NEGATIVE SURFACE IONISATION OF HYPERTHERMAL HALOGEN ATOMS

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Negative surface ionisation of hyperthermal halogen atoms was studied as a function of their kinetic energy on thoriated tungsten and on niobium wires. The transition from a thermal equilibrium process to direct reflection causes the ionisation to increase drastically above thermal energies: efficiencies up to 40% were found for 30 eV Cl atoms impinging on thoriated tungsten.

1. Introduction

Positive surface ionisation (PSI) of atoms on surfaces is a well known phenomenon. It is used extensively for the measurement of particle fluxes in molecular beam experiments. Atoms striking the surface with thermal energies will stick to it for a time of about 10^{-4}–10^{-3} sec. This is long enough to establish a thermodynamic equilibrium between the particles and the surface. The evaporation of ions is described by the well known Saha–Langmuir equation. For alkali atoms and hot surfaces with a high work function this results in an ionisation efficiency of almost 100% [1]. At higher energies however a fraction of the impinging atoms is reflected directly, partly as ions, partly as neutrals. The latter particles cause a slight decrease in ionisation efficiency with increasing energy [2, 3]; reflected ions are formed even at the lowest temperature of the surface [4, 5]. At energies of some tens of eV this "fast" ionisation is the dominant mechanism of PSI, the efficiency is then almost independent of the temperature of the surface [6, 7].

Negative surface ionisation (NSI) is much less known. The ionisation of molecules containing atoms with high electron affinities, striking a surface with a low work function at thermal energies, has been studied recently [8, 9]. Even in the most favourable case the ionisation efficiency is only 2%. For negative surface ionisation, "fast" ionisation at higher energies might increase the ionisation efficiency. In this paper we report measurements on NSI of hyperthermal halogen atoms impinging on thoriated tungsten and niobium wires. We have found indeed that "fast" ionisation occurs in this energy range with an efficiency which is an order of magnitude higher than NSI efficiency for thermal halogen compounds.

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2. Experimental method

A detailed description of the apparatus will be given elsewhere [10]. Halogen beams were obtained by sputtering on alkalihalide (MX) surfaces with a 6 keV Ar^+ ion beam. After velocity selection the alkali component of the sputtered beam was measured by PSI on an Re 75 $\mu\Phi$ wire at 1400°K, giving currents of 5×10^{-14} to 2×10^{-13} A. At this temperature the ionisation efficiency for thermal alkali beams is known to be unity even for Na because of oxidation of the wire [11]. The NSI detector on which the measurements for velocity selected halogens were performed, consisted of a wire surrounded by a cylindrical collector of 2 cm Φ. The wire was placed in a permanent magnetic field of 350 G to prevent electrons from reaching the collector. A potential difference of 30 to 60 V was maintained between wire and collector, so that energetic positive ions which may be formed

on the wire could not reach the collector. The experiments were done with 100 $\mu\varnothing$ Nb and 75 $\mu\varnothing$ thoriated tungsten (W–Th) wires, the latter carbonised and activated according to Perski et al. [8]. We did not succeed in detecting low energetic sputtered halogens because the fluxes are low and because of the relatively high electron background at a temperature of 1600 to 1800°K at which most efficient NSI of thermal halogen compounds takes place [8]. For energies above some eV however, we found a temperature independent NSI signal. During the measurements of these hyperthermal halogens the temperature of the wire was kept at a temperature of 1300°K to avoid poisoning. At this temperature the electron background is negligible.

For the present research, halogen and alkali atoms were sputtered from MX targets with the lowest possible difference in mass between the M and the X atom: NaF, KCl, RbBr and CsI. In earlier experiments the sputtered beam was analysed by mass spectroscopy [10]. From these measurements we know that above a few eV the energy distributions of isobaric alkali and halogen atoms are the same.

From sputtering theory we infer that for the targets used by us at energies of some eV also the number of ejected alkali and halogen atoms are about equal [12].

Taking the PSI efficiency of energetic alkali atoms on Re to be unity, which may be true within 20% [2, 3], the efficiency β of the NSI detector at a given energy is given by

$$\beta = (I^{-}/I^{+})\,G\,, \qquad (1)$$

in which I^{-} and I^{+} are the signals on the NSI and PSI detector, respectively, and G is a geometry factor. To determine G we reversed the potentials of the NSI detector and deactivated the W–Th wire. The PSI signal of a thermal K beam was now measured on both detectors. Because the ionisation efficiency is known to be unity for K on deactivated W–Th and on Re [8, 11], the ratio of these signals equals G. For Nb this measurement was done with thermal Cs. Because the work function of Nb and Re is higher than the ionisation potential of Cs we assumed the ionisation efficiency to be unity. The obtained values for G were in agreement with the calculated ones from the distances of the wires with respect to the source.

