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D + C(CH₃)₄ → HD (ν', j') + C(CH₃)₃CH₂: possible concerted flow of vibration energy into translation

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The HD (ν', j') product speed distributions from the D + C(CH₃)₄ → HD(ν', j') + C(CH₃)₃CH₂ reaction at a centre-of-mass collision energy of 1.20 eV (27.7 kcal/mol) were measured using a three-dimensional ion imaging apparatus. Anomalously fast HD (ν', j') molecules are observed that move at speeds beyond the energetically allowed limit for reagents in their ground states plus the average thermal vibrational energy present in neopentane. These products are attributed to a reaction between D atoms and thermally excited C(CH₃)₄ molecules in which it is speculated that vibrational energy from more than one vibrational mode of neopentane is funneled into product translation in what seems to be an unprecedented coordinated process.

Keywords: Hydrogen atom abstraction; hydrocarbon reaction dynamics; concerted energy flow

1. Introduction

The H-atom abstraction reaction by hot H atoms to form molecular hydrogen

\[ H + RH \rightarrow H_2 + R \]  \hspace{1cm} (1)

is a topic of immense interest because of what it can teach us about how reactions occur. Clearly, the most famous and fruitful examples are atom-diatom reactions where R = H or R = F, Cl, Br, or I. Less attention has been given to R as a polyatomic molecule [1], but some studies have been made of alkanes as the target. For example, studies have been carried out for fast H atoms reacting with CH₄ [2,3], CD₄ [2, 4–8] CHD₃ [9], CDCl₃ [10–12], C₂H₆ [13], C₃H₈ [13], CD₃(CH₂)₂CD₃ [14], n-C₅H₁₂ [15], n-C₆H₁₂ [15] and c-C₆H₁₂ [16]. These experiments have concentrated primarily on the rovibrational distribution of the molecular hydrogen product, H₂, or its isotopic cousin HD, because the internal state distribution is readily measured by coherent anti-Stokes Raman spectroscopy (CARS) or resonance enhanced multiphoton ionization (REMPI) spectroscopy. We report here the use of a three-dimensional ion imaging technique to measure the speed distribution of selected rovibrational states of HD in the reaction

\[ D + C(CH₃)₄ \rightarrow HD(ν', j') + C(CH₃)₃CH₂ \]  \hspace{1cm} (2)

Our choice for the alkane target of neopentane, which we affectionately refer to as ‘megamethane’, was based on the idea that it is a ‘ball of hydrogen’ having 12 identical H atoms that can participate in the reaction with the translationally hot D atom and therefore have a much larger cross section than for the reaction with methane. This intuition has been borne out, but to our initial surprise, we found that the HD (ν', j') speed distribution shows a maximum value greatly in excess of what is energetically allowed for the reaction of D with C(CH₃)₄ that is excited with its average thermal vibrational energy (T = 300 K). In previous studies the reactions of fast H atoms with alkanes have been regarded as direct, that is, proceeding by a collision in which the incoming D atom strikes the alkane target and then recoils as the HD product without lingering in the vicinity of the target [17]. The present work suggests that a different reaction mechanism involving some type of trapping also contributes to the formation of the molecular hydrogen product.

1.1. Experimental

Figure 1 presents the experimental setup. Only the most relevant features are given here because a detailed description of the instrument can be found elsewhere [18]. A three-dimensional ion imaging apparatus was employed to measure the speed distribution of the HD...
reaction product in the laboratory frame using the Photoloc method [19]. The detector consisted of Chevron-mounted multichannel plates (MCPs) coupled to a delay line anode. The reactive mixture was prepared by combining 3 psi of neopentane (Scott Specialty Gases, 99%) with 1.5 psi of DI (synthesized in house) and topping off the mix with Ar (Liquid Carbonic, 99.998%) to a total pressure of 50 psi. We found that the use of Ar was superior to that of He because the latter causes a time-of-flight baseline distortion around mass 4 Da, which in some cases was so large as to obscure the neighbouring HD signal.

