Population of 3s, 3p, and 3d Sublevels of Atomic Hydrogen after Dissociative Excitation of some Alkanes by Electron Impact

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The intensity ratios within the Balmer-line $H_a$ have been determined after pulsed electron impact excitation and dissociation of the alkanes $CH_4$, $C_2H_6$, $C_3H_8$, $C_5H_{12}$, $C_6H_{14}$, $C_7H_{16}$, and $C_8H_{18}$. A time resolved technique has been used to separate the line-components by their different lifetimes.

We report in this paper measurements of the first ionization potential.

The threshold energies for Balmer emission are well above the first ionization potential of the target molecules, so that the first step in the production of hydrogen atoms with $n=3$ is the excitation of the molecule to a so called super excited state $E^{(*)} >$ First ionisation potential.

At least 3 concurring decay-modes lead off the electronic excitation energy:

1. Autoionisation, leading to an (most often) excited, ionized molecular fragment $M^{**} \rightarrow (M^*)^+ + e^-$

2. Internal conversion, converting electronic energy into vibrational energy of the molecule $M^{**} \rightarrow M^* + E_{ vib}$

3. Dissociation or presdissociation, producing excited fragments, atomic or molecular or both, easily identified by their emission.

$M^{**} \rightarrow A^* + B$,

B may be a molecular fragment.

This paper deals with the third case, where $A^*$ is a hydrogen atom in the 3s, 3p or 3d state leading to Balmer radiation.

The total intensity of $H_a$ is composed of 7 transitions, if fine structure and Lamb-shift is included (Table 1). These cannot be separated spectroscopically, but because the lifetimes of the hydrogen-states depend only on $n$ and $I_6$, the 7 transitions can be condensed into 3 ones, originating from states with different $I$. These can be still separated by a time resolved technique, because the lifetimes of the states with different $I$ differ by about one order of magnitude (Table 1). Therefore, the registration of the $H_a$-curve after pulsed electron impact excitation allows to determine the relative portions of the $3 I$ sublevels. Considering statistical excitation conditions, the relative intensities are expected to be as given in Table 1.

| Table I. Atomic states of hydrogen, leading to $H_a$ radiation, lifetimes of states with equal $I$ and intensity-ratios due to statistical excitation conditions. |
|-----------------|-----------------|-----------------|
| $n=3$           | $\tau_0 = 15.6$ ns | $\tau_0 = 5.4$ ns |
| $n=4$           | $\tau_0 = 80$ ns  | $\tau_0 = 60$ ns  |
| $n=5$           | $\tau_0 = 1210$ ns | $\tau_0 = 1210$ ns |

$E_{ vib} = \frac{(2n+1)\pi^2}{6562.8 \text{ Å}}$ for $H_a$

$J(3s) / J(Ha) = 15.6\%$

$J(3p) / J(Ha) = 5.6\%$

$J(3d) / J(Ha) = 78.7\%$
Method

The independent decay of the 3l sublevels should be described by the sum of exponentials

\[ J(t) = J_0^s \cdot e^{-t/\tau_s} + J_0^p \cdot e^{-t/\tau_p} + J_0^d \cdot e^{-t/\tau_d}. \]

But because of the short decay time of the 3p state of only 5.4 ns, the 4.8 ns decay of the excitation pulse must be considered.

This leads to an observed decay-curve, represented by

\[ J_{\text{obs}}(t) = \sum_{n=s,p,d} J_0^n \cdot (\tau_n \cdot e^{-t/\tau_n} - \tau_A \cdot e^{-t/\tau_A}) + U. \]  

(1)

U is the uncorrelated background, mainly caused by dark pulses of the photomultiplier. The parameters \( J_0^s, J_0^p, J_0^d \) and \( \tau_s, \tau_p, \tau_d \) and \( U \) respectively are fitted by a computer routine to the measured curves. We found good agreement between the fitted \( \tau \)-values and the theoretical ones. Therefore the theoretical lifetimes are used in the expression and only the intensities are still fitted by the computer.

