

Internal Energy Distribution of Benzene Molecular Ions in Surface-Induced Dissociation

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The so-called 'deconvolution' method has been used to determine the internal energy distribution of molecular ions of an organic compound, benzene, excited by collisions with self-assembled monolayer surfaces formed on gold. The average internal energy was found to increase linearly with the laboratory collision energy. The kinetic energy–internal energy (T–V) conversion was 17% for the octadecanethiolate monolayer and 28% for the 2-(perfluorooctyl)-ethanethiolate monolayer surface. The results are similar to those obtained for metal carbonyl projectiles, though they indicate somewhat higher energy conversion. In addition, excitation of the projectile ion well beyond 20 eV internal energy is observed.

INTRODUCTION

Surface-induced dissociation (SID)¹ is an alternative ion activation method that has been applied recently to different kinds of ions including atomic and small organic molecular ions,^{2–7} as well as protonated peptides.^{8–14} Among other important aspects of ion–surface collisions, such as the reactions^{1b} between the projectile and self-assembled monolayer surfaces, the internal energy deposited to the projectile ion by the collision with a surface is of particular interest. This is an important quantity, especially if one wants to compare SID using various surfaces with gas-phase collisional activation (CA).

Internal energy distributions of ions activated by various means are often calculated by a method¹⁵ developed by Cooks and co-workers (usually called the 'thermometer' molecule (or ion) method). This method has been used for the calculation of the distribution of the internal energy deposited by surface-induced dissociation (SID).^{1,3,16,17} In the great majority of cases, molecular ions of transition metal carbonyls, e.g. W(CO)₆⁺, have been used as 'thermometer' ions. It has been found that: (i) on average, much more kinetic energy is converted to internal energy by SID than by CA; (ii) SID provides a narrower internal energy distribution than CA;^{1,16} (iii) a relatively well defined amount of kinetic energy is transferred to internal energy of the projectile ion in the collision; and that (iv) energy transfer does not depend on the type of instrument used, as far as similar instruments and/or similar time windows are concerned.¹⁷ For example, 13% kinetic energy–internal energy transfer was reported for

a hydrocarbon-covered stainless steel (untreated metal) surface.¹⁷ More recently, self-assembled monolayer films prepared on gold have been successfully applied in SID studies. It was found that alkanethiolate monolayers provide about 12% kinetic energy–internal energy conversion (comparable to that of the stainless steel), and that fluorinated alkanethiolate monolayers provide much more effective conversion of kinetic energy to internal energy (19%).³ More recently, Cooks and co-workers¹⁸ estimated the kinetic energy–internal energy transfer for ferrocene molecular ions at fluorinated and perdeuterated alkanethiolate surfaces. Their estimate was based on thermochemical appearance energies and led to the values of 24% and 15% for the fluorinated and the perdeuterated monolayer surfaces, respectively.¹⁸ A larger value of 60% for the T–V conversion has also been reported by Whetten and co-workers,¹⁹ for C₆₀⁺ collided with a graphite surface. These results show that the chemical composition of the projectile may play a role in the T–V conversion.

The 'thermometer' ion method, though very useful, is based on several assumptions, and is limited mainly to ions that have thermodynamically well characterized consecutive fragmentation processes. Although the method is not limited to transition metal carbonyls, these are the main ions that have been used as thermometer ions. This leads to a limitation, because the highest energy fragments of metal carbonyls are formed at around 15 eV internal energy. This means that limited information is available for energy transfers much beyond 15 eV for metal carbonyls. In this paper, an attempt is made to apply a different method for the determination of internal energy distributions, the so-called 'deconvolution' method.^{20,21} This has been developed in the course of electron capture collisions^{20,21} to determine the internal energy content of fragmenting singly charged ions. The application of the deconvolution method requires the knowledge of the accurate breakdown curves²² of an ion. This is a severe limitation, because accurate breakdown curves have been

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determined only for a few ions. Nevertheless, for benzene molecular ions, the breakdown curves have been published.²³ In addition, the time windows of the breakdown curve determination²³ and that of the surface-induced dissociation processes are comparable (μs), so it is reasonable to use the breakdown curves in our study even from a kinetic point of view.

