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# Internal energy deposition through collision of hyperthermal neutral molecules with energies up to 5 eV with a surface

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## Abstract

When a hyperthermal molecule collides with a solid surface, its positive ions are scattered from the surface. In this hyperthermal surface ionization (HSI) process, some of the translational energy is used in the ionization of the molecule. At the same time, vibrational degrees of freedom in the molecule are also excited, resulting in the formation of fragment ions. This article describes the process of internal energy deposition through collisions of high kinetic energy molecules with a solid surface. The solid surface used was rhenium oxide ( $\text{ReO}_2$ ) and the molecule tested was iron pentacarbonyl  $\text{Fe}(\text{CO})_5$  with translational energies in the range of 0–5 eV. The internal energy distribution was estimated using the intensities of the fragment ions and the threshold energies for these fragments. The experimental results show that the ratio of the average internal energy to the translational energy amounts to some 30%. This is quite high compared with that previously reported for the HSI process and the ion/surface collision process. The mechanism giving this high conversion rate and the effect of the surface thermal energy on the internal energy is discussed. (Int J Mass Spectrom 194 (2000) 75–83) © 2000 Elsevier Science B.V.

**Keywords:** Internal energy; Molecule/surface collision; Surface ionization;  $\text{Fe}(\text{CO})_5$ ;  $\text{ReO}_2$

## 1. Introduction

In previous articles we have reported mass spectrometric studies on the mechanism of the hyperthermal surface ionization (HSI) process where aerodynamical acceleration of molecules, seeded into the supersonic free jet of He carrier gas, was used to enhance the efficiency of ionization. The sample molecules were benzene, toluene [1], aliphatic alcohols [2], and monoterpenes [3]. The results confirmed that (1) surface ionization appears to be dramatically

affected by incident kinetic energy ( $E_k$ ), (2) the kinetic energy is partially used for surface ionization (SI), and (3) the mechanism involves conversion of  $E_k$  to ionization through an impulsive process.

Recently, there has been much interest in the dynamics of the gas/surface energy transfer, and quite a few intensive studies have been carried out [4–7]. These energy transfer studies can provide great insight into the nature of gas/surface interactions in general. Studies of the ionization process at the surface are included in this exciting research area. An interesting question about the way the translational energy contributes to ionization at surfaces was discussed in a previous report [5] where we estimated the

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value  $\gamma$ , defined as the fraction of the kinetic energy effectively used for ionization. We used two unique methods: (1) the dependence of ion yield on the kinetic energy of the incident beam, and (2) the dependence of ion yield on the surface temperature. The results confirmed that (1) the kinetic energy is partially used for ionization, whereas (2) the efficiency of energy conversion varies with the molecule. These findings are consistent with the simple mechanism suggested earlier [1,2] that the energy required for surface ionization may be associated with the energy gap caused by the difference in ionization energy (IE) of the molecule and the work function ( $\phi$ ) of the surface.

Another particularly interesting problem is related to how the kinetic energy is transferred to the internal energy of the molecule. The energy deposited in the molecule, rearranged to each vibrational degree of freedom through a quasiequilibrium process, directly relates to the dissociation of the molecule and determines the mass spectral patterns observed in hyperthermal surface ionization mass spectrometry (HSIMS).

Danon et al. [6] reported a theoretical procedure based on quasiequilibrium theory, to estimate the mean energy content of the molecule for EI-induced fragmentation, and this method was applied to the HSI process, inferring the transfer of kinetic energy to vibrational–rotational energy for 1-iodopropane/diamond [6] and for the cholesterol/ReO<sub>2</sub> system [7].

Many studies of analogous ion/surface phenomenon have been reported [8–10] where mass-selected molecular ions, with kinetic energies in the range of 10–10<sup>3</sup> eV, were beamed against various solid surfaces. In these surface-induced dissociation (SID) processes, the large internal energies available have been shown to facilitate structural characterization in polyatomic molecules. Application to ion chemistry has also been illustrated [10].

In the present study, we report the method and the results of estimating the internal energy through collisions of hyperthermal molecules with a solid surface. The objectives of this report are: (1) to report the results of an experimental study of high kinetic energy molecule scattering from a Re-oxide surface; the molecule tested was ironpentacarbonyl [Fe(CO)<sub>5</sub>].

This scattering results in dissociative ionization due to energy transfer from the molecular kinetic energy; (2) to apply the method of Cooks et al. [8–10] to the present gas molecule/solid surface scattering process for estimating internal energy distribution of the molecular ions; (3) to discuss the effect of molecular kinetic energy ( $E_k$ ) and surface temperature ( $T_s$ ) on the internal energy distribution of the molecular ion; and (4) to discuss the main ideas behind this method and to compare the results with those obtained from other analogous experiments.

The kinetic energy of the colliding molecules in the present study covers up to 5 eV. This is a much smaller energy range than that examined in the SID process [8–10].

## 2. Experimental

### 2.1. Apparatus

The apparatus used was essentially identical to that of the hyperthermal ionization studies described elsewhere [1,2]. It basically consists of a large main chamber with a supersonic nozzle, and a second chamber with a surface and a quadrupole mass spectrometer (QMS), each chamber being pumped differentially. The supersonic nozzle was made of alumina with an 80- $\mu\text{m}$ - $\phi$  pinhole; the end 1.5 cm of the nozzle was electrically heated.

