate coefficients of the reactions  $\text{H} + \text{CH}_2\text{D} \leftrightarrow \text{D} + \text{CH}_3$  are different in the forward and backward directions. Models incorporating the above mechanisms show that the  $(\text{D}/\text{H})_{\text{C}_2\text{H}_6}$  may be enriched 1 order of magnitude relative to the  $(\text{D}/\text{H})_{\text{CH}_4}$  in the upper atmosphere of giant planets. This result implies that  $\text{C}_2\text{H}_5\text{D}$  may be readily detectable.

### 2. MEASUREMENTS OF $\text{CH}_3\text{D}$ AND $\text{C}_2\text{H}_5\text{D}$ ABSORPTION CROSS SECTIONS

A double-beam absorption cell, described previously (Cheng et al. 1999), was used to determine the cross sections of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and their deuterium isotopomers. The light source was synchrotron radiation dispersed by 1 m Seya Namioka monochromator. The monochromator was typically scanned in 0.1 nm steps

with a signal-averaging period of 2 s at each step. The absorption cell has an inner diameter of 39.5 mm and a path length of 171.7, 1133, 3288 mm (for  $\text{CH}_4$  and  $\text{CH}_3\text{D}$ ), or 553.9 mm (for  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_5\text{D}$ ). It has a pressure port connected with five calibrated MKS Baratron capacitance pressure meters (with varied ranges 1–10,000 torr, in steps of factors of 10). To avoid interference resulting from desorbed impurities and variations in cell temperature due to irradiation, a reservoir of 600  $\text{cm}^3$  in volume was connected to the cell.

One of the most important factors that demands great attention is to eliminate and to quantify minor impurities in samples.  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$  (both Matheson),  $\text{CH}_3\text{D}$ , and  $\text{C}_2\text{H}_5\text{D}$  (both Cambridge Isotope Laboratories, isotopic purity 98.8%) have listed chemical purities of 99.999%, 99.99%, 98.7%, and 99.8%, respectively. To purify  $\text{CH}_4$  and  $\text{CH}_3\text{D}$ , we set up a vacuum distillation system and connected it with a White cell coupled with a Fourier transform infrared spectrometer. A copper cell  $\sim 15 \text{ cm}^3$  in volume was affixed on one end to a cold head of a cryostat cooled by a compressor so that the sample may be trapped at varied temperature for distillation. From IR analysis of the purified  $\text{CH}_4$  sample we found no evidence of  $\text{H}_2\text{O}$  or  $\text{CO}_2$ . We estimated an upper limit of 0.2 parts per million (ppm) for these impurities. About 620 ppm of  $\text{CH}_3\text{D}$  in natural abundance was also determined. For the purified  $\text{CH}_3\text{D}$  sample, impurities  $\text{CDCl}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and other organics were successfully eliminated at the first cycle of the purification. The impurity level of CO ( $\sim 0.3\%$ ) remained roughly the same even after repeated cycles of vacuum distillation. No spectroscopic evidence of  $\text{CH}_4$  or higher deuterated species  $\text{CH}_2\text{D}_2$ ,  $\text{CHD}_3$ , and  $\text{CD}_4$  was detected. The remaining fraction of oxygen is 2970 ppm, indicating a reduction by  $\sim 45\%$  after purification. It appears that traces of CO and  $\text{O}_2$  cannot be separated from  $\text{CH}_4$  ( $\text{CH}_3\text{D}$ ) by vacuum distillation.  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_5\text{D}$  were vacuum-distilled between 77 and 195 K and then slowly passed through a Pd/charcoal activated absorbant at 195 K. After purification, no  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ , or  $\text{O}_2$  was detectable in the vacuum UV spectrum.