The principle of the 'deconvolution' method is the following: If the breakdown graph and the internal energy distribution are known, the mass spectrum can be determined by the convolution of the two curves. If, on the other hand, the breakdown curve and the mass spectrum are known, the internal energy distribution can be calculated by a deconvolution process. The 'thermometer molecule method' uses a similar idea, but instead of experimentally determined breakdown curves, relies on threshold appearance energies of fragment ions formed by consecutive bond cleavages. For most organic compounds, where rearrangements and parallel reactions are frequent, the use of experimental breakdown curves and a deconvolution procedure is necessary.

The deconvolution process was originally developed for benzene,^{20,21} and has been successfully applied for acetone²⁴ and pyridine,²⁵ as well. For benzene, the breakdown curve has been determined²³ in the 0–15.3 eV internal energy range, and was extrapolated to 20 eV internal energy. Deconvolution was performed by a simple approximate method, and the results have been tested thoroughly both qualitatively and quantitatively up to 15 eV internal energy. At higher energies the method could not be tested, as there is no suitable means of producing benzene ions with a known internal energy above 15 eV. The shapes of the internal energy distribution curves were reasonable, and the accuracy of mean internal energy determination was estimated to be ± 1 eV based on charge exchange experiments.^{20,21}

In the present paper, an attempt is made to apply the 'deconvolution' method^{20,21} to estimate kinetic energy–internal energy conversion in the SID process of an organic molecule, benzene, using a fluorinated alkanethiolate (2-perfluorooctyl-ethanethiolate; F-surface) and an alkanethiolate monolayer surface (octadecanethiolate, C_{18} -surface). It was found that at higher laboratory collision energies ($E_{\text{LAB}} > 40$ eV), highly excited species are formed in relatively large abundances, resulting in fragment ions not encountered in collision induced decomposition. To obtain more accurate results the original deconvolution method has been extended to higher SID internal energies (up to 40 eV), and this modification is also described in the present paper. The two, somewhat different, versions of the deconvolution method will be referred to as 'original' and 'extended' below.

RESULTS AND DISCUSSION

Internal energy distributions of benzene molecular ions, activated by collisions both with 2-(perfluorooctyl)-ethanethiolate (F-surface) and with octadecanethiolate (C_{18} -surface) monolayer surfaces, were determined. In the following discussion, for the sake of simplicity, results obtained for the F surface will be discussed in detail. The treatment of the data, and the results

obtained for the C_{18} -surface were analogous, and these will be summarized at the end of this section.

Internal energy distributions, determined by the original deconvolution method, give the relative proportion of ions in very broad ranges between zero and 20 eV internal energy. Assuming uniform distribution within each internal energy range, energy distribution curves and mean internal energies can be determined. Internal energy distribution curves determined in this way at 10, 30, 50 and 70 eV collision energies are shown in Fig. 1. The first two are almost totally 'complete' in the 0–20 eV internal energy range. The curves corresponding to 50 and 70 eV show, however, a cutoff at 20 eV internal energy, indicating a limitation in the original deconvolution method at unusually high internal energies. Figure 1 suggests that, at high collision energies, benzene ions with more than 20 eV internal energy are formed.

The original deconvolution method uses only a few selected ions from the spectra, m/z 78, 77, 52, 51, and 50, to determine the internal energy distributions for benzene molecular ions. From the measured intensities of these peaks, following the deconvolution procedure, the total ion current of benzene can be calculated. Comparison of the calculated and the actually measured total ion current offers a simple check on the validity of the original deconvolution method. Up to 30 eV collision energy the calculated and measured total ion currents agree within 5%, but at higher energies the calculated value decreases significantly. At 70 eV collision energy, for example, the calculated value is only 53% of the measured one. This suggests, in agreement with Fig. 1, that at high collision energies a significant percentage of the fragment ions are not accounted for in the original deconvolution procedure. Indeed, the spectra⁷ show abundant ions at m/z 26, 27, 38 and 37, which are not observed in the breakdown diagram, because their formation requires more energy than that available from photon sources or from charge exchange. In fact, there is no readily available method currently which can impart a well defined energy over 24 eV (ionization energy of He) into a molecule or ion. After the ionization energy of benzene is subtracted, this