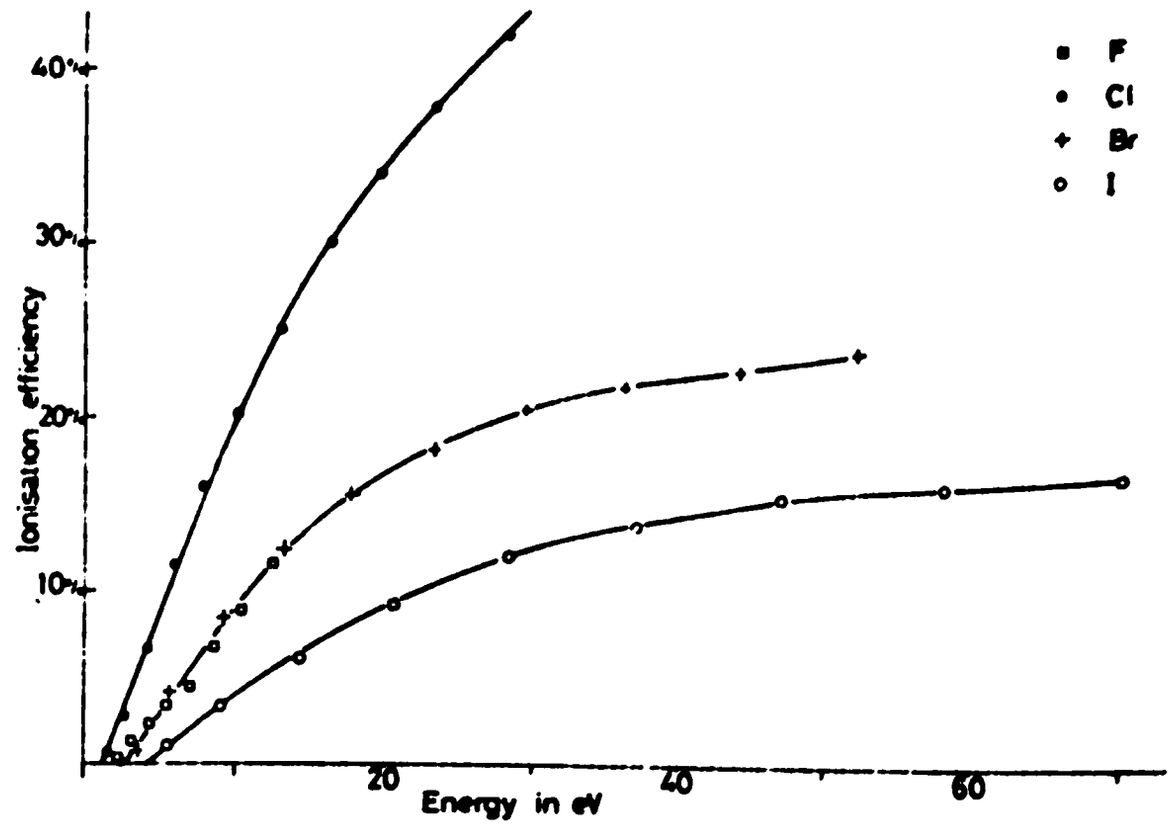

Fig. 1. Negative surface ionisation efficiency for F, Cl, Br and I atoms on thoriated tungsten as a function of their kinetic energy.