The mixture was then supersonically expanded into a vacuum chamber through a pulsed nozzle (General Valve Series 9, 0.76 mm orifice) at a backing pressure of about 1000 Torr. The background pressure in the chamber exhausted by two turbo pumps was \( \approx 8 \times 10^{-9} \) Torr and about \( 5 \times 10^{-7} \) Torr when the nozzle was running. The nozzle and the lasers were operated at 10 Hz.

Although the probe laser beam is able to both dissociate DI and to detect HD, we use two beams from dedicated photolysis and probe lasers. Such a setup has the advantages: (1) the collision energy is fixed and does not vary as the probe laser wavelength is scanned across the different HD \((v', j')\) REMPI lines, and (2) any background is eliminated that could arise from the probe laser beam. A Nd\(^{3+}\):YAG laser (GCR Series, Quanta-Ray) pumped a dye laser (LPD3000, Lambda Physik) that operated on pyromethene 597. The tunable dye laser output was subsequently frequency-doubled in a BBO crystal to generate a 286.5 nm photolysis laser beam. Under these conditions, the D(slow) + \(^1\)H\(^2\)O photolysis channel does not have sufficient energy to produce the HD states we observe, i.e. all HD products we study come from the D(fast) + \(^1\)H photolysis channel. Another Nd\(^{3+}\):YAG laser (DCR-3, Quanta-Ray) pumped a dye laser (LPD3000, Lambda Physik) that operated with Exalite 428 dye. The output of this laser was then frequency-doubled using a BBO crystal to produce the following REMPI wavelengths: 205.769 nm for HD \((v' = 0, j' = 10), 211.855 \) nm for HD \((v' = 1, j' = 8)\) and 215.918 nm for HD \((v' = 1, j' = 13)\). The probe laser power was between 200 \(\mu J\) and 300 \(\mu J\) while the photolysis laser power was maintained at around 1500 \(\mu J\). Probe and photolysis beams were focused onto the molecular beam by means of 50 cm and 45 cm lenses, respectively. The \([2 + 1]\) REMPI detection scheme of HD \((v', j')\) was used, via the \(Q(j')\) members of the \(0, v'\) vibrational band of the \(E, F^1\Sigma^+_g - X^1\Sigma^+_g\) electronic transition.

The experimental HD \((v', j')\) signal was obtained by subtracting ‘Signal 1’ from ‘Signal 2’ on an every-other-shot basis. Signal 1 was obtained by recording the signal from the probe laser alone. Signal 2 is the signal recorded when the probe laser came \((\approx 15 \text{ ns})\) after the photolysis laser. In this case, the signal should be exactly like Signal 1 plus the extra HD \((v', j')\) product that formed as a result of D atoms, generated by the photolysis laser, colliding and reacting with neopentane molecules. Subtraction of Signal 1 from Signal 2 therefore gives the amount of HD \((v', j')\) product exclusively coming from the photolysis-laser-induced \(D + \text{C(CH}_3)_4 \rightarrow \text{HD}(v', j') + \text{C(CH}_3)_2\text{CH}_2\) reaction.

All wavelengths were measured with a laser wavelength meter (Wavemaster, Coherent). Each REMPI line was scanned over 20 pm to take into account line broadening. About once every ten days, the signal would deteriorate dramatically, evidently from buildup of some deposit. This problem was solved by regularly replacing the mesh of the extractor plate (Figure 1).