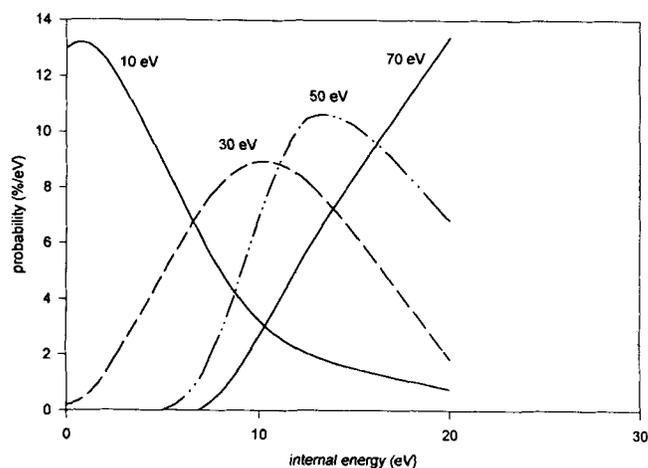


Figure 1. Internal energy distributions of benzene molecular ions determined by the original deconvolution method. Collisions using a fluorinated monolayer surface at 10, 30, 50 and 70 eV collision energies.

leaves less than 15 eV available for excitation of the ion. Note that the above mentioned high energy m/z 26 and 37 ions can also be observed in the 70 eV electron impact spectra, although in low abundance.

Difficulties above *ca.* 40 eV SID collision energy indicate that the 0–20 eV internal energy range, considered in the original deconvolution method,^{20,21} is not sufficient to describe SID processes using high collision energies. An extension of the deconvolution procedure seemed, therefore, necessary to cover a larger internal energy range. An advantage of using benzene instead of metal carbonyls in studies on energy transfer is that benzene molecular ions with over 20 eV internal energy give fragments which are not observed at lower internal energy. Breakdown curves are, however, not available (and difficult to measure) for this range, so approximations had to be made. In the 'extended' version of the deconvolution method two new ions, m/z 26 and 37 have also been considered, adding two internal energy ranges to those used in Refs 20 and 21.

The extended version of the deconvolution method is based on the following scheme, closely related to the 'original' version described in Refs 20 and 21: (i) Below 4.6 eV internal energy (Range 1) the molecular ion (m/z 78) will not decompose, and above this range, only fragmentation ions will be observed; (ii) Between 4.6 eV and 9.6 eV (Range 2) two major ions will be formed, $C_6H_5^+$ (m/z 77) and $C_4H_4^{+}$ (m/z 52). These ions represent 75% of all the ions in this energy range and they are not formed outside this range; (iii) Between 9.6 and 14.9 eV internal energy (Range 3), mainly $C_4H_3^+$ (m/z 51) ions are formed, representing 50% of all ions in this range, and $C_4H_3^+$ is not formed to a significant degree outside this energy window; (iv) The fourth energy range (Range 4) is from 14.9 to 20 eV, in which mainly $C_4H_2^{+}$ (m/z 50) ions are formed and these represent 50% of all ions in this range. $C_4H_2^{+}$ ions are, however, formed also in Range 3; their abundance is about 10% that of $C_4H_3^+$. As was mentioned above, additional energy ranges are necessary to account for the total ion current at higher SID collision energies. Because the appearance energies and breakdown curves of the additional low mass ions that appear in the SID spectra are not known, the definition of these ranges is, admittedly, arbitrary. The relative abundances of the high energy fragments m/z 26 and m/z 37 in the 60 and 70 eV SID spectra account for 25–30% of the total ion current. These ions were thus selected to define ranges 5 and 6. The criteria used to determine the ranges were to provide internal energy distribution peaks shapes above 20 eV internal energy analogous to those determined by the original method below 20 eV, and also to obtain a linear relationship between collision energy and mean internal energies over a wider SID collision energy range: (v) Range 5 is estimated to extend from 20 to 30 eV internal energy. Here mainly $C_2H_2^{+}$ (m/z 26) ions are formed representing about 2/3 of all ions in this range; (vi) The last range (Range 6) is estimated to extend from 30 to 40 eV, where C_3H^+ (m/z 37) is the major ion representing 2/3 of the total ion current in this range. Finally, the last assumption is that no ions are formed with more than 40 eV internal energy.

