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# Double photoionisation of toluene

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#### Abstract

Spectra of doubly ionised toluene have been taken by the TOF-PEPECO method at photon energies of 26.91, 32.69 and 40.81 eV. The location of the adiabatic double ionisation threshold near 23.6 eV, as recently proposed by Roithová et al. is confirmed. Photoionisation to the ground state of the doubly charged ion is found to be dominated by autoionisation, at least at photon energies above 26 eV. Dissociation of the doubly charged ion, examined by PEPIPICO experiments, sets in at energies above 25.5 eV; the products formed at the lowest energies are  $C_7H_6^{2+} + H_2$  and  $C_2H_3^{+} + C_5H_5^{+}$ . © 2006 Elsevier B.V. All rights reserved.

1. Introduction

Because of toluene's importance as a calibration standard in charge stripping, Roithová et al. [1] recently studied the formation of its doubly charged ions by photon impact and by charge exchange. On the basis of calculations incorporating Franck-Condon factors with thermal excitation, derived from high-level molecular structure theory and compared with the experimental photoionisation yield curve, they proposed a substantial revision of the double ionisation energy, reducing it by 0.9 eV from the previous value. Because of the significance of this revision, it seemed appropriate to examine the spectrum of this doubly charged ion directly by the newly developed time-of-flight photoelectron-photoelectron coincidence (TOF-PEPECO) technique [2-4]. This paper reports measurements of complete double photoionisation spectra of toluene and toluene- $d_8$  with light of 46.1, 37.9 and 30.4 nm wavelength (26.91, 32.68 and 40.81 eV photon energy). The revised adiabatic double ionisation energy is confirmed and several aspects of the dication term manifold, as well as the photoionisation mechanism, are clarified.

To discover the fate of toluene dications of low internal energy, we also measured the mass spectra and ion pair for-

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mation spectra of toluene by photoelectron-photoionphotoion coincidence (PEPIPICO) spectroscopy at a number of wavelengths. These measurements clearly identify the major dication dissociation pathways and cast new light on the mechanisms, which have also been the object of a detailed study in another paper by Roithová et al. [5].

## 2. Experimental

In the TOF-PEPECO experiment, wavelength-selected light from a fast pulsed discharge in He or Ne ionises target molecules in the strongly divergent field of a conical permanent magnet. The photoelectrons are collimated by the field and are guided to a 5.5 m distant detector by a weaker solenoid field. Electron flight times are recorded by a multi-hit time-to-digital converter and are calibrated as energies using the oxygen photoelectron spectrum as standard, measured before and after each experimental run. Details have been given in earlier papers [2–4].

For measurements of PEPIPICO spectra, an apparatus developed for angular correlation experiments [6] has been modified. Photoionisation is by wavelength-selected light from an electron cyclotron resonance (ECR) lamp [7], which impinges on target molecules in a uniform electric field of  $100 \text{ V cm}^{-1}$  between two plane grids. Electrons are accelerated to a nearby channel electron multiplier while positive ions are accelerated through a two-field

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time-of-flight mass spectrometer to a microchannel plate detector.

### 3. Results and discussion

## 3.1. Double photoionisation spectra

Double ionisation spectra of toluene and toluene- $d_8$ have been taken at three photon energies, 26.91, 32.69, and 40.81 eV. Spectra of the two isotopomers covering the full energy range are shown in Fig. 1, while comparison spectra covering the low energy region are given in Fig. 2. Because the electron energy resolution is energy dependent and better at low than at high energy, the ionisation energies can best be derived from measurements at the lowest photon energy. For both toluene- $h_8$  and toluene- $d_8$  the onset is at  $23.55 \pm 0.05$  eV; centres of the estimated three bands are at 24.0, 24.5, and 25.1 eV. The most notable difference between the spectra of the isotopomers is that the third band is more clearly delineated in the deuterium compound. A fourth band, which may be composite, has its peak near 26.5 eV. The electron pair distributions giving rise to these ionisations can be seen in an energy distribution map taken at 32.69 eV, shown as a grey scale image in Fig. 3.