In a detailed discussion of all the cascade-processes is given, leading to \( n = 3 \)-population, with the result that no significant contribution to Balmer \( \alpha \)-radiation is due to cascading from higher levels; so with good accuracy the expression (1) can be used to describe the Balmer \( \alpha \)-decay.

The points in Fig. 1 are an example of a typical decay-curve, taken on methane. The drawn curve is a function given by the expression (1) but with background subtracted. Deviations in the time range above 500 ns might be due to a small amount of cascading.

Khayrallah has emphasized the importance of equilibrium excitation conditions, which require excitation pulse lengths of at least 1 \( \mu \text{sec} \). We think that this is not necessary if the finite pulse length is considered in the evaluation of the decay-curves. The intensity after an excitation time \( T \) is given by the integral

\[ i(T) = \int_0^T E(t) \cdot i(T-t) \, dt, \]

where \( E(t) \) describes the excitation pulse and \( i(T-t) \) the decay. \( E(t) \) is a pulse of rectangular shape, independent of \( t \) between 0 and \( T \), so

\[ i(T) = E \cdot \tau (1 - e^{-T/\tau}) \]

\( E \cdot \tau \) is the intensity at equilibrium between excitation and decay.

Therefore each of the decay-components must be corrected by the reciprocal of \( (1 - e^{-T/\tau}) \), where \( \tau \) is the lifetime of the component to be corrected.

After this procedure intensity ratios can be formed and should be independent of \( T \).

We have varied \( T \) over a wide range (see below) and found no significant change of the corrected intensity-ratios within the H\(_\alpha\)-line.

Experimental

The experimental arrangement has been described in detail in previous papers. So only a brief description should be given here.

A molecular beam (\( p \leq 4 \cdot 10^{-4} \text{Torr}, \) background pressure \( \approx 1 \cdot 10^{-6} \text{Torr} \)) is crossed under 90° by a pulsed electron beam of variable energy (80 to 500 eV, \( i \leq 30 \mu \text{A} \)).

Photons are detected perpendicular to both beams through a narrow band interference filter by a cooled photomultiplier. Decay curves were registered by means of the method of delayed coincidences, using a time to height converter and a multichannel analyzer.

All decay curves were measured at least 5 times. Total collection time to get some thousands of pulses at \( t = 0 \) is between 2 and 15 hours, dependent on the energy (emission cross sections are greatest at about 150 eV) and the target molecule used, because Balmer emission decreases with increasing number of
atoms of the molecule from CH$_4$ to C$_9$H$_{20}$, due to the increasing influence of internal conversion.

Most of the difficulties arise from the fact that the terms with different $\ell$ (different lifetimes) but equal $j$-values, are very close together, so small perturbations by electric or magnetic fields are sufficient to mix these nearly degenerate states to an appreciable extent, which causes drastic changes in lifetimes. The fields may be caused by space charge of ionic fragments. The ion density depends on the target gas pressure, the exciting electron current density and the velocity of the electrons. Therefore some test measurements have been carried out to make sure that the perturbing influence of the static and dynamic Stark-effect is negligible (Figure 2).

In reference an estimation has been given, which shows that the ion densities obtained in our experiment of about $1 \cdot 10^7$/cm$^3$ are too low by nearly a factor of 10, to cause a measurable change in lifetime. This is confirmed by the tests.