This model implies that the total ion current of benzene, irrespective of the internal energy distribution,

can be calculated from the intensities of the 7 selected ions (m/z 78, 77, 52, 51, 50, 37, and 26) if we correct for the contribution of each to the total. The total ion current (TIC) can be expressed by the following expression ($[i]$ indicating the abundance of the ion of mass i):

$$\text{TIC}_{\text{calc}} = [78] + 4/3\{[77] + [52]\} + 2[51] + 2\{[50] - 0.1[51]\} + 3/2[26] + 3/2[37] \quad (1)$$

The coefficients in expression (1) are the inverse of the fraction of ion $[i]$ in a given energy range, e.g. $\{[77] + [52]\}$ accounts for 3/4 (75%) of all ions formed with energies between 4.6 and 9.6 eV, so $4/3\{[77] + [52]\}$ accounts for *all* ions formed in that energy range. The TIC_{calc} values, determined according to the 'extended' deconvolution method by equation (1), can be compared with the total ion current measured directly. In all cases between 10 and 70 eV collision energy, the measured and calculated total ion abundance values agreed within 5%. This suggests that the extended deconvolution model based on 7 selected ions, as described above, does account for the fragmentation processes of benzene molecular ions over a wide energy range. This is a significant improvement over the 'original' deconvolution procedure based on 5 ions, which showed similar agreement only up to 30 eV SID collision energy.

Using TIC_{calc} the internal energy distribution in various energy ranges (Ranges 1–6) can be expressed. $P(n)$ denotes the probability of an ion having internal energy in Range (n), shown in %/eV units:

$$P(1) = ([78]/\text{TIC}_{\text{calc}})/4.6 \quad (2a)$$

$$P(2) = (4/3\{[77] + [52]\}/\text{TIC}_{\text{calc}})/5.0 \quad (2b)$$

$$P(3) = (2[51]/\text{TIC}_{\text{calc}})/5.3 \quad (2c)$$

$$P(4) = (2\{[50] - 0.1[51]\}/\text{TIC}_{\text{calc}})/5.1 \quad (2d)$$

$$P(5) = (3/2[26]/\text{TIC}_{\text{calc}})/10 \quad (2e)$$

$$P(6) = (3/2[37]/\text{TIC}_{\text{calc}})/10 \quad (2f)$$

The 'deconvolution' method gives the proportion of ions, $P(n)$, in each energy range, but there is no information on the distribution *within* the given range. The simplest assumption, used also in the 'original' version,^{20,21} is that the distribution is uniform *within* an energy range. Using this approximation the mean internal energy (E_m) can be calculated from the internal energy distribution by the following equation, and the results are shown in Table 1. (The general formula: $E_m = \sum_i [P(i) \cdot \text{width}(i) \cdot E_{\text{mean}}(i)]$; i denotes the energy range i .)

$$E_m = P(1) \cdot 4.6 \cdot 2.3 + P(2) \cdot 5.0 \cdot 7.1 + P(3) \cdot 5.3 \cdot 12.3 + P(4) \cdot 5.1 \cdot 17.5 + P(5) \cdot 10 \cdot 25 + P(6) \cdot 10 \cdot 35 \quad (3)$$

The internal energy distribution diagrams obtained by equations (2a–f) are histograms; that corresponding to 30 eV collision energy is shown in Fig. 2 (histogram). A distribution with such sudden changes is, however, physically unreasonable. The object is, therefore, to obtain a distribution which is 'smooth' (its derivative and second derivative should be continuous and preferably small), and the area below the curve in each energy range (as defined above) is equal to that determined by equations (2a–f). The result of such a fitting procedure