From the spectra in Figs. 1 and 2 it is immediately evident that a state or group of dication states is populated at ionisation energies around 24.5 eV, rather isolated from an undifferentiated continuous population of states at energies above 26 eV. This accords well with the theoretical prediction [1] that three dication states,  ${}^{1}A'$ ,  ${}^{3}A''$  and  ${}^{1}A''$  should be accessible at the lowest energies, followed by more states at energies some 2 eV higher. The contour of the low energy band is consistent with the presence of three contributing states with intensity maxima near 24, 24.5 and



Fig. 2. Double photoionisation spectra of toluene- $h_8$  taken at 32.69 eV photon energy (b) and toluene- $d_8$  taken at 26.91 and 40.81 eV photon energies, (a) and (c), respectively.

25 eV, but whether or not these can be interpreted as vertical ionisation energies requires further discussion. Band maxima approximate vertical ionisation energies only if the ionisation process is a direct transition from the neutral ground state to the ionic state. The electron pair energy distribution, Fig. 3, casts doubt upon such a proposition.

The electron pair distribution in formation of the low energy band is seen in Fig. 3 to favour pairs with one electron of high energy and one low, with few electrons of near equal energy. Examination reveals a broad peak in the distributions measured at both 32.69 and 40.81 eV, where one



Fig. 1. Complete double photoionisation spectra of toluene and toluene- $d_8$  at 40.81 eV photon energy with part of the photoelectron spectrum shown under the same conditions.



Fig. 3. Complete electron pair energy distribution map at 32.69 eV photon energy.

electron has energy of about 1 eV and the other has the complementary energy hv - DIP - 1 eV. At 26.91 eV, where the excess energy is only 2 eV, the distribution is again peaked at 1 eV, which in this case represents equal energy sharing. The appearance of these distributions indicates that a major part of the double ionisation process at all these photon energies must be autoionisation, via a state of the singly charged ion about 1 eV above the peak of the low energy double ionisation band, i.e. at about 25.5 eV. The (partial) photoelectron spectrum included in Fig. 1 shows the existence of just such a state, or group of states, with its peak at about 26 eV and extension up to 27 eV. This may be a configuration interaction satellite band or a simple direct one-electron ionisation, in either case deriving its intensity from the allowed ejection of an electron from the C2s-based molecular orbitals of toluene. One calculation [8] locates an orbital of this character at 25.97 eV. The direct ionisation and autoionisation processes cannot be separated quantitatively at any wavelength, partly because even the direct part will produce a hollow distribution at high excess energy; nevertheless the form of distributions indicates a strong autoionisation contribution. Thus we cannot agree with the assumption of purely direct ionisation made by Roithová et al. in applying the Wannier model to their analysis [1]. We note that they were aware of this possible weakness in their treatment.

The existence of autoionisation via a monocation state is likely to broaden the ionisation bands beyond the purely vertical Franck–Condon region, possibly enhancing the probability of access to the adiabatic threshold. It is therefore interesting to extract double ionisation spectra which emphasise 'direct' and 'autoionisation' contributions, insofar as they can be separated by selecting electron pairs with the appropriate energy sharing. Examination of the data suggests that a different autoionisation process may be involved for electrons of the lowest energies, below 0.5 eV. At 32.69 eV photon energy we therefore take pairs with near equal energy ( $\Delta E < 2.0 \text{ eV}$ ) to represent direct double photoionisation, pairs with either electron having an energy of  $1 \pm 0.5 \text{ eV}$ , or one energy below 0.5 eV to represent autoionisation. The resulting spectra are compared in Fig. 4. In the spectrum from pairs of nearly equal energy ('direct' process, Fig. 4b) the intensity of the low energy band is significantly weakened relative to the higher energy ones, as must be expected. The opposite happens when pairs emphasising autoionisation (Fig. 4c and d) are selected. There are minor differences in other characteristics, particularly the relative intensities of the components making up the low energy double ionisation band, but the lowest onset remains essentially constant at  $23.55 \pm 0.05$  eV. The lowest energy component, which may represent the <sup>1</sup>A' state, is particularly enhanced and also sharpened when electron pairs with one energy below 0.5 eV are selected. This and the other differences visible in Figs. 2 and 4 confirm the involvement of autoionisation via states or levels of different geometry from that of neutral toluene.



Fig. 4. Lower energy band in the spectrum of toluene at 32.69 eV from all electron pairs (a), electron pairs with near equal energy (b), electron pairs including one at 0.5-1.5 eV (c) and electron pairs including one at 0-0.5 eV (d).