TABLE 1  
PARTIAL LIST OF DEUTERIUM-RELATED HYDROCARBON REACTIONS

Base Reaction	Base Rate Coefficient	References	Branchings	Ratio
Photodissociation Reactions				
(R1) $\text{CH}_4 + h\nu \rightarrow \text{CH}_3 + \text{H}$ .....	$J_1$	1	(R2) $\text{CH}_3\text{D} + h\nu \rightarrow \text{CH}_2\text{D} + \text{H}$	3/4
(R4) $\text{CH}_4 + h\nu \rightarrow {}^1\text{CH}_2 + \text{H}_2$ .....	$J_4$	2	(R3) $\text{CH}_3\text{D} + h\nu \rightarrow \text{CH}_3 + \text{D}$	1/4
(R7) $\text{CH}_4 + h\nu \rightarrow {}^1\text{CH}_2 + 2\text{H}$ .....	$J_7$	2	(R5) $\text{CH}_3\text{D} + h\nu \rightarrow {}^1\text{CHD} + \text{H}_2$	1/2
(R10) $\text{CH}_4 + h\nu \rightarrow {}^3\text{CH}_2 + 2\text{H}$ .....	$J_{10}$	2	(R6) $\text{CH}_3\text{D} + h\nu \rightarrow {}^1\text{CH}_2 + \text{HD}$	1/2
(R13) $\text{CH}_4 + h\nu \rightarrow \text{CH} + \text{H} + \text{H}_2$ .....	$J_{13}$	2	(R8) $\text{CH}_3\text{D} + h\nu \rightarrow {}^1\text{CHD} + 2\text{H}$	1/2
(R17) $\text{C}_2\text{H}_2 + h\nu \rightarrow \text{C}_2\text{H} + \text{H}$ .....	$J_{17}$	2	(R9) $\text{CH}_3\text{D} + h\nu \rightarrow {}^1\text{CH}_2 + \text{H} + \text{D}$	1/2
(R20) $\text{C}_2\text{H}_4 + h\nu \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$ .....	$J_{20}$	2	(R11) $\text{CH}_3\text{D} + h\nu \rightarrow {}^3\text{CHD} + 2\text{H}$	1/2
(R23) $\text{C}_2\text{H}_4 + h\nu \rightarrow \text{C}_2\text{H}_2 + 2\text{H}$ .....	$J_{23}$	2	(R12) $\text{CH}_3\text{D} + h\nu \rightarrow {}^3\text{CH}_2 + \text{H} + \text{D}$	1/2
(R26) $\text{C}_2\text{H}_6 + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ .....	$J_{26}$	2	(R14) $\text{CH}_3\text{D} + h\nu \rightarrow \text{CD} + \text{H} + \text{H}_2$	1/4
(R29) $\text{C}_2\text{H}_6 + h\nu \rightarrow \text{C}_2\text{H}_4 + 2\text{H}$ .....	$J_{29}$	2	(R15) $\text{CH}_3\text{D} + h\nu \rightarrow \text{CH} + \text{D} + \text{H}_2$	1/4
			(R16) $\text{CH}_3\text{D} + h\nu \rightarrow \text{CH} + \text{H} + \text{HD}$	1/2
			(R18) $\text{C}_2\text{HD} + h\nu \rightarrow \text{C}_2\text{D} + \text{H}$	1/2
			(R19) $\text{C}_2\text{HD} + h\nu \rightarrow \text{C}_2\text{H} + \text{D}$	1/2
			(R21) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{HD} + \text{H}_2$	1/2
			(R22) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{H}_2 + \text{HD}$	1/2
			(R24) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{HD} + 2\text{H}$	1/2
			(R25) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{H}_2 + \text{H} + \text{D}$	1/2
			(R27) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}_2$	2/3
			(R28) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{HD}$	1/3
			(R30) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{H}_3\text{D} + 2\text{H}$	2/3
			(R31) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{H} + \text{D}$	1/3
Chemical Reactions				
(R32) $\text{H} + {}^1\text{CH}_2 \rightarrow \text{CH} + \text{H}_2$ .....	$2.0 \times 10^{-10}$	3	(R33) $\text{H} + {}^1\text{CHD} \rightarrow \text{CD} + \text{H}_2$	1/2
(R35) $\text{H} + {}^3\text{CH}_2 \rightarrow \text{CH} + \text{H}_2$ .....	$2.66 \times 10^{-10}$	4	(R34) $\text{H} + {}^1\text{CHD} \rightarrow \text{CH} + \text{HD}$	1/2
(R38) $\text{H} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2$ .....	$3.37 \times 10^{-20} T^3 e^{-4406/T}$	2	(R36) $\text{H} + {}^3\text{CHD} \rightarrow \text{CD} + \text{H}_2$	1/2