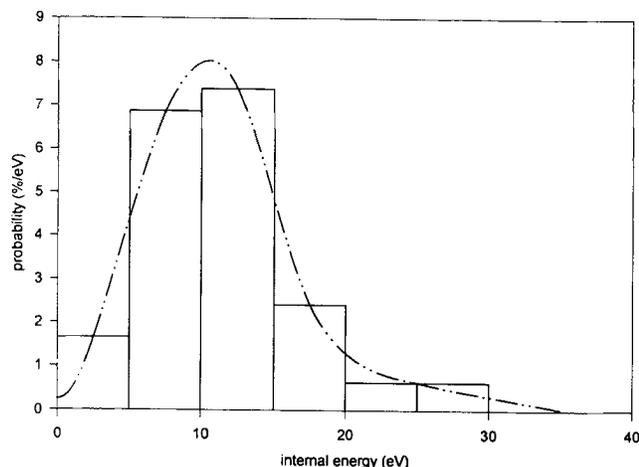


Figure 2. Internal energy distributions of benzene molecular ions determined by the extended deconvolution method. Collisions using a fluorinated monolayer surface at 30 eV collision energy. Assuming a uniform internal energy distribution within each energy range (continuous line) and assuming a smooth distribution (broken line). For details, see text.

is shown by the dashed curve in Fig. 2, for 30 eV collision energy. Such smooth internal energy distributions have been determined. As examples, results at 10, 30, 50 and 70 eV SID collision energies are shown in Fig. 3. It is worth mentioning, however, that mean internal energies are not affected significantly by 'smoothing'.

Comparison of internal energy distribution curves obtained by the 'original' (Fig. 1) and the 'extended' (Fig. 3) method show that the distributions up to 30 eV SID collision energy are very similar, although there is some 'tailing' to above 20 eV internal energy. The mean internal energies are also similar (Table 1). Above 30 eV collision energy, however, the probability of an ion having more than 20 eV internal energy will be very likely. Neglecting these high energy fragments would result in very unlikely distributions and large errors in the mean internal energy values.

The shape of the internal energy distribution curves obtained at various collision energies are quite similar.

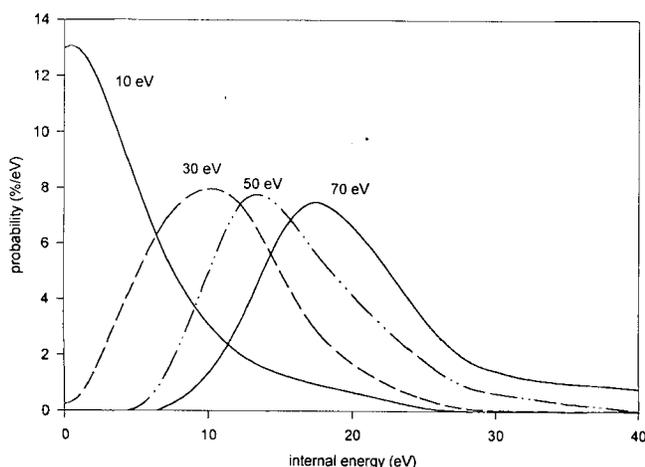


Figure 3. Internal energy distributions of benzene molecular ions determined by the extended deconvolution method. Collisions using a fluorinated monolayer surface at 10, 30, 50 and 70 eV collision energies.

Table 1. Mean internal energies of benzene molecular ions colliding on 2-(perfluorooctyl)-ethanethiolate (F-surface) and octadecanethiolate (C_{18} -surface) monolayer surfaces. Data were evaluated by the original and the extended versions of the deconvolution method.

Collision energy (eV)	Mean Internal Energy (eV)			
	Original method		Extended method	
	F surface	C_{18} surface	F surface	C_{18} surface
10	5.30	4.07	5.66	4.06
20	7.64	4.86	8.23	4.83
30	9.92	6.38	11.23	6.37
40	11.97	8.40	14.47	8.63
50	13.54	9.97	16.81	10.54
60	14.95	10.48	19.26	13.56
70	15.71	11.44	20.70	13.56

The ascending portion of the curves have a similar slope, or more precisely, a similar change in slope. The same is true for the descending portion of the curves. The similarity of the shape of the internal energy distribution curves, e.g. at 30 and at 70 eV collision energy (Fig. 3) is a further indication that internal energy ranges above 20 eV have been properly selected in the 'extended' version of the deconvolution method. The internal energy distribution curves are relatively narrow, but are, nevertheless, wider than those determined in the case of metal carbonyls. The full widths at half height are between 6 and 9 eV, showing only modest increase with increasing collision energy.

