

# YIELDS OF IONS AND EXCITED STATES IN NONPOLAR LIQUIDS EXPOSED TO X-RAYS OF 1 TO 30 KEV ENERGY - Richard A. Holroyd

## INTRODUCTION

When x-rays from a synchrotron source are absorbed in a liquid, the x-ray energy ( $E_x$ ) is converted by the photoelectric effect into the kinetic energy of the electrons released. For hydrocarbons, absorption by the K-electrons of carbon dominates. Thus the energy of the photoelectron ( $E_{pe}$ ) is  $E_x - E_b$ , where  $E_b$  is the K-shell binding energy of carbon. Additional electrons with energy equal to  $E_b$  will be released in the Auger process that fills the hole in the K-shell. These energetic electrons will produce many ionizations, excitations and products. The consequences of the high density of ionizations and excitations along the track of the photoelectron and special effects near the K-edge are examined here.

## FREE ION YIELDS

For photoelectrons as well as for electrons of very high energy, kinetic energy is imparted to secondary electrons that thermalize some distance from the parent ion. These secondary electrons can either recombine or escape from the spur to become free ions. The probability of escape depends on the separation distance. However, free ions yields measured for several hydrocarbons are much less for x-rays than for high-energy radiation like gamma rays. Results are shown for n-hexane, 2,2,4-trimethylpentane and 2,2,4,4-tetramethylpentane in figure 1.

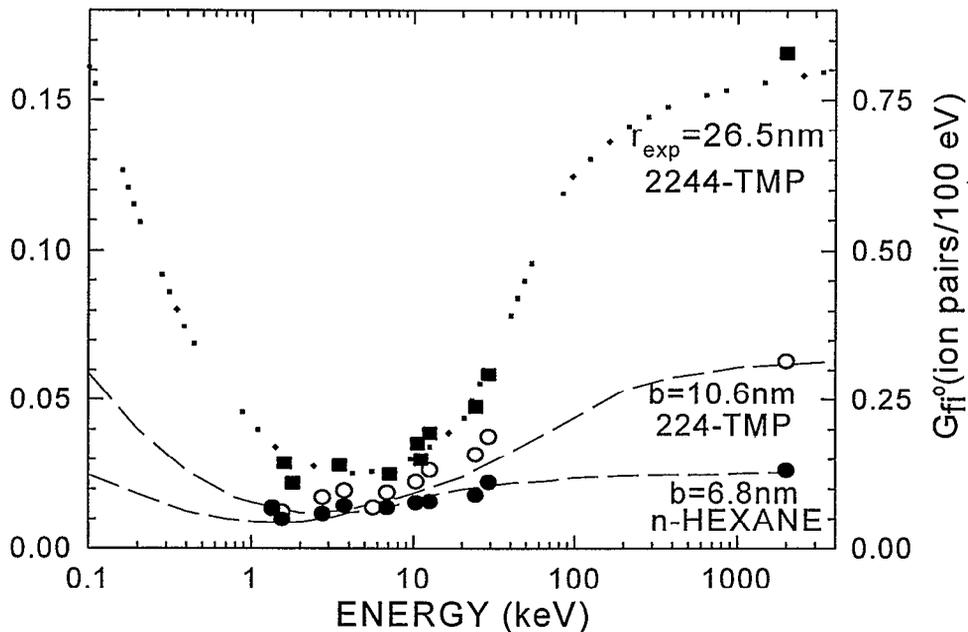


Figure 1. Ion yield data. Points are experimental - Refs 1-3. Dotted line is calculated, see Ref 4. Dashed lines are calculated, see Ref 5.

The yields are lowest around 2 keV. Because of the high brightness of synchrotron radiation, extra care was taken in these experiments to avoid volume recombination and to collect the free

ions with high efficiency. The low yield of ions for x-rays is attributed to the high density of ionizations along the track of the photoelectron. As the x-ray energy decreases the ionizations occur closer and closer together until at 2 keV they are (on average) 3 nm apart. This higher density of ionization maximizes track recombination.