(R41) $\text{H} + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$ .....	$2.0 \times 10^{-11}$	5	(R37) $\text{H} + {}^3\text{CHD} \rightarrow \text{CH} + \text{HD}$	1/2
(R44) $\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ .....	$3.0 \times 10^{-12}$	6	(R39) $\text{H} + \text{CH}_3\text{D} \rightarrow \text{CH}_2\text{D} + \text{H}_2$	3/4
(R47) $\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{H}_2$ .....	$2.35 \times 10^{-15} T^{-1.5} e^{-3725/T}$	7	(R40) $\text{H} + \text{CH}_3\text{D} \rightarrow \text{CH}_3 + \text{HD}$	1/4
(R50) $\text{CH} + \text{H}_2 \rightarrow {}^3\text{CH}_2 + \text{H}$ .....	$3.75 \times 10^{-11} e^{-1662/T}$	8	(R42) $\text{H} + \text{C}_2\text{H}_2\text{D} \rightarrow \text{C}_2\text{HD} + \text{H}_2$	2/3
(R53) $\text{CH} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + \text{H}$ .....	$5.0 \times 10^{-11} e^{200/T}$	9	(R43) $\text{H} + \text{C}_2\text{H}_2\text{D} \rightarrow \text{C}_2\text{H}_2 + \text{HD}$	1/3
(R58) $\text{CH} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3$ .....	$2.23 \times 10^{-10} e^{173/T}$	10	(R45) $\text{H} + \text{C}_2\text{H}_4\text{D} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}_2$	3/5
(R61) ${}^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$ .....	$9.24 \times 10^{-11}$	11	(R46) $\text{H} + \text{C}_2\text{H}_4\text{D} \rightarrow \text{C}_2\text{H}_4 + \text{HD}$	2/5
(R64) ${}^3\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}$ .....	$7.0 \times 10^{-11}$	7	(R48) $\text{H} + \text{C}_2\text{H}_3\text{D} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}_2$	5/6
(R67) ${}^3\text{CH}_2 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3$ .....	$8.0 \times 10^{-11}$	3	(R49) $\text{H} + \text{C}_2\text{H}_3\text{D} \rightarrow \text{C}_2\text{H}_3 + \text{HD}$	1/6
(R70) ${}^3\text{CH}_2 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$ .....	$8.0 \times 10^{-11}$	3	(R51) $\text{CH} + \text{HD} \rightarrow {}^3\text{CHD} + \text{H}$	1/2
(R73) $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$ .....	$6.6 \times 10^{-20} T^{2.24} e^{-3220/T}$	12	(R52) $\text{CH} + \text{HD} \rightarrow {}^3\text{CH}_3 + \text{D}$	1/2
(R76) $\text{CH}_3 + \text{C}_2\text{H}_3 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_2$ .....	$3.4 \times 10^{-11}$	13	(R54) $\text{CH} + \text{CH}_3\text{D} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}$	4/5
(R79) $\text{CH}_3 + \text{C}_2\text{H}_5 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4$ .....	$2.0 \times 10^{-12}$	7	(R55) $\text{CH} + \text{CH}_3\text{D} \rightarrow \text{C}_2\text{H}_4 + \text{D}$	1/5
(R82) $\text{C}_2 + \text{CH}_4 \rightarrow \text{C}_2\text{H} + \text{CH}_3$ .....	$5.05 \times 10^{-11} e^{-297/T}$	14	(R56) $\text{CD} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}$	4/5
(R85) $\text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}$ .....	$1.2 \times 10^{-11} e^{-998/T}$	15	(R57) $\text{CD} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + \text{D}$	1/5
(R88) $\text{C}_2\text{H} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3$ .....	$1.2 \times 10^{-11} e^{-491/T}$	16	(R59) $\text{CH} + \text{C}_2\text{H}_2\text{D} \rightarrow \text{C}_2\text{HD} + \text{CH}_3$	1/2
(R91) $\text{C}_2\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_5$ .....	$3.5 \times 10^{-11} e^{3/T}$	15	(R60) $\text{CH} + \text{C}_2\text{H}_3\text{D} \rightarrow \text{C}_2\text{H}_2 + \text{CH}_2\text{D}$	1/2