Results obtained for the C_{18} monolayer surface give analogous results; the only difference is that the internal energy deposition at a given collision energy is smaller than for the fluorinated surface. The mean internal energies calculated both by the original (broken lines) and the extended deconvolution method (continuous line) are shown in Fig. 4 and in Table 1. These show that up to ca. 10 eV mean internal energy the use of the 'extended' or the 'original' version yields similar results. At higher collision energies the original deconvolution method, due to the neglect of high-energy fragment ions, results in smaller mean internal energies.

Using the extended deconvolution method (continuous lines in Fig. 4) the calculated mean internal energies show a very good linear dependence on the collision energy (up to 60 eV collision energy). Statistical analysis of the data in the range of 10–60 eV collision energies indicates 0.999% and 0.992% linear regression coefficient using fluorinated and C_{18} monolayer surfaces, respectively. The mean internal energy at 70 eV SID collision energy on a fluorinated surface is slightly lower than estimated by the linear fit. The internal energy extrapolated to zero SID collision energy (intercept) is 2.9 eV and 1.7 eV for the F and C_{18} surfaces, respectively. These values can be used to predict the mean internal energy of benzene molecular ions deposited by electron impact ionization, i.e., before collision occurs with the surface. The mean value of the intercepts is 2.3 eV, which is the same as the mean internal energy assuming uniform distribution from zero to the fragmentation threshold of benzene (i.e., the half of Range 1: $4.6/2 = 2.3$ eV).

The slope of the plot of mean internal energy vs. SID collision energy gives the proportion of collisional

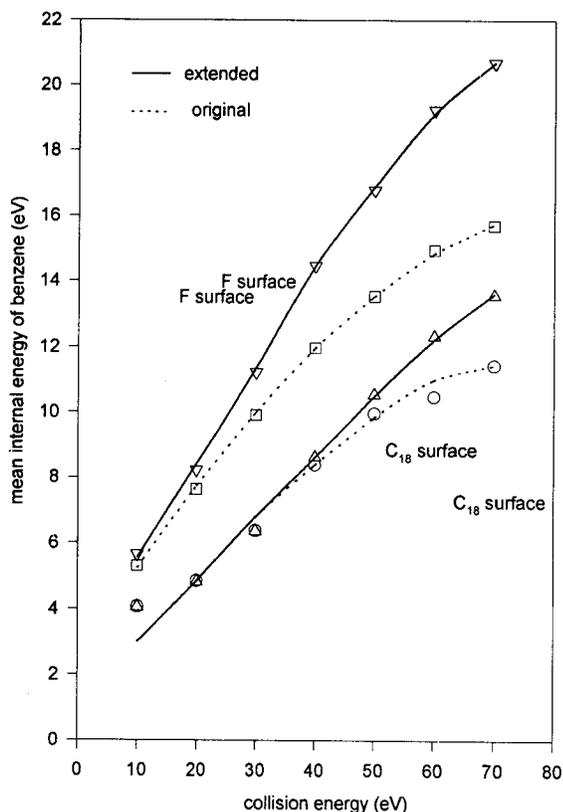


Figure 4. Mean internal energy distributions (eV) of benzene molecular ions determined by the original (broken lines) and the extended (continuous line) deconvolution method. Collisions using a fluorinated and a C_{18} monolayer surface between 10 and 70 eV collision energies.

energy converted to internal energy. The slope observed in Fig. 4 for the fluorinated surface is 0.28. This indicates that, on average, 28% of the kinetic (collision) energy of the benzene molecular ion is converted to internal energy. This is a high value, larger than the 19% determined in the case of $W(CO)_6^{+}$ using the thermometer method¹⁵ but closer to the 24% calculated for ferrocene¹⁸ ($Au-S(CH_2)_2(CF_2)_{11}CF_3$ surface). The C_{18} surface results in smaller energy conversion calculated for benzene, 17%, compared to 12% in the case of $W(CO)_6^{+}$ and 15% in the case of ferrocene ($Au-S(CD_2)_{15}CD_3$ surface). It is worth mentioning that the ratio of energy conversion on a fluorinated and on a C_{18} monolayer surface is practically the same (within the errors of determination) using the deconvolution method on benzene and the thermometer ion method on $W(CO)_6^{+}$ (1.65 and 1.58, respectively).