Model calculations<sup>4,5</sup> of this track effect are shown by the lines in Figure 1. In these computer calculations, initial positions of ions along the track are first determined based on range data, and then either a Gaussian or exponential distribution of electrons around the track is assumed. The charges are subsequently allowed to diffuse randomly and drift subject to the electric fields present. Good fits to the results are obtained using, in the case of n-hexane and 2,2,4-trimethylpentane, Gaussian distributions and, in the case of 2,2,4,4-tetramethylpentane a wider exponential distribution. The distribution parameters are indicated on the figure.

The computer calculations were done for electrons of a given energy, while the experiments were done with x-rays of that energy. At high x-ray energy most of the energy will be in the photoelectron. However, at low energy the observed ion yields  $G_{\text{obs}}$  include a significant contribution from the Auger electron from carbon and observed yields are the sum of the yields of both electrons. The carbon Auger spectrum peaks around 250 eV,<sup>6</sup> thus:

$$G_{\text{obs}} \times E_x = G_{\text{pe}} \times (E_x - 250) + G_{\text{Auger}} \times 250 \quad (1)$$

To calculate the free ion yield of the photoelectron requires knowing the ion yield for a 250 eV electron, which we assume for n-hexane and 2,2,4-trimethylpentane to be the values calculated by the models at that energy (see lines in Fig. 1). The value of  $G_{\text{pe}}$  can then be calculated from the data using Eq. 1. The results of such a calculation, using for  $G_{\text{Auger}}$  0.084 per 100 eV, are shown as the points in Fig 2 for n-pentane. The original data<sup>2,3</sup> are shown by the solid line; the dotted lines are calculated lines. There are two effects of this reevaluation. Each point is shifted

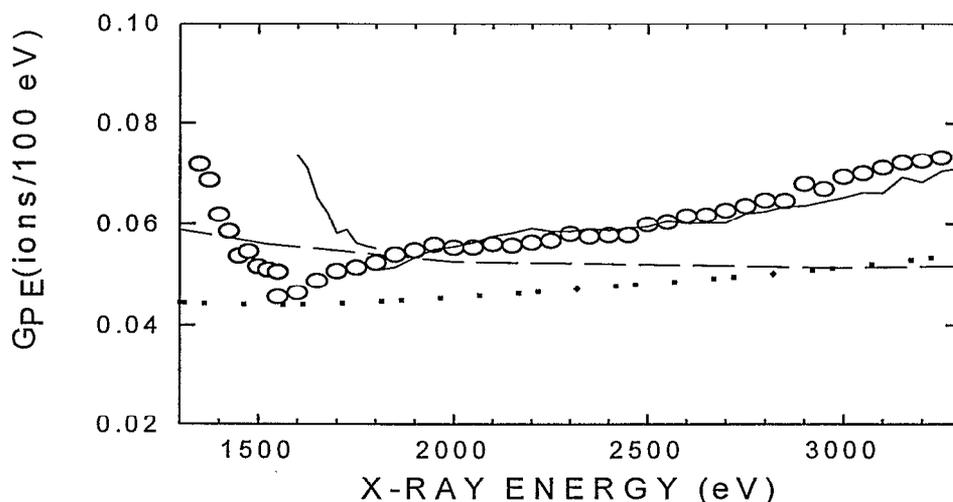


Figure 2. Ion yield data for n-pentane. Solid line is original data - Refs 2 & 3. Points are  $G_{\text{PE}}$ . Dashed line from Ref 4 using  $b=6.8$  nm. Dotted line from ref 5 for 6.8 nm. (by 250 eV) to lower energy such that the minimum in yield occurs at lower energy. The ion yield at the minimum is slightly lower than in the raw data. Similar results were obtained for

nhexane. The data points shown in Fig1 for n-hexane and 2,2,4-trimethylpentane have also had this correction applied and are thus  $G_{pe}$ . The correction was not applied to 2,2,4,4-tetramethylpentane because the calculated value of  $G_{Auger}$  of 0.5 per 100 eV led to unrealistically low values of  $G_{pe}$ .