#### 3.2. Dissociation of doubly charged toluene

Photoionisation mass spectra and PEPIPICO spectra of toluene- $d_8$  have been measured at six photon energies (wavelengths): 25.32 eV (48.9 nm), 26.91 eV (46.1 nm), 27.69 eV (44.7 nm), 30.45 eV (40.7 nm), 33.91 eV (36.5 nm) and 40.81 eV (30.4 nm). The relative intensities of the major processes are listed in Table 1, corrected for our known ion and electron collection efficiencies. The PEPIPICO spectrum at 36.5 nm is shown as an example in Fig. 5.

No significant dissociation of the toluene dication is detected at 25.3 eV and neutral hydrogen  $(D_2)$  loss, leaving a  $C_7 D_6^{2+}$  dication, is the only significant process at 26.9 eV. The charge separation reactions illustrated in Fig. 5 do not set in below 27.8 eV, where our double ionisation spectra show the existence of many states. The most abundant ion pair at all shorter wavelengths is  $C_2D_3^+ + C_5D_5^+$ , the second most abundant is  $C_2D_3^+ + C_5D_3^+$  which is clearly shown by a metastable signature (diagonal tailing) [9] in the PEPIPICO spectrum to originate in intermediate  $C_7 D_6^{2+}$  ions. The eight most abundant ion pair dissociation pathways at 33.91 eV (36.5 nm) are listed in Table 2. The slopes of three of the peaks in the PEPIPICO spectrum are distinctly different from unity; these slopes and weak vertical tailing metastable signatures strongly suggest the secondary dissociation mechanisms given in Table 2.

Because  $H_2$  loss starts only above 26 eV where many states of the dications are populated, we are not convinced by the arguments of Roithová et al. [5] ascribing the frag-

Table 1

The major dissociation pathways of doubly charged toluene- $d_8$  ions at different photon energies, corrected for ion and electron detection efficiencies

Photon energy (eV)	Intensity relative to the summed $C_7D_8^+$ and $C_7D_7^+$ peaks = 10,000					
	$C_7 D_8^{++}$	$C_7 D_6^{++}$	$C_{2}D_{3}^{+}+C_{5}D_{5}^{+}\\$	$C_2D_3^+ + C_5D_3^+$		
40.81	278	120	142	129		
33.91	165	86	92	48		
30.45	138	75	35	7.7		
27.69	81	18	1.2	_		
26.91	61	4	$0.2 \pm 0.1$	_		
25.33	20	$0\pm 0.02$	$0.2\pm0.2$	$0.2\pm0.2$		

Table 2

Relative intensities of the eight major ion pair products from toluene-d<sub>8</sub> at 33.9 eV



Fig. 5. PEPIPICO spectrum of toluene- $d_8$  at 33.91 eV.

mentation pathways to decay from the lowest singlet or lowest triplet states. The 'strong' assumption of quasi-equilibrium theory [10] that all higher states decay by internal conversions to the ground state before dissociation is not valid for all monocations [11] and is untested (to say the least) for dications. Furthermore, as usually applied, it also includes intersystem crossings and does not preserve distinctions of multiplicity. The removal of two bonding electrons and the presence of strong coulombic forces suggest that in many dication states dissociation may be very rapid, or even direct.

# 4. Conclusions

The revision of the adiabatic double ionisation threshold of toluene put forward by Roithová et al. is confirmed. Details of the full spectrum of the doubly charged ion and of the electron distributions suggest that the processes of double photoionisation and dication dissociation are more complex than initially assumed.

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Ion pair	Intensity (relative to the main reaction $= 1000$ counts)	Slope	Probable mechanism	I heoretical slope
$C_2D_3^+ + C_5D_5^+$	1000	$-1.02\pm-0.03$	_	_
$C_2D_3^+ + C_5D_3^+$	527	$-0.96\pm0.03$	_	_
$C_2D_3^+ + C_3D_3^+$	462	$-0.75\pm0.05$	$\mathrm{C}_5\mathrm{D}_5^+  ightarrow \mathrm{C}_3\mathrm{D}_3^+$	-0.60
$CD_{3}^{+} + C_{4}D_{3}^{+}$	434	$-0.70\pm0.05$	$C_6D_5^+ \rightarrow C_4D_3^+$	-0.66
$CD_{3}^{+} + C_{6}D_{5}^{+}$	414	$-1.01\pm0.03$	_	-
$C_3D_3^+ + C_4D_4^+$	187	_	_	-
$C_3D_3^+ + C_4D_3^+$	178	_	_	_
$C_3D_3^+ + C_4D_2^+$	59	-	_	_

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