(R94) $\text{C}_2\text{H}_3 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}$ .....	$5 \times 10^{-20} T^{2.63} e^{-4298/T}$	17	(R62) ${}^1\text{CH}_2 + \text{HD} \rightarrow \text{CH}_2\text{D} + \text{H}$	1/2
(R97) $2\text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$ .....	$2.4 \times 10^{-11}$	13	(R63) ${}^1\text{CH}_2 + \text{HD} \rightarrow \text{CH}_3 + \text{D}$	1/2
(R100) $2\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$ .....	$2.4 \times 10^{-12}$	7	(R65) ${}^3\text{CH}_2 + \text{CH}_2\text{D} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}$	4/5
			(R66) ${}^3\text{CH}_2 + \text{CH}_2\text{D} \rightarrow \text{C}_2\text{H}_4 + \text{D}$	1/5
			(R68) ${}^3\text{CH}_2 + \text{C}_2\text{H}_2\text{D} \rightarrow \text{C}_2\text{HD} + \text{CH}_2$	2/3
			(R69) ${}^3\text{CH}_2 + \text{C}_2\text{H}_3\text{D} \rightarrow \text{C}_2\text{H}_2 + \text{CH}_2\text{D}$	1/3
			(R71) ${}^3\text{CH}_2 + \text{C}_2\text{H}_3\text{D} \rightarrow \text{C}_2\text{H}_2\text{D} + \text{CH}_3$	4/5
			(R72) ${}^3\text{CH}_2 + \text{C}_2\text{H}_4\text{D} \rightarrow \text{C}_2\text{H}_4 + \text{CH}_2\text{D}$	1/5
			(R74) $\text{CH}_3 + \text{HD} \rightarrow \text{CH}_2\text{D} + \text{H}$	1/2
			(R75) $\text{CH}_3 + \text{HD} \rightarrow \text{CH}_4 + \text{D}$	1/2
			(R77) $\text{CH}_3 + \text{C}_2\text{H}_2\text{D} \rightarrow \text{CH}_4 + \text{C}_2\text{HD}$	2/3
			(R78) $\text{CH}_3 + \text{C}_2\text{H}_2\text{D} \rightarrow \text{CH}_3\text{D} + \text{C}_2\text{H}_2$	1/3
			(R80) $\text{CH}_3 + \text{C}_2\text{H}_4\text{D} \rightarrow \text{CH}_4 + \text{C}_2\text{H}_3\text{D}$	4/5
			(R81) $\text{CH}_3 + \text{C}_2\text{H}_4\text{D} \rightarrow \text{CH}_3\text{D} + \text{C}_2\text{H}_4$	1/5
			(R83) $\text{C}_2 + \text{CH}_3\text{D} \rightarrow \text{C}_2\text{H} + \text{CH}_2\text{D}$	3/4
			(R84) $\text{C}_2 + \text{CH}_3\text{D} \rightarrow \text{C}_2\text{D} + \text{CH}_3$	1/4
			(R86) $\text{C}_2\text{H} + \text{HD} \rightarrow \text{C}_2\text{H}_2 + \text{D}$	1/2
			(R87) $\text{C}_2\text{H} + \text{HD} \rightarrow \text{C}_2\text{HD} + \text{H}$	1/2
			(R89) $\text{C}_2\text{H} + \text{CH}_3\text{D} \rightarrow \text{C}_2\text{H}_2 + \text{CH}_2\text{D}$	3/4
			(R90) $\text{C}_2\text{H} + \text{CH}_3\text{D} \rightarrow \text{C}_2\text{HD} + \text{CH}_3$	1/4
			(R92) $\text{C}_2\text{H} + \text{C}_2\text{H}_5\text{D} \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4\text{D}$	5/6
			(R93) $\text{C}_2\text{H} + \text{C}_2\text{H}_5\text{D} \rightarrow \text{C}_2\text{HD} + \text{C}_2\text{H}_5$	1/6
			(R95) $\text{C}_2\text{H}_3 + \text{HD} \rightarrow \text{C}_2\text{H}_4 + \text{D}$	1/2
			(R96) $\text{C}_2\text{H}_3 + \text{HD} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}$	1/2
			(R98) $\text{C}_2\text{H}_3 + \text{C}_2\text{H}_2\text{D} \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{HD}$	2/3
			(R99) $\text{C}_2\text{H}_3 + \text{C}_2\text{H}_2\text{D} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{C}_2\text{H}_2$	1/3
			(R101) $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4\text{D} \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_3\text{D}$	4/5
			(R102) $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4\text{D} \rightarrow \text{C}_2\text{H}_5\text{D} + \text{C}_2\text{H}_4$	1/5