### ION YIELDS AT K-EDGES

Conductivity studies in which the x-ray energy is scanned across a K-edge of a constituent atom show inverted ion yield spectra for samples that are optically thick. That is, minima in ion yield are observed at positions of absorption maxima. An early example of this was for a solution of ferrocene in 2,2,4-trimethylpentane.<sup>7</sup> Even though inverted, a useful EXAFS spectrum was obtained which gave valid structural information. Striking results were obtained for tetramethylsilane<sup>8</sup> and  $CCl_4$ ,<sup>9</sup> which both showed sharp minima in free ion yields at the K-edge of silicon and chlorine, respectively. In the Si case the minimum occurs at the position of the  $1s \rightarrow \sigma^*$  transition where there is a peak in the absorption spectra. Inefficiency of charge collection<sup>7</sup> and a fundamental change in primary process<sup>10</sup> have been suggested as explanations for the observed minima in ion yield at edges.

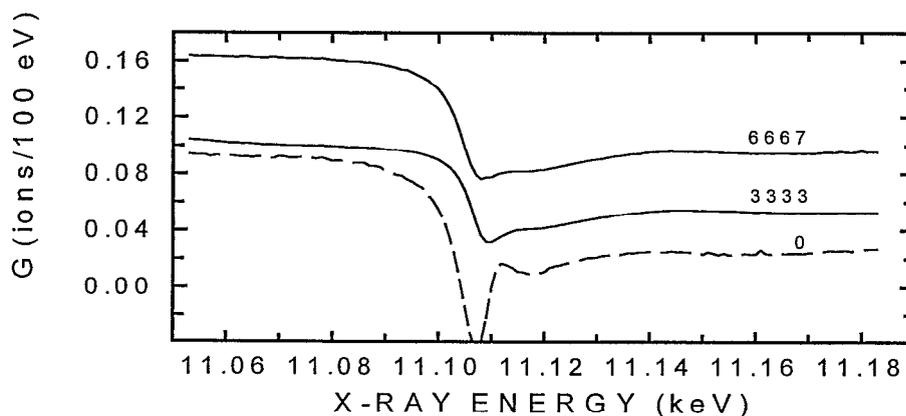
Experiments were done with Kr gas to determine if the primary yield of ions changes across a K-edge, which is at 14.3 keV.<sup>11</sup> The pulse size did not change by more than 0.5% across the K-edge, indicating that the initial ion yield is constant, independent of whether the ions are created by the energetic photoelectron emitted below the edge or by the electrons emitted in the Auger decay at and above the edge.

The free ion yield for liquid tetramethylgermane (TMG) was measured in the vicinity of the K-edge at 11.1 keV.<sup>11</sup> At this energy the x-rays are totally absorbed; below the edge the half-depth of penetration is 0.45 mm. The results obtained at 0, 1000 and 2000 V applied are shown in figure 3. A dip is observed at the K-edge and the yield above the edge is less than that below; very similar to the results found for  $CCl_4$  and tetramethylsilane. Some decrease above the edge is expected since the fluorescence yield is 0.53,<sup>12</sup> and the fluorescent x-rays are not all reabsorbed by the liquid. The spectrum at 0 V was obtained by linear extrapolation of data at high voltages. The yield of ions below the edge, 0.093 ions/100eV, is quite reasonable but at and above the edge unrealistically low yields of free ions are obtained.

Figure 3. Ion yields from liquid TMG for applied fields (V/cm) indicated

Experiments were also done with TMG vapor at room temperature to measure ion yields and provide cross section data near the K-edge of Ge. In this case the fraction of photons absorbed,  $F_a$ , is given by:

$$F_a = 1 - \exp[-l \times (\rho_C \sigma_C + \rho_H \sigma_H + \rho_{Ge} \sigma_{Ge})] \quad (2)$$



The length  $l$  of the cell used was 3 cm,  $\rho$ 's are densities and the  $\sigma$ 's cross sections. This fraction is less than unity but increases at the edge. The spectrum obtained is quite similar to the transmission spectrum of TMG<sup>13</sup> showing two peaks separated by 10 eV. The ion yield,  $G^0$ , was calculated from this data using published cross sections<sup>14</sup> and the concentration of TMG based on vapor pressure data. The yield thus found is 4.2 ions/100 eV below the edge. Since the Kr results showed no change in the initial yield of ions across an edge, this value of  $G^0 = 4.2$  was assumed to apply and the Ge cross section as a function of x-ray energy was calculated across the K-edge using Eq 2 and known values of  $\sigma_C$  and  $\sigma_H$ .