CONCLUSIONS

The present paper has addressed the calculation of internal energy distributions deposited to a projectile ion in low-energy ion-surface collisions. It has been demonstrated that the original deconvolution method can be extended to higher internal energy ranges (20–40 eV) that are necessary if higher energy fragments are

formed upon ion-surface collision. The present results obtained for low-energy collisions of benzene molecular ions with 2-(perfluorooctyl)-ethanethiolate and octadecanethiolate monolayer surfaces by using the extended deconvolution method are analogous to, even if quantitatively different than, those obtained for metal carbonyls^{3,16,17} and for ferrocene.¹⁸ The comparison of the present results with the previous ones indicate that: (i) There are differences in the kinetic energy-internal energy conversion calculated for benzene and metal carbonyl projectile ions. Calculations for benzene lead to excitation energies *ca.* 50% higher than those for metal carbonyls^{3,16,17} but only *ca.* 20% higher than calculated for ferrocene.¹⁸ This difference may be related to the method of determining internal energy distributions or to differences in chemical composition or structure. Benzene, like all organic compounds, contains hydrogen atoms. H-atoms may significantly influence energy conversion, as suggested for CA.^{26,27} Vibrational frequencies (again, mainly due to the low mass of hydrogen) are significantly different, and these may effect vibrational coupling between the projectile and the surface molecules. (ii) The internal energy distribution curves are wider in the case of benzene than in the case of metal carbonyls (also by about 50%). This may be a consequence of the higher internal energy calculated for benzene, or an *overestimate* of the width as a result of the broad energy ranges in the higher energy region associated with the 'extended' deconvolution method. Alternatively, the thermometer ion method may *underestimate* the energy range of the higher energy fragments. (iii) Molecular ions with internal energy well in excess of 20 eV are formed by SID in the case of benzene. It is also very likely in the case of other molecules, and further investigations for other ions are necessary to describe this high-energy region. [For a recent study on $Fe(CO)_6$, see Ref. 28.] (iv) Conversion of kinetic to internal energy is *ca.* 60% more efficient using a fluorinated, rather than a hydrocarbon monolayer surface; this ratio does not depend significantly on the projectile ion structure. (v) Surface collisions impart a much narrower distribution of internal energy to the projectile compared with high energy gas phase collisional activation (CA).^{20,21}

EXPERIMENTAL

The tandem mass spectrometer used in this investigation has been described¹⁷ and has been applied recently in several surface-induced dissociation studies.^{6,7,12–14,17} The instrument consists of two Extrel 4000 u quadrupoles positioned at 90°, with a surface placed to intersect the ion optical path of the two quadrupoles (45°). A surface holder designed originally for four surfaces⁷ was used to guarantee a similar laboratory environment from one surface to another.

Self-assembled monolayer surfaces were prepared by the spontaneous assembly of 2-(perfluorooctyl)-ethanethiolate (F-surface) and octadecanethiolate (C_{18} -surface) on vapor deposited gold. (For further details of surface preparation, see Ref. 7).

Energy resolved mass spectra for the molecular ion of benzene were determined in the 10–70 eV laboratory collision energy region by maintaining a potential difference between the ion source and the surface. To limit surface contamination, the pressure in the analyzer region was kept below the range of $5.0\text{--}5.5 \times 10^{-7}$ Torr. In the case of the C_{18} monolayer surface, interferences due to sputtering from the surface prevented the measurement of some fragment ions of benzene (e.g. m/z 26). These problems were resolved by using the

molecular ion of perdeuterobenzene ($C_6D_6^{+}$) or a perdeuterioeicosanethiolate monolayer surface.

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