TABLE 1  
(CONTINUED)

Base Reaction	Base Rate Coefficient	References	Branchings	Ratio
(R103) $D + H_2 \rightarrow H + HD$ .....	$4.0 \times 10^{-18} T^{2.29} e^{-2627/T}$	18	...	...
(R104) $H + HD \rightarrow D + H_2$ .....	$2.0 \times 10^{-18} T^{2.29} e^{-2627/T}$ (est. by $k_{103}/2$ )		...	...
(R105) $D + CH_3 \rightarrow H + CH_2D$ .....	$2.3 \times 10^{-10}$	19	...	...
(R106) $H + CH_2D \rightarrow D + CH_3$ .....	$1.34 \times 10^{-10} e^{-810/T}$ (est. by $k_{105}/K$ )	20	...	...

NOTE.—Rate constants are relative to nondeuterated reactions.

REFERENCES.—(1) Heck, Zare, & Chandler 1996; (2) Gladstone et al. 1996; (3) Moses et al. 2000; (4) Boullart & Peeters 1992; (5) Baulch et al. 1994; (6) Tsang & Hampson 1986; (7) Baulch et al. 1992; (8) Becker et al. 1991; (9) Berman & Lin 1983; (10) Berman et al. 1982; (11) Langford, Petek, & Moore 1983; (12) Rabinowitz et al. 1991; (13) Fahr et al. 1991; (14) Pitts et al. 1982; (15) Opansky & Leone 1996b; (16) Opansky & Leone 1996a; (17) Fahr & Laufer 1995; (18) Michael & Fisher 1990; (19) Seakins et al. 1997; (20) Yung et al. 1988.

At each wavelength, absorbance was plotted against number density and fitted to a line by least-squares to yield the absorption cross section of the sample. The resultant absorption cross sections of  $CH_4$  and  $CH_3D$  (and  $C_2H_6$  and  $C_2H_5D$ ) in the spectral range 105–150 (and 105–161) nm are shown in Figure 1. Our  $CH_4$  and  $C_2H_6$  spectra are nearly identical to those of Mount, Warden, & Moos (1977). Near the threshold region, our values are smaller because our samples are free from interferences from absorption of trace impurities (M. Bahou et al. 2001, in preparation). Note that the cross sections of the heavier isotopomers deviate around 132 nm, as would be expected on the basis of the zero-point energy theory of Yung & Miller (1997).