The extent to which inefficient collection efficiency can cause the observed minima in free ion yields for liquid TMG was assessed as follows. The efficiency,  $F$ , increases as the applied field,  $E$ , increases and decreases as the dose rate,  $Q(x)$ , increases. The dose rate depends on the distance,  $x$ , from the window. In general, conditions were adjusted to maximize  $F$  and thus minimize loss of ions due to volume recombination. To first order  $F(x)$  is given by:  $F(x) = 1 - C dQ/dx$ , where  $C$  depends inversely on  $E^2$ . If the carbon and hydrogen cross sections are ignored  $dQ/dx = B \times \sigma_{Ge} \rho_{Ge} \exp(-\sigma_{Ge} \rho_{Ge} x)$  and the dose rate will be largest near the entrance window. The term  $B$  is proportional to the x-ray beam intensity. Averaged over the cell, the efficiency becomes:

$$F_{ave} = 1 - B C \sigma_{Ge} \rho_{Ge}$$

Thus, as  $\sigma_{Ge}$  increases the efficiency of charge collection decreases and vice versa. Plots of  $F_{ave}$  for the experimental conditions used, constructed using the Ge cross sections determined in the gas phase experiments, are very similar to the experimental ion yield curves shown in figure 3. Thus inefficiency of ion collection accounts qualitatively for the inverted ion yield curves observed for TMG.

#### ACKNOWLEDGEMENT

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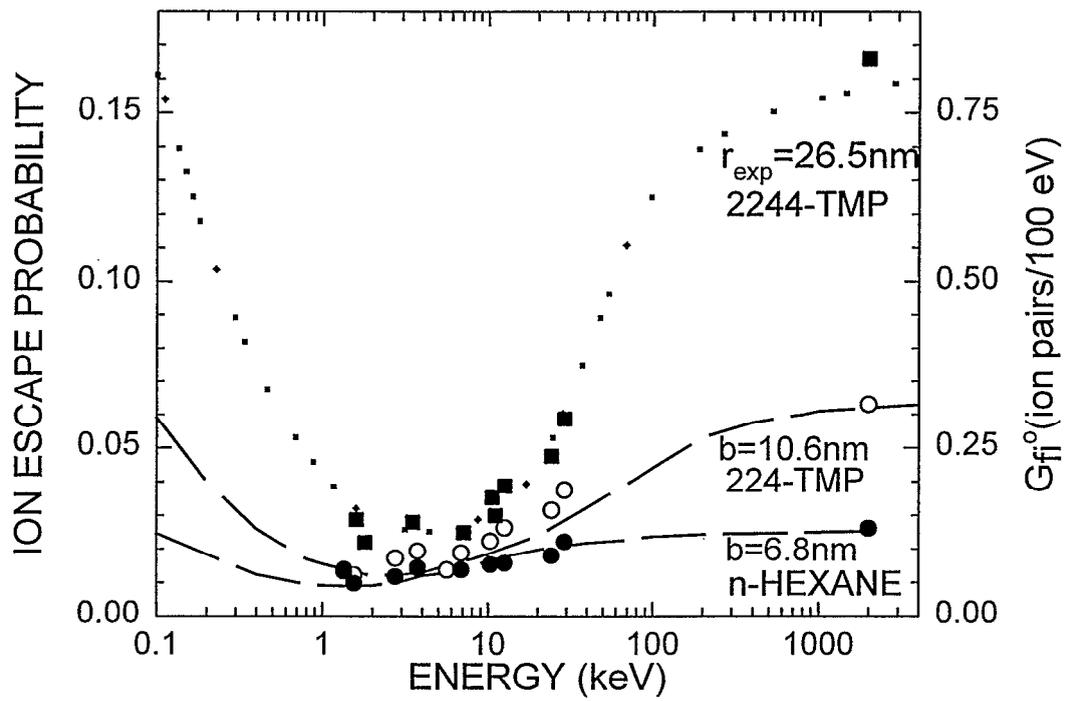