2. Results

Figure 2 presents the raw data for HD \((v' = 0, j' = 10)\), HD \((v' = 1, j' = 8)\), and HD \((v' = 1, j' = 13)\) products from the \(D + \text{C(CH}_3)_4 \rightarrow \text{HD}(v', j') + \text{C(CH}_3)_2\text{CH}_2\) reaction at \(E_{\text{coll}} = 1.20 \text{ eV}\). Figure 2(a), 2(b), and 2(c) show both Signal 1 and Signal 2, i.e. the probe-only and the probe-15-ns-after-photolysis traces. Figure 2(d), 2(e), and 2(f) show the result obtained by subtracting Signal 1 from Signal 2.
Figure 2. Raw HD ($\nu', j'$) speed distributions: (a) HD($\nu' = 0, j' = 10$), (b) HD($\nu' = 1, j' = 8$) and (c) HD($\nu' = 1, j' = 13$), showing Signal 1, the signal from probe laser alone (dashed curve) and Signal 2, the signal when the probe laser arrives $\sim$15 ns after the photolysis laser (solid curve). (d), (e), and (f) correspond to the processed speed distribution found by subtracting Signal 1 from Signal 2.
Figure 3 shows the HD speed distribution obtained by averaging three scans for each HD state studied. It is evident that the three distributions have a very similar appearance, which is particularly evident in Figure 3(d) where the three speed distributions are plotted on the same graph with error bars omitted for clarity.

The total energy available to be distributed among the product degrees of freedom is calculated from the expression

\[ E_{\text{total}} = E_{\text{coll}} + \Delta H + E_{\text{int}}(\text{neopentane}) \]  

(3)

where \( E_{\text{coll}} = 1.203 \pm 0.050 \text{ eV} \), as determined from the photolysis wavelength and the known bond dissociation energy of DI [20] where we have included the uncertainty arising from incomplete DI cooling in the supersonic expansion, \( \Delta H = 0.178 \pm 0.086 \text{ eV} \), is the value of the exothermicity based on the \( \text{D}_2(\text{C–H in neopentane}) \) [21] and the \( \text{D}_2(\text{H–D}) \) [20], and \( E_{\text{int}}(\text{neopentane}) = 0.087 \text{ eV} \) is the average thermal vibrational energy in neopentane calculated from the 45 vibrational degrees of freedom (Table 1) at \( T = 300 \text{ K} \). This treatment neglects the rotational energy of neopentane because this molecule is expected to be cooled in the supersonic jet expansion. Thus, we estimate \( E_{\text{total}} = 1.47 \pm 0.07 \text{ eV} \).

Table 2 tabulates the average speed of HD (\( v', j' \)) product for each reaction channel studied, the average translational energy deposited in the two recoiling products, the fraction of the total energy appearing in product translation, and the minimum and maximum speeds in the HD (\( v', j' \)) product if the neopentyl radical remains a complete structureless spectator. This behaviour would be that of a reaction

\[ \text{D} + \text{H} - \text{M} \rightarrow \text{HD}(v', j') + \text{M} \]  

(4)

where M is a hypothetical structureless particle with a mass of 71 Da.

The information presented in Figures 2 and 3 is the HD speed as measured in the laboratory frame. Because of unfavorable kinematics for this reaction, the inversion of the data to a differential cross-section is not possible [22]. On the other hand, because the center-of-mass (COM) speed at 1.20 eV collision energy is small, 292 m/s, compared to the HD speed in the COM frame for reaction (4), i.e. 7441 m/s for HD (\( v' = 0, j' = 10 \)), 6448 m/s for HD (\( v' = 1, j' = 8 \)) and 3819 m/s for HD (\( v' = 1, j' = 13 \)), it is a good approximation to equate \( v_{\text{LAB}}(\text{HD}) \) to \( v_{\text{COM}}(\text{HD}) \). We use this approximation when calculating the relative translational energy of the products shown in Table 2, which is given by (using conservation of linear
momentum in the COM frame):

\[
E_{T,\text{products}} = \frac{1}{2} m' v^2_{rel} = \frac{1}{2} \left( \frac{m_{HD} m_{C_6H_11}}{m_{HD} + m_{C_6H_11}} \right) (v_{HD} - v_{C_6H_11})^2
\]

\[
= \frac{1}{2} \left( \frac{m_{HD} m_{C_6H_11}}{m_{HD} + m_{C_6H_11}} \right) (v_{HD} - \frac{m_{HD}}{m_{C_6H_11}} v_{HD})^2
\]

\[
= \frac{1}{2} m_{HD} v_{HD}^2 \left( \frac{71}{74} \right)
\]

