Dear Sir,

Reactions Between Doubly Charged $[\text{C}_6\text{H}_5\text{I}_2]^{2+}$ Ions and Self-assembled Monolayer Surfaces

Self-assembled monolayer films prepared on gold surfaces have been used extensively in recent ion-surface collision experiments. A portion of the kinetic energy of the projectile is converted into ion internal energy on collision and this energy transfer leads to dissociation of the projectile. This process is referred to as surface-induced dissociation (SID). In addition to dissociation, another interesting feature of these experiments is the detection of ions corresponding to reactions between the projectile ion and the monolayer films. Addition of H or CH$_3$ to singly charged benzene and pyrazine$^{1,2}$ molecular ions from alkane alcohols monolayers (n-C$_{18}$H$_{37}$, n = 4, 18) have been observed, in addition to analogous reactions involving D and CD$_3$ additions from perdeuterocarboxylic monoester monolayers$^{3,4,5}$ (n-C$_{18}$D$_{37}$Sb). We used a tandem quadrupole mass spectrometer that has been described previously.$^6$ The collision energy was varied from 15 to 60 eV. Singly and doubly charged molecular ions were produced by 70 eV electron impact ionization. The pressure in the analyser region was kept within the range 5.0 × 10$^{-5}$ - 5.5 × 10$^{-7}$ Torr (1 Torr = 133.3 Pa). For further details of surface preparations and instrument parameters, see Refs 5 and 10.

Figure 1 shows the ion-surface collision spectra obtained by colliding (a) singly charged benzene, (b) doubly charged benzene, (c) singly charged hexa-2,4-diyne and (d) doubly charged hexa-2,4-diyne at 30 eV collision energy with a surface prepared from CF$_3$(CF$_2$)$_2$CH$_2$CH$_2$SH on vapour-deposited gold. Spectra obtained with alkane alcohols surfaces are not shown owing to space limitations, but are discussed below.

Unfortunately, the ions selected at m/z 39 contain both singly charged m/z 39 ([C$_6$H$_5$I]$^+$) and doubly charged m/z 78 ([C$_6$H$_5$I]$_2$$^{2+}$) ions. However, the collision of this beam with the hydrocarbon, deuterocarbon and fluorocarbon monolayers [see, e.g., Figs 1(b) and (d)] yields peaks in the range m/z 40-78, which can be explained by reduction of the doubly charged ions (m/z 78) and to subsequent fragmentations (e.g m/z 75, 52, 51, 50). The intensities of these peaks are about 1.0-3.5% of the selected beam (m/z 39) in the 30 eV ion-surface collision spectra of the doubly charged benzene on the fluorocarbon surface [Fig. 1(b)]. In principle, these ions could also originate from reactions between the singly charged [C$_6$H$_5$I]$^+$ cation (m/z 39) and the monolayer. However, the intensities of these peaks are less than 0.3% of the main beam (m/z 39) in the corresponding 30 eV ion-surface collision spectra of a 'pure' [C$_6$H$_5$I]$^+$ ion formed in the ion source from the molecular ion of benzonitrile. In this case, the doubly charged molecular ion (m/z 51.5) does not contribute to the ion beam of [C$_6$H$_5$I]$_2^+$ at m/z 39. The spectrum for the doubly charged benzene shows enhanced fragmentation of the singly charged ion formed by charge exchange at the surface in comparison with the singly charged ions formed in the source (compare Fig. 1(b) and Fig. 1(a)). The singly charged hexa-2,4-diyne ion (m/z 78) was not detectable in the 30 eV ion surface collision spectra of the doubly charged ion obtained with the fluorocarbon surface, and only a very weak peak was observed at m/z 78 in the corresponding spectrum obtained on the octadecanethiolate surface. This ion has also not been observed at 42 eV collision energy with a stainless-steel surface.$^8$ We suggest, therefore, that the singly charged molecular ion of the hexa-2,4-diyne isomer formed by charge exchange process with the surface is less stable than that of benzene. Note that the ions at m/z 31, 45, 57 and 70 in the ion-surface collision spectra shown in Fig. 1 are presumably F-containing ions with the formulae [CF$_3$]$^+$, [C$_2$H$_3$F]$^+$, [C$_3$H$_7$F]$^+$ and [C$_4$H$_9$F]$^+$, respectively.

Peaks at m/z values higher than 78 indicate reactions between projectile ions and monolayers. The spectra for singly and doubly charged deuterobenzene (CD$_3$I) confirm that, similarly to the singly charged spectra,$^{2,3}$ the peaks at m/z 96 and 95 are due to an F-addition reaction with benzene ions followed by subsequent H and H$_2$ losses, respectively [Figs 1(a) and (b)]. (The peaks at m/z 96 and 95 are shifted to m/z 101 and 99, respectively.) Although deuterated hexa-2,4-diyne was not available to us, it is reasonable to assume that the peak at m/z 96 and 95 in the singly charged spectrum [Fig. 1(a)] originate also from an initial F addition. The peaks at m/z 96 and 95 are not observed in the spectrum of the doubly charged hexa-2,4-diyne ion [Fig. 1(d)]. However, peaks at m/z 94, 93 and 92 together with, e.g., m/z 74 appear in the spectrum when the ion at m/z 37 is selected from the ion source. This suggests that an ion [C$_6$H$_5$I]$_2^+$ (m/z 37) is also formed in the ion source. This doubly charged ion undergoes charge exchange with the surface forming the ion at m/z 74 and reacts with the fluorocarbon surface, forming e.g. [C$_6$H$_5$F]$^+$ (m/z 92) and [C$_6$H$_5$F]$^+$ (m/z 93). A peak at m/z 91 appears in the ion-surface collision spectra of both the singly and doubly charged C$_6$H$_5$I ions obtained with alkane alcohols surfaces. This peak results from CH$_2$I addition following by H$_2$ loss, as supported by the reactions with the perdeuterocarboxylic monoester surface. In the case of the deuterated surface, three peaks are observed at m/z 94, 93 and 92, which correspond to CD$_3$I addition and the subsequent loss of H$_2$ (m/z 94), HD (m/z 93) and D$_2$ (m/z 92). The relative abundances of the ions corresponding to F addition remain roughly the same in comparison with the total ion abundances for both the singly and doubly charged ions of benzene; the intensities of the 'methyl addition' peaks are significantly lower for the doubly charged ions of both isomers.

Additional experiments are in progress to obtain more information on the isomeric [C$_6$H$_5$I]$_2^+$ structures and the
energetics of the ion–surface reactions. Our preliminary results are in better agreement with the assumption of a closed-ring (but not necessarily planar) \(^{11}\) form of the doubly charged benzene, although a mixture of isomer ions may be present.

Yours

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