### 3. KINETICS AND PHOTOCHEMICAL MODEL

On the basis of the models of Gladstone, Allen, & Yung (1996) and Lee et al. (2000), we develop a model with deuterated C1 and C2 species. We assume no difference between kinetics of deuterated hydrocarbons and their corresponding nondeuterated hydrocarbons for most reactions. However, the branching ratios for photodissociation of the deuterated species could be different. A partial list of deuterated reactions is presented in Table 1. Two pairs of fast isotope exchange reactions between  $HD/H_2$  and  $CH_3D/CH_4$ ,  $H + HD \leftrightarrow D + H_2$  and  $CH_3 + D \leftrightarrow CH_2D + H$ , have been included in the model. We adopt rate constants for  $H + HD \leftrightarrow D + H_2$  (R103 and R104 in Table 1) suggested by Michael & Fisher (1990). Seakins et

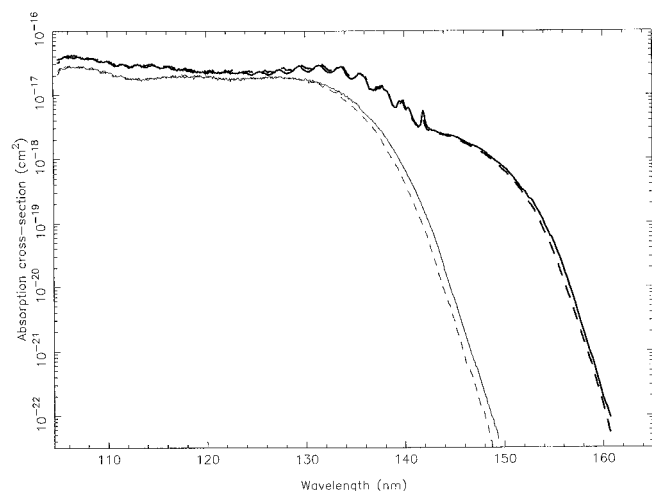


FIG. 1.—Laboratory measurements of absorption cross sections of  $CH_4$  (thin solid line) and  $CH_3D$  (thin dashed line) for wavelengths from 105 to 150 nm and cross sections of  $C_2H_6$  (thick solid line) and  $C_2H_5D$  (thick dashed line) for wavelengths from 105 to 161 nm. The measurements were taken at 295 K with approximately 0.1 nm resolution.

al. (1997) determined the rate constant for reaction of methyl radical and deuterium atom,  $CH_3 + D \rightarrow CH_2D + H$  (R105). Since there is no reliable kinetics measurement for its reverse reaction,  $CH_2D + H \rightarrow CH_3 + D$  (R106), we use the value derived by Yung et al. (1988). These authors computed the equilibrium constant  $K = 1.72e^{810/T}$  for the  $D + CH_3 \leftrightarrow H + CH_2D$  exchange reaction.

### 4. RESULTS AND DISCUSSION

We studied several cases for testing the isotopic fractionation of hydrocarbons in the upper atmosphere of Jupiter. In all models, we assume that  $[HD]/[H_2] = 4.4 \times 10^{-5}$  and the mixing ratio for  $CH_3D$  is  $2.5 \times 10^{-7}$  at the lower boundary. These cases include the following: (1) identical weight for H and D, no fractionation for cross sections, and exclusion of the isotopic exchange reactions; (2) different atomic weights for diffusive separation of H and D; (3) new cross sections of  $CH_3D$  and  $C_2H_5D$ ; (4) no fractionation for  $D + CH_3 \leftrightarrow H + CH_2D$  exchange reactions; and (5) inclusion of fractionation for the previous exchange reactions. Results of the model calculations are shown in Figure 2. In all the figures, solid lines represent  $(D/H)_{CH_4}$ , and dashed lines represent  $(D/H)_{C_2H_6}$ . In Figure 2a