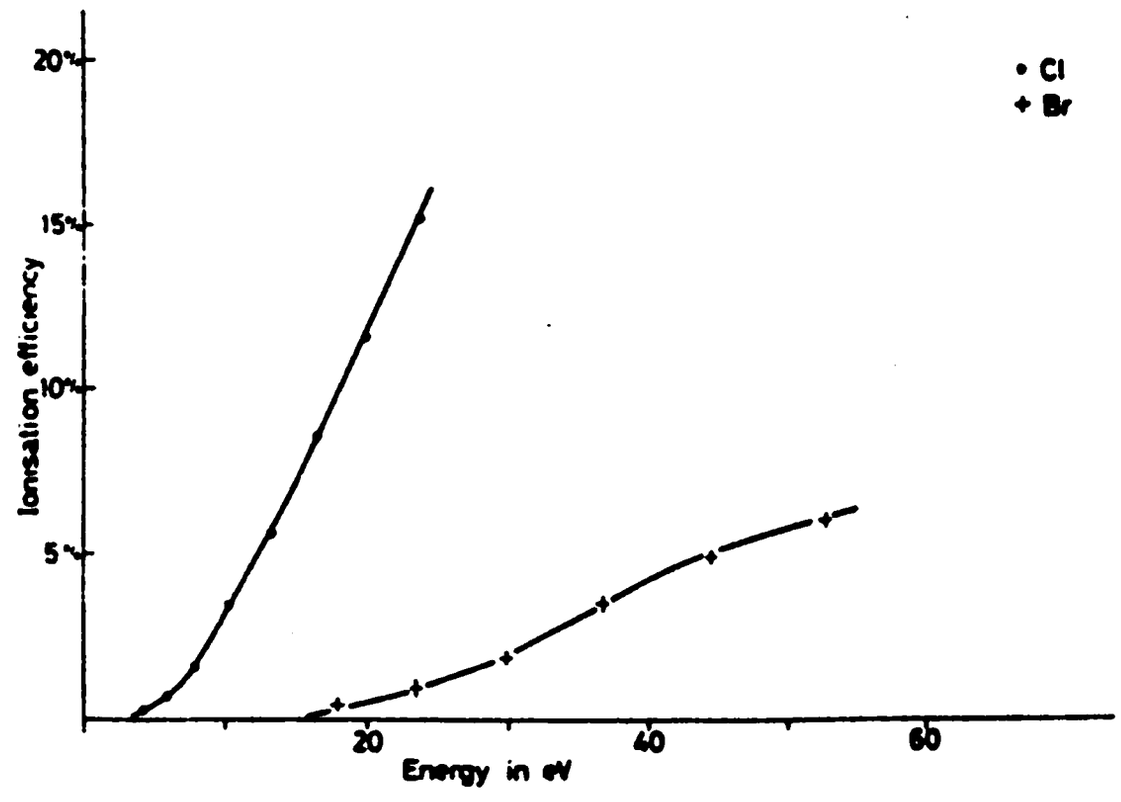

Fig. 2. Negative surface ionisation efficiency for Cl and Br atoms on niobium as a function of their kinetic energy.

3. Results and discussion

In figs. 1 and 2 the NSI efficiencies of the halogens on W–Th and on Nb wires are given as a function of energy. The NSI of F and I on Nb could not be measured, being lower than 1%. Because we used velocity selected beams, the maximum energy is different for the different halogens. Figs. 1 and 2 show a dramatic increase of the efficiency, similar to that of the PSI of alkalis on cold surfaces [6, 7].

Two remarks can be made concerning the results

Table 1
Electron affinities and measured ionisation efficiencies on W–Th at 10 eV kinetic energy for different halogen atoms

	Electron affinity in eV [13]		Ionisation efficiency at 10 eV kinetic energy
	$^2P_{1/2}$	$^2P_{3/2}$	
F	3.49	3.45	9%
Cl	3.72	3.61	20%
Br	3.82	3.36	9%
I	4.00	3.06	4%

of figs. 1 and 2. Firstly, it was found earlier that sputtered halogens are formed in the excited $^2P_{1/2}$ state for about 30 to 50% [10]. One might expect, that the NSI efficiency at a given energy will increase with increasing electron affinity of the atom and with decreasing work function of the detection wire. In table 1 the electron affinities of the halogens in the $^2P_{3/2}$ ground state and in the $^2P_{1/2}$ state are given as well as the ionisation efficiencies at 10 eV kinetic energy on W–Th.

From table 1 we see that the ionisation efficiencies show for F, Cl, Br and I the same tendency as the electron affinities of the $^2P_{3/2}$ ground state. From this we infer that the excitation does not play an important role in hyperthermal NSI.

Secondly, we found from our investigations on particles sputtered from various salt surfaces that MX molecules are present up to about 10 eV [10]. The maximum flux of these particles occurs at a few eV. At these velocities the flux of the MX molecules is about 30% of the halogen atoms. However, sputtering on all possible alkali chlorides, we found the same NSI signals as a function of velocity and the same thresholds [10]. Because the heavy MX molecules have relatively large energies at the threshold velocity, this indicates that highly efficient NSI of energetic molecules does not occur. This can be understood by the following arguments. The formation of MX^- is unlikely since the MX molecules have a closed shell configuration. An alternative mechanism for hyperthermal NSI would be dissociation of the MX molecules and formation of X^-, as is known to occur in NSI of thermal MX molecules. However, in thermal NSI the molecules are dissociated during the equilibrium with the surface, while reflected hyperthermal MX molecules have to take the dissociation energy directly from their kinetic energy. Therefore, the energy required for formation of X^- from hyperthermal MX on surfaces is much larger than for formation of X^- from X, and consequently the efficiency for the former process is expected to be very low. Finally, we want to mention the fact that the sputtered MX molecules can be detected on the PSI detector. For this reason the ionisation efficiencies in figs. 1 and 2 may be somewhat too low for energies below 5 eV.

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