The most striking feature of the HD \((v', j')\) speed distributions in Figure 3 is their width. The solid lines in Figure 3(a)–3(c) represents the speed distribution of the HD that would have been observed had the neopentyl product acted purely as a spectator, i.e. according to Equation (4). Conservation of energy therefore dictates the following conclusions: the signal to the left of the dashed blue curve in Figure 3 corresponds to internal excitation of the neopentyl product. The signal to the right of the dashed green curve indicates HD molecules moving at speeds greater than energetically allowed for neopentane reagent with an average internal energy of 300 K. Figure 3 shows that an appreciable population of HD \((v', j')\) products have speeds in significant excess of this value. This behavior is particularly apparent for the HD \((v' = 1, j' = 13)\) product state (Figure 3(c)). Obviously, this excess energy must come from internal excitation of the neopentane, a topic that is discussed in more detail later.

For the speed distribution corresponding to neopentyl internal excitation, we list in Table 3 the average product translational energy and the fractions of the total energy that appears in HD \((v', j')\) internal excitation and average neopentyl internal excitation for the specific state of HD \((v', j')\). As the internal energy of the HD \((v', j')\) product increases, the corresponding fractions of total energy available to product translation and neopentyl internal energy decrease, as expected.

The speed distributions in Figure 3 have a distorted bell-shaped appearance, parabolic at low speeds and exponentially trailing off at high speeds. Figure 4 presents a fit of these speed distributions to a Maxwell-Boltzmann speed function. The matches are striking. They suggest that each speed distribution is well represented by a temperature. Moreover, the temperatures for the three different HD product states are nearly the same.

### 3. Discussion

Previous theoretical treatments of the reaction of fast hydrogen atoms with hydrocarbons have been carried out using quasiclassical trajectory calculations assuming a direct reaction [17]. It is found that most of the available energy is channeled into product translation.

### Table 1. C(CH₃)₄ normal modes, associated degeneracies and population ratios compared with the lowest energetic level at \(T = 300\) K.

<table>
<thead>
<tr>
<th>(v_i)</th>
<th>(E_i) (cm(^{-1}))</th>
<th>(\omega_i)</th>
<th>(N_i/N_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1.000000</td>
</tr>
<tr>
<td>1</td>
<td>202</td>
<td>1</td>
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<td>1</td>
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<tr>
<td>6</td>
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<td>3</td>
<td>0.035344</td>
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<tr>
<td>7</td>
<td>945</td>
<td>3</td>
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<tr>
<td>8</td>
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<td>2</td>
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<td>3</td>
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<td>1</td>
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<td>3</td>
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<td>2960</td>
<td>3</td>
<td>0.000002</td>
</tr>
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<td>2960</td>
<td>2</td>
<td>0.000001</td>
</tr>
<tr>
<td>19</td>
<td>2967</td>
<td>3</td>
<td>0.000002</td>
</tr>
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</table>

### Table 2. Some kinematic data for the D + C(CH₃)₄ → HD \((v', j')\) + C(CH₂)(CH₃)₂ reaction and the average measured quantities. Column 2 contains the average speed, \(\langle |v|\rangle\), of each HD \((v', j')\) state (Figure 3) and the resulting uncertainty. The third column is the relative translational energy of the products. The fourth column is \(E_{T,\text{products}}\) divided by the total available energy (1.47 eV, see Equation (3)). The fifth and sixth columns indicate the theoretical HD \((v', j')\) speed limits corresponding to the spectator reaction, i.e. D + HM → HD + M for the mass of M equal to 71 Da.