FIGURE 1

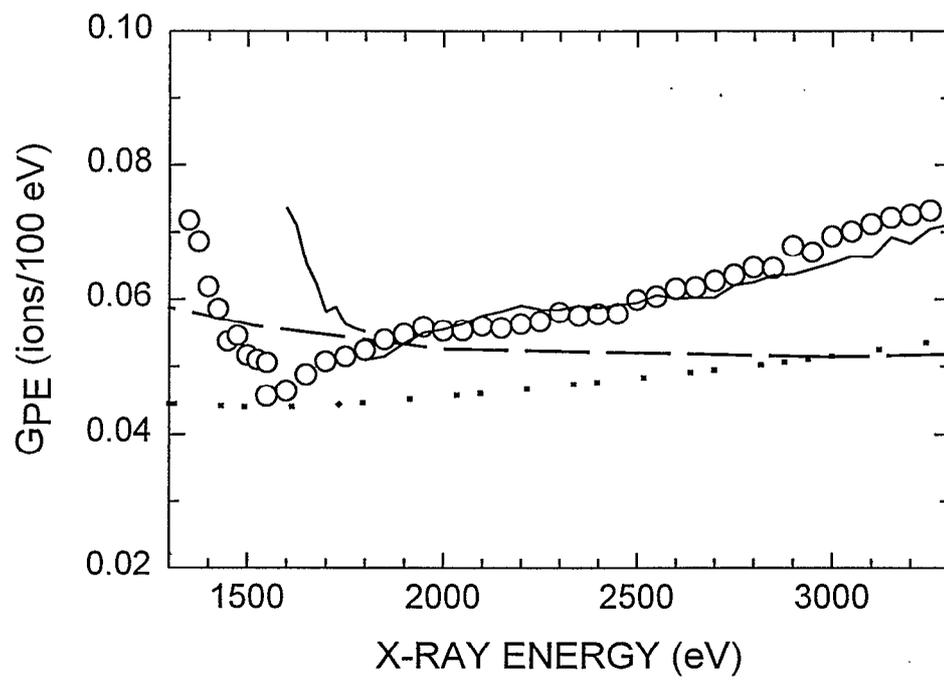


Figure 2

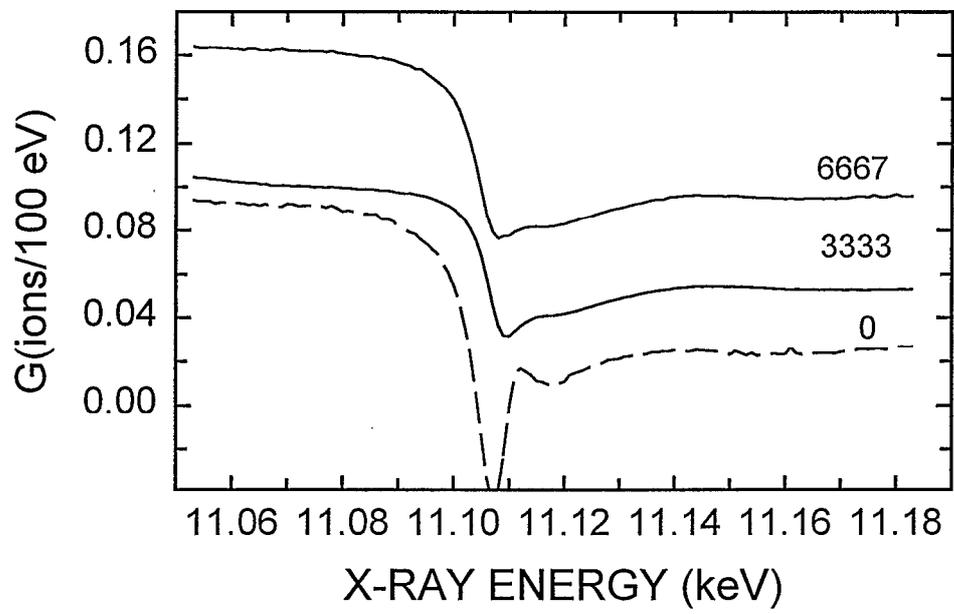


Figure 3