H/D fragment ratio in Lyman-α photolysis of CH₂D₂

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The photofragment imaging technique is used to study the formation of H and D in the photolysis of CH₂D₂. From the images different reaction channels are distinguished that lead to hydrogen fragments. For the channel that leads to hydrogen atoms concomitant with methyl fragments a H/D ratio of 3.5±0.6 is found. © 1996 American Institute of Physics. [S0021-9606(96)03709-0]

INTRODUCTION

Methane photolysis is of interest in the atmospheres of the earth and other planets.¹,² The first excited electronic state of methane is located approximately 8.7 eV above the ground state.³,⁴ Therefore, the photochemistry of methane in the atmosphere is mostly driven by intense solar atomic emission lines, such as Lyman-α radiation. At photon energies corresponding to Lyman α only the lowest singlet, ¹T₂, electronic state can be accessed. The ¹T₂ electronic state is believed to have a short lifetime with respect to dissociation, which partly explains the observed broad and diffuse absorption band.³,⁴ The ¹T₂ state correlates adiabatically with the ¹CH₂ (¹B₁) + H₂ products.⁵,⁶ A study by Mordaunt et al.⁷ and our study on methane⁸ revealed that the formation of methyl fragments concomitant with hydrogen atoms is the dominant channel in the Lyman-α photolysis of methane. Additionally, these studies indicated that at least one alternative channel produces hydrogen atoms in the VUV photolysis of methane.

In this paper we present results on the formation of H and D from the Lyman-α photolysis of CH₂D₂. The photofragment imaging technique⁹,¹⁰ enables us to derive the relative contributions from the channels that lead to formation of H and/or D fragments from the photolysis of CH₂D₂. We find that the dominant channel (>80%) leads to hydrogen fragments concomitant with methyl fragments; an alternative channel proceeds via three-body dissociations, which lead to CH⁺H⁺H₂ fragments and/or CH₂⁺H⁺H fragments. We observe a significant preference for formation of H over D photofragments from the photolysis of CH₂D₂. The isotope effects are very different for the channels that lead to (a) H atoms concomitant with CH₃ fragments, and (b) H atoms concomitant with CH⁺H₂ and/or CH₂⁺H fragments. We compare this H/D isotope effect with the results from studies on other small polyatomics, such as water and triplet methylene, and note interesting similarities.

RESULTS

In Fig. 1 a REMPI spectrum of the atomic photofragments from CH₂D₂ is shown, for which the laser is scanned over a wavelength range that includes the H and D transitions, while collecting all ions with masses between 0.1 and 5. The signals are centered around 121.53 nm and 121.57 nm correspond with m/z = 2 signal (D atoms) and m/z = 1 (H atoms), respectively. By integrating these ion signals separately we find that the σH/σD branching ratio is 3.0 for this particular scan. From a series of 8 repeated scans an averaged σH/σD value of 3.1±0.5 is found. When the molecular beam is not fired, a small (less than 2%) H-atom background signal is observed (no significant D-atom background signal), which is neglected. To extract quantitative data from these ion spectra care is taken that the UV laser power is constant over the wavelength range scanned. Although frequency tripling in a phase-matched Kr/Ar mixture is bandwidth limited, our experimental arrangement (the length of the tripling cell and focal length of the used lens being im-
important parameters) ensures that the generated VUV power is constant over the 0.07 nm VUV wavelength range scanned. Nonetheless, scans were taken with the Ar/Kr mixture optimized on the H, and alternatively the D ion signals. This procedure leads to similar $\sigma_H/\sigma_D$ branching ratios.

Additionally, we measured images of H and D photofragments from the photolysis of CH2D2. These photofragment images are recorded while the laser is scanned over the entire H or D atom Doppler profiles. An H-atom photofragment image of the Lyman-$\alpha$ photolysis of CH4 has been presented previously. Qualitatively, the recorded H and D photofragment images of the photolysis of CH2D2 are similar to the photofragment image of the H-atom photofragments from the Lyman-$\alpha$ photolysis of CH4. Two distinct rings are observed in all images—the inner one is isotropic and the outer one anisotropic. Figures 2(a)–(d) show the speed distributions of the hydrogen-atom photofragments following the photolysis of CH2D2 [Figs. 2(c) and 2(d)], and, for comparison, CH4 [Fig. 2(a)] and CD4 [Fig. 2(b)]. These speed distributions show the two distinct channels that lead to hydrogen atoms in the photolysis of methane.