| Product state | \(\langle |v|\rangle\) (m/s) | \(\langle E_{T,\text{products}}\rangle\) (eV) | \(\langle f_{T,\text{products}}\rangle\) (eV) | \(|v|_{\text{min}}\) (m/s) | \(|v|_{\text{max}}\) (m/s) |
|---|---|---|---|---|---|
| HD \((v' = 0, j' = 10)\) | 4840 ± 740 | 0.38 ± 0.08 | 0.26 ± 0.05 | 6791 | 8070 |
| HD \((v' = 1, j' = 8)\) | 4840 ± 610 | 0.38 ± 0.07 | 0.26 ± 0.05 | 5740 | 7127 |
| HD \((v' = 1, j' = 13)\) | 4680 ± 610 | 0.35 ± 0.07 | 0.24 ± 0.05 | 2773 | 4733 |
Moreover, the average fraction in translation decreases with collision energy, indicating that product internal excitation is favoured at high collision energies. Larger alkanes seem to promote energy release into product internal excitation. Layfield and Troya [17] conclude that the molecular degrees of freedom of the alkane not directly involved in the process of bond making/breaking are not entirely orthogonal to the reaction coordinate, particularly at high energies. We also find that the neopentyl radical is internally excited (all the signals to the left of the blue dashed curve in Figure 3), in agreement with this picture.

Although there appears to be no other studies of H+neopentane, we do have some information on the related reaction of Cl + neopentane. Rose, Greaves, and Orr-Ewing [23] reported that about 33% of the total available energy ends up as neopentyl internal excitation in the Cl + C(CH₃)₄ → HCl + C(CH₃)₃CH₂ reaction at \( E_{\text{coll}} = 0.35 \text{ eV} \) (8 kcal/mol), where the HCl product was probed state-selectively. We compare our findings by averaging the three average fractions of the total energy in the neopentyl fragment, which gives \( \langle f_{\text{int, neopentyl}} \rangle = 26 \pm 3\% \). Estillore, Visger and Suits [24] investigated the same hydrogen abstraction reaction by a Cl atom by probing the neopentyl product non-state-specifically at 157 nm. They found that the internal energy of the neopentyl product was at most \( \approx 20\% \) of the total energy available. A theoretical QCT study by Layfield and Troya on H + RH → H₂(\( \nu' \), \( j' \)) + R, where R = CH₃, C₂H₅ and C₃H₇ (both primary and secondary radicals), found that R product contained about 15% of the total energy. These observations are in rough agreement with what we find, although it is admittedly difficult to make detailed comparisons because we have measured only three HD product states.

It is natural to wonder whether neopentane can really be treated as a C(CH₃)M₃ species where M is an hypothetical structureless particle of mass 15 Da. This treatment reduced the number of normal modes from 45 to 18. A quasiclassical trajectory calculation with histogram binning was carried out, and the results are presented in Figure 5. There were too few reactive trajectories leading to HD (\( \nu' = 1 \), \( j' = 13 \)) product to allow its inclusion in Figure 5. The comparison with the experimental observations suggests that this

<table>
<thead>
<tr>
<th>Product State</th>
<th>( v_{\text{ref}} ) (m/s)</th>
<th>( \langle E_{\text{T,products}} \rangle ) (eV)</th>
<th>( \langle f_{\text{T, products}} \rangle )</th>
<th>( f_{\text{int,HD}} )</th>
<th>( f_{\text{int, neopentyl}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD (( \nu' = 0 ), ( j' = 10 ))</td>
<td>7780</td>
<td>0.30 ± 0.03</td>
<td>0.21 ± 0.02</td>
<td>0.38</td>
<td>0.42 ± 0.04</td>
</tr>
<tr>
<td>HD (( \nu' = 1 ), ( j' = 8 ))</td>
<td>6766</td>
<td>0.27 ± 0.02</td>
<td>0.19 ± 0.01</td>
<td>0.54</td>
<td>0.28 ± 0.01</td>
</tr>
<tr>
<td>HD (( \nu' = 1 ), ( j' = 13 ))</td>
<td>3712</td>
<td>0.11 ± 0.01</td>
<td>0.080 ± 0.007</td>
<td>0.84</td>
<td>0.080 ± 0.007</td>
</tr>
</tbody>
</table>