### Results

The results are very similar to those found earlier. The most surprising result is reproduced, namely, that no significant contribution of 3p-states to Balmer-radiation has been found for all the molecules studied, CH$_4$ to C$_9$H$_{20}$. Under statistical excitation conditions of the $n=3$ sublevels of atomic hydrogen, about 6% contribution from 3p should be present (Table 1). The evaluation of our decay-curves lead to less than 1%, most often to zero. This agrees with the emission cross sections given by Vroom and de Heer. They found a ratio of about 10 to 1 in the cross sections for total Balmer $\alpha$-compared with Lyman $\beta$-radiation in the case of methane at 50 eV impact energy. If this is correct, the 3p-contribution to Balmer $\alpha$ is below the limit of reliable proof. It can be stated that Balmer $\alpha$-emission after dissociative excitation by electron impact of the alkanes CH$_4$ and C$_5$H$_{12}$ to C$_9$H$_{12}$ consists almost exclusively of emission resulting from transitions 3s$\rightarrow$2p and 3d$\rightarrow$2p respectively and only to a very small amount of 3p$\rightarrow$2s transitions, as found earlier for H$_2$, H$_2$O and C$_6$H$_6$ and the molecules studied in Ref. 2, respectively.

We therefore give in Table 2 only the intensity ratios $I(3s)/I(H\alpha)$, the relative amount of 3s states to the total H$\alpha$-emission. As can be seen, this ratio does not change systematically with molecular size, but varies by nearly 10%. Errors given are not absolute ones, but ems-values deduced from 5 to 10 measurements carried out at each of the molecules. For reasons of comparison the earlier published results obtained on C$_6$H$_6$ and H$_2$ are added to the table together with the results of two other groups.

Table II. Intensity ratios $I(3s)/I(H\alpha)$ after electron impact induced dissociative excitation of the molecules given in the first column.

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>THIS WORK</th>
<th>OTHER WORK</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>0.57 ± 0.01</td>
<td>0.33 ± 0.04$^2$</td>
</tr>
<tr>
<td>C$_4$H$_2$</td>
<td>0.66 ± 0.00</td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>0.64 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>C$_7$H$_6$</td>
<td>0.66 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>C$_8$H$_6$</td>
<td>0.60 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>C$<em>9$H$</em>{12}$</td>
<td>0.61 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.38 ± 0.02</td>
<td>0.39 ± 0.04$^3$</td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>0.62 ± 0.04</td>
<td>0.17 ± 0.04 [200 eV]$^4$</td>
</tr>
</tbody>
</table>

### Discussion

The values given in the table are mean values of measurements taken at different impact energies. This procedure is possible because no systematic
change of the ratios was found with impact energy between 80 and 500 eV. All the test measurements of Fig. 2 are carried out on methane. No deviating results were obtained with the other molecules studied (including $\text{H}_2$, $\text{C}_6\text{H}_6$, and $\text{H}_2\text{O}$).

As discussed above excitation to equilibrium is no necessary condition if the pulse-length of the excitation pulse is known and the error is corrected. To show this, pulse-lengths are varied from 50 ns to 1.2 $\mu$s and corrected to infinite excitation duration. No systematic change of the ratios can be observed. Because the uncorrected intensity ratios change with decreasing duration of the excitation pulse in favour of the faster decaying components, pulse length variation could be a method to discover a low intensity component of short decay time among others. But even in the case of a 50 ns excitation, where the 3s contribution is diminished by a factor of about 4, no 3p contribution could be detected. Because the excitation length has turned out to be of no influence on the ratios, all measurements were done at 300 ns pulse length, determined by the pulse generator used.

Further tests are concerned with the perturbing influence of particle and fragment densities. So the pressure on the entrance-side of the capillary-array, forming the molecular beam, was varied from $1 \cdot 10^{-2}$ to 0.5 Torr. The corresponding pressure at the beam center is then between $2 \cdot 10^{-4}$ and $1 \cdot 10^{-3}$ Torr.

In this range no influence on the ratio $J(3\text{s})/J(\text{H}_\alpha)$ is found, the same is true for the variation of the mean current over a 10 to 1 range.

We conclude that the experimental conditions guarantee unperturbed excitation and especially decay-conditions. Absolute errors of the intensity ratios should be about a few percent.

To proof wether the sublevel occupation following dissociative excitation is similar in the $n = 2$-state, decay curve measurement on Lyman $\alpha$ are just being carried out at this laboratory.

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7 G. A. Khayrallah and S. J. Smith, to be published.