**DISCUSSION**

**Ion images**

The fast channel observed in the photofragment images can only be attributed to hydrogen atoms formed concomitant with methyl fragments,

$I(\theta) \approx 1 + \beta_2 P_2(\cos \theta),$

where $P_2(\cos \theta)$ is the second-order Legendre polynomial and $\beta_2$ is the anisotropy parameter. The resulting anisotropy parameters are compared to those for CH4 and CD4 in Table I. The anisotropy parameters range between 0.20 and 0.28, which indicates that the excited methane molecules have a relatively short lifetime prior to dissociation via this channel and that the transition has predominately parallel character.

The mechanism that leads to the slower hydrogen atoms cannot be assigned unambiguously. Contributions from the following channels are possible:

![Graphical representation of ion intensity versus VUV wavelength](image)

**FIG. 1.** REMPI spectrum of the atomic photofragments from the Lyman-$\alpha$ photolysis of CH2D2. The laser is scanned over the 121.52 to 121.59 nm wavelength range, which includes H and D transitions. The signal centered around 121.53 nm corresponds to $m/z=2$ signal (D atoms), the signal centered near 121.57 nm corresponds to $m/z=1$ (H atoms). By integrating these ion signals a $\sigma_H/\sigma_D$ branching ratio of 3.0 is found for this particular scan.

**FIG. 2.** Speed distributions of atomic hydrogen photofragments following absorption of a Lyman-$\alpha$ photon in methane. (a) H-photofragments of CH4. (b) D-photofragments of CD4. (c) H-photofragments of CH2D2. (d) D-photofragments of CH2D2.

**TABLE I.** Branching ratios of the slow and fast channel, and anisotropy parameter for the fast channel in the H/D photofragment images.

<table>
<thead>
<tr>
<th>Parent</th>
<th>Fragment</th>
<th>% Slow channel</th>
<th>% Fast channel</th>
<th>$\beta$ Fast channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>H</td>
<td>13</td>
<td>87</td>
<td>0.28</td>
</tr>
<tr>
<td>CH2D2</td>
<td>H</td>
<td>8</td>
<td>92</td>
<td>0.25</td>
</tr>
<tr>
<td>CH3D2</td>
<td>D</td>
<td>19</td>
<td>81</td>
<td>0.25</td>
</tr>
<tr>
<td>CD4</td>
<td>D</td>
<td>12</td>
<td>88</td>
<td>0.20</td>
</tr>
</tbody>
</table>
calculated and exhibits no activation barrier.\textsuperscript{14,15} The energetic threshold for this channel is only 4.48 eV. Therefore, excitation of methane at Lyman \(\alpha\) brings the molecule high above the energetic threshold for formation of atomic hydrogen photofragments. Additionally, excitation at Lyman \(\alpha\) is approximately 1.5 eV higher in energy than the bandhead of the first absorption band of methane.\textsuperscript{7} The large isotope effect may seem at first to be somewhat surprising, but it is not unprecedented. Studies on other small polyatomics have revealed large H/D isotope effects.\textsuperscript{16}