Figure 4. Fit of the speed distributions to a Maxwell-Boltzmann function for (a) HD(\( \nu' = 0 \), \( j' = 10 \)), (b) HD(\( \nu' = 1 \), \( j' = 8 \)), and (c) HD(\( \nu' = 1 \), \( j' = 13 \)). The error bars represent one standard deviation from three different measurements.
simplification is unable to describe correctly the reaction dynamics. We conclude that the extra degrees of freedom of neopentane do play an important role in governing the total energy partitioning among the various degrees of freedom of the products for this reaction.

The most remarkable feature of the reactions of neopentane molecules with translationally hot D atoms is the observation that the speed distribution of the HD ($v' = 0, j' = 10$) product significantly exceeds the energy available if only the average thermal energy of 0.09 eV at 300 K is taken into account (all the signals to the right of the green dashed curves in Figure 3). Clearly, this extra energy must come from internal excitation of the neopentane reagent. Table 1 lists the 19 different normal modes of neopentane with their associated degeneracies, which constitute the 45 vibrational degrees of freedom. We also list the fundamental frequencies of each mode. The first four vibrational modes have thermal populations similar to the population of the ground state neopentane. These low-frequency modes however are not sufficiently energetic to produce the fastest HD ($v' = 1, j' = 13$) products observed (Figure 3(c)). For example, roughly 0.25 eV (2080 cm$^{-1}$) must be transferred to the recoiling HD ($v' = 1, j' = 13$) travelling at 6000 m/s.

We have also wondered whether these conclusions about excess HD speed come from some other source or wrong assumption. No signal is observed when neopentane is not present. Thus, we are led to believe that the HD signal we observe is from D + neopentane. When the pulse sequence is probe laser followed 50 ns later by the photolysis laser, we do observe an HD signal that originates from the photolysis of DI by the probe laser followed by prompt reaction of D + neopentane during the width (8 ns) of the probe laser and small nonresonant HD signal from the photolysis laser. However, this signal is subtracted from the signal that arises when the photolysis laser is fired 15 ns before the probe laser on an every other shot basis. We have confidence in this approach because it has succeeded in the past in yielding results for the H + D$_2$ → HD + D reaction that so closely agree with theoretical calculations [25]. It may be asked whether some misestimate has been made in the C–H bond energy of neopentane and its uncertainty and we cannot rule out this possibility.

Some precedent exists for the observation of excess product speed. Kandel and Zare [26] found anomalously fast products in the reactions of Cl$^+$CH$_4$ and Cl$^+$CD$_4$, which they attributed to reaction of ground-state chlorine with methane vibrationally excited in trace quantities into low-energy bending and torsional modes. We believe the fast HD ($v' = 1, j' = 13$) molecules in our experiment to be similar in this respect to this study. We also suspect that the cross section for reaction is enhanced by internal excitation of the neopentane reagent.

Examining the energies of the different normal modes of neopentane and their relative populations (Table 1), we suggest that the energy found in recoiling HD originates from more than one normal mode being transferred to the HD product. If true, this implies that another reaction mechanism is at play. We imagine that the reacting D atom forms a temporary complex with neopentane (indirect reaction) and the energy of reaction combined with internal energy of the neopentane can be transferred to the HD product, which emerges from the complex translationally thermalized. This model, if dominant, would account for our experimental observations that (1) the HD product speed distribution is fit well by a Maxwell-Boltzmann function with approximately the same temperature for different HD product states, and (2) we observe very fast HD product speeds. There is some precedence for extraordinarily large vibration to translation (V–T) energy transfer in inelastic collisions between rare gas atoms and vibrationally excited polyatomic...
molecules [27–30]. These are referred to as supercollisions. However, much less is known about such behavior in reactive scattering. Further studies are needed, both experimentally and theoretically, to determine whether these anomalously fast product recoils arise from such an indirect mechanism.

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References