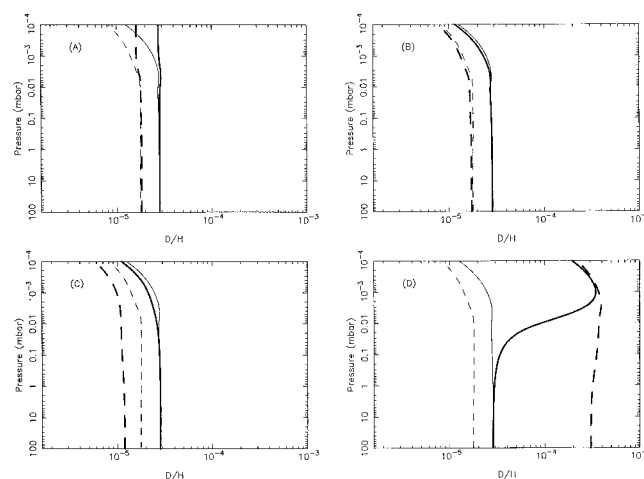


FIG. 2.—D/H ratios for  $CH_4$  and  $C_2H_6$  in our model. Solid lines are values of  $(D/H)_{CH_4}$ , and dashed lines are values of  $(D/H)_{C_2H_6}$ . (a) The thick lines are for the case assuming H and D species have identical masses, no difference in EUV cross sections, and no  $D + CH_3 \leftrightarrow H + CH_2D$  exchange reactions. The thin lines are for the case in which H and D species have different atomic weights. (b) The thin lines denote the same case as in (a). The thick lines are for the case in which  $CH_3D$  and  $C_2H_5D$  have different cross sections. (c) The thin lines denote the same case as in (a). The thick lines are for the case with rate constants for the forward and backward reactions  $D + CH_3 \leftrightarrow H + CH_2D$  in the ratio of 3 : 1. (d) The standard model. The thin lines denote the same case as in (a). The thick lines are for the case with different rate constants for both directions of the exchange reaction, as given in Table 1.

the thick lines are for the case assuming identical masses for H and D species, no difference in EUV cross sections, and no  $D + CH_3 \leftrightarrow H + CH_2D$  exchange reactions. The thin lines are for the case in which H and D species have different atomic weights. Note that the decrease of D/H values in the upper atmosphere for thin lines is due to different molecular masses. In Figure 2*b*, thin lines denote the same case as in Figure 2*a*. The thick lines are for the case in which  $CH_3D$  and  $C_2H_5D$  have different cross sections, taken from Figure 1. The small difference indicates that fractionation due to photolysis is less important than that of chemical reactions (see below). The two cases described above do not include the exchange reactions  $D + CH_3 \leftrightarrow H + CH_2D$ .

Figure 2*c* shows the effect of including the exchange reaction  $D + CH_3 \leftrightarrow H + CH_2D$  in the model. The thin lines denote the same case as in Fig. 2*a*. The thick lines are for the case in which the ratio of rate coefficients for the forward and the backward reaction is taken to be the stoichiometric value of 3 (Yung et al. 1988). A similar estimate for exchange reactions  $D + H_2 \leftrightarrow H + HD$  in this case adopts the ratio of 2 : 1 rate coefficients for the forward and the backward reaction. The standard model is shown in Figure 2*d*. The thin lines denote the same case as in Figure 2*a*. The thick lines are for the case with different rate constants for both directions of the exchange

reaction, as given in Table 1. The highly enriched  $(D/H)_{CH_4}$  and  $(D/H)_{C_2H_6}$  values for the last case are caused by the temperature-dependent equilibrium constant for the exchange reaction. At a typical temperature of 150 K for the Jovian upper stratosphere, the equilibrium constant  $K$  for  $D + CH_3 \leftrightarrow H + CH_2D$  is 381, which results in a much higher production rate for  $CH_2D$ . Consequently, the D/H ratio for  $C_2H_6$  is an order of magnitude larger than that for  $CH_4$ . Thus, the model predicts a result that can be tested by the determination of the abundance of  $C_2H_5D$  in the upper atmosphere of Jupiter. The nature of the temperature dependence of this fractionation factor implies even larger isotopic enrichment in the outer solar system. Thus, we expect that in the other giant planets' atmospheres, such as Saturn's, the D/H fractionation factor is even larger than in Jupiter because of their lower stratospheric temperatures. However, the fractionation may be modified by the exchange of D atoms with vibrationally excited  $H_2$  (C. Parkinson 2000, private communication). The Cassini mission may provide observational evidence for the enrichment of deuterated ethane in the upper atmosphere of Saturn.

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