Selective photolytic X–H/X–D bond breaking has been demonstrated experimentally and predicted theoretically for small molecules such as water,\textsuperscript{17–22} triplet methylene,\textsuperscript{23} acetylene,\textsuperscript{24} and ethylene.\textsuperscript{25} These studies reveal that, in general, the \(\sigma_{H}/\sigma_{D}\) branching ratios depend on the excitation energy, and the initial state of the molecules. Although the largest isotope effects are predicted to occur when the excitation is at the leading, low-energy part of the absorption band, recent theoretical calculations also predict large isotope effects when the excitation is significantly shifted to higher energies.\textsuperscript{17–20,23} A similar feature was found in the correlation between \(\sigma_{H}/\sigma_{D}\) branching ratio and the excitation energy in theoretical studies on both HOD (Refs. 17–20) and triplet CHD (Ref. 23). The \(\sigma_{H}/\sigma_{D}\) branching ratio is calculated to be very high (>10) for excitation energies corresponding to the low energy side of the absorption spectrum. The \(\sigma_{H}/\sigma_{D}\) branching ratio drops to approximately 2 at “intermediate” excitation energies, but increases again at even higher excitation energies. The HOD dissociation has been studied experimentally\textsuperscript{21} and modeled theoretically\textsuperscript{18–20} following absorption of a 157 nm photon.\textsuperscript{18–20} This radiation excites the HOD molecule approximately 1.1 eV above the bandhead of the absorption band and 2.8 eV above the energetic threshold for dissociation. A \(\sigma_{H}/\sigma_{D}\) branching ratio of 4 is observed\textsuperscript{21} and theoretically predicted.\textsuperscript{18,20} Similarly, calculations predict a \(\sigma_{H}/\sigma_{D}\) branching ratio of 12 when triplet CHD is excited 1.5 eV above the bandhead of the absorption band, i.e., 2.6 eV above the dissociation threshold.\textsuperscript{23} In our experiments methane is excited 1.5 eV above the leading edge of the absorption spectrum and 5.7 eV above the threshold for dissociation. We observe a \(\sigma_{H}/\sigma_{D}\) branching ratio of 3.5±0.6 for the channel that produces hydrogen atoms concomitant with methyl fragments. The similarities observed in these different systems are quite remarkable.

The observed \(\sigma_{H}/\sigma_{D}\) branching ratio isotope effect of 3.5±0.6 following absorption at Lyman \(\alpha\) is certainly consistent with earlier studies. A more detailed interpretation of these isotope effects in the \(\sigma_{H}/\sigma_{D}\) branching ratio must

<p>| Table II. Branching ratios ((\sigma_{H}/\sigma_{D})) in the photolysis of CH(<em>{2})D(</em>{2}). |
|---------------------------------|---------------------------------|</p>
<table>
<thead>
<tr>
<th></th>
<th>(\sigma_{H}/\sigma_{D})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integrated</td>
<td>3.1±0.5</td>
<td>total yield of H/D atoms</td>
</tr>
<tr>
<td>Slow channel</td>
<td>1.3±0.4</td>
<td>CH(<em>{1})=CH(</em>{2})+H+H and/or</td>
</tr>
<tr>
<td>Fast channel</td>
<td>3.5±0.6</td>
<td>CH(_{2})=CH+H+H</td>
</tr>
</tbody>
</table>

Isotope effect in the photolysis of CH\(_{2}\)D\(_{2}\)

The integrated, relative yield of H and D photofragments from the photolysis of CH\(_{2}\)D\(_{2}\) is obtained from the REMPI scans (Fig. 1), and is 3.1±0.5. Our H and D photofragment images reveal, however, that different channels contribute to the formation of hydrogen atoms from the photolysis of methane. Using the photofragment imaging technique we can distinguish these channels, and derive their relative importance (see Table I), and obtain the \(\sigma_{H}/\sigma_{D}\) branching ratios for the different channels (see Table II). We find that the CH\(_{2}\)D\(_{2}\)=CHD\(_{2}\)+H channel is favored over the CH\(_{2}\)D\(_{2}\)=CH\(_{2}\)D+D by a factor 3.5±0.6. In the formation of hydrogen atoms via the combined channels II, III, and IV, the H over D ratio is much smaller, i.e., 1.3±0.4. Owing to the difficulty in assigning this channel we will not discuss it further here.

We consider the isotope effect observed in channel I as this channel is unambiguously assigned. The minimum energy path for breaking the CH\(_{2}\)=H bond in methane has been
await a theoretical calculation of the methane (and \( \text{CH}_2\text{D}_2 \))
dissociation dynamics on a reliable potential energy surface.

**ACKNOWLEDGMENTS**

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