Sample materials were introduced through a sampling interface connected to a diffusion cell [11]. Samples of about 500 mg were placed in the cell located in a temperature-controlled oven. Either different oven temperatures or different dimensions of the diffusion tube prepared the desired concentration of sample molecule in the carrier gas (He). The sample introduction rate was 1–8  $\times 10^{-8}$  mol s<sup>-1</sup>, and sample concentration was 0.02–0.05% in He.

The seeded supersonic free jet can provide neutral molecules that are characterized by narrow kinetic energy distribution. The kinetic energy ( $E_k$ ) of seeded molecules can be determined by the well established method using nozzle temperature ( $T_n$ ), nozzle stagnation pressure ( $P_0$ ), and the ratio  $M_h/M_1$ , where  $M_h$

and  $M_1$  are the molecular mass of the seeded molecule and the carrier gas molecule, respectively [12,13]. We assume the width of the beam energy ( $\Delta V/V$ ) to be around 0.1 [5,13].

The angle of the incident and emerging beams was selected as  $45^\circ$  to the normal of the surface. The solid surface used was Re ribbon ( $0.025 \times 0.75 \times 15$  mm), which could be electrically heated up to 1500 °C. This surface was oxidized by the presence of  $O_2$  at a pressure of  $1 \times 10^{-5}$  Torr for 1–2 h. The treated surface could be used for at least one day in the temperature range 700–1200 K. However, in the present study,  $2 \times 10^{-5}$  Torr  $O_2$  gas was supplied constantly to the surface during the scattering experiment to ensure surface oxidation. This procedure also ensures that the surface reaction with dissociation products like CO or the other residual molecules in the chamber is negligible. The Re-oxide surface has been favorably used [1,2] because of its high work function ( $\varphi = 6.4$  eV [14]).

A quadrupole mass filter (ANELVA, Tokyo; AQA-200) placed normal to the beam axis served as a detector of ions emitted from the surface. All the ion currents reported here were output from a microchannel plate multiplier with the gain set to 500.

## 2.2. Mass discrimination in QMS

In principle, the method depends on the accurate measurement of the ion intensities; however, quadrupole mass spectrometers are known to have a large mass discrimination, depending on the operational conditions. We corrected this effect by comparing the mass spectral pattern of perfluoro-tri-*n*-butylamine [ $N(C_4F_9)_3$ ; PFTBA] with that obtained from a magnetic sector type mass spectrometer (NIST MS database [15]).

## 3. Results and discussion

### 3.1. Method for estimating the internal energy

The ionization process in HSI is considered to be impulsive—no molecular adsorption on the surface is

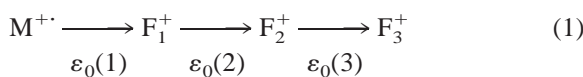
Table 1  
Ionic species,  $m/z$ , and their threshold energies for  $Fe(CO)_5$

Ion	$m/z$	Threshold energy/eV <sup>a</sup>
$Fe(CO)_5^+$	196	0
$Fe(CO)_4^+$	168	1.15
$Fe(CO)_3^+$	140	2.11
$Fe(CO)_2^+$	112	3.33
$Fe(CO)^+$	84	5.16
$Fe^+$	56	7.58

<sup>a</sup> Threshold energy was obtained by subtracting the appearance energy of each ionic species from the ionization energy of the molecular ion  $Fe(CO)_5^+$ . The appearance energies and the ionization energies were selected from [22–24].

involved. This has been proved by many measurements through HSIMS [3,16,17]. For example, HSIMS of limonene exhibits a very similar pattern to that of electron impact mass spectrometry (EIMS) [3]; the peak  $m/z$  of 68, which comprises the base peak in both spectra, is derived from the retro-Diels–Alder cleavage of the cyclohexene ring in the molecular ion and is known to be formed within 50 ps after the molecular ion formation [18].

Quasiequilibrium theory (QET) has been successfully applied to interpret EIMS, and the mass-spectral findings described above suggest the possible application of QET to the HSI process as well. On the assumption that the mechanism is explicable by QET, the following procedure can be applied to estimate the internal energy distribution function  $P(\epsilon)$  of the molecular ion. The method uses fragment ion abundance from a series of consecutive reactions with known threshold energies ( $\epsilon_0$ ) [Eqs. (1) and (2)]



$$P(\epsilon) = \frac{[F_i^+]}{\epsilon_0(i+1) - \epsilon_0(i)} \quad (2)$$

The threshold energy  $\epsilon_0(i)$  for the fragment ion  $F_i^+$  is defined as the energy required for it to dissociate from the molecular ion  $M^+$ , and is equal to the difference of their appearance energies (Table 1). This method is similar to that developed by Cooks et al., which has been successfully applied to estimate the internal energy deposition for a number of SID processes [9].

### 3.2. Contribution of thermal decomposition behind the nozzle

Another requirement for the method described above to be valid is that the molecules should be intact before the collision process. The contribution to the dissociative reaction behind the nozzle may be negligible for the following reason. The residence time of the gas molecules in the heated part of the nozzle (0.5 mm i.d.  $\times$  15 mm long = volume 3.0  $\mu$ L) is calculated to be  $1.5 \times 10^{-3}$  s, using a carrier gas flow of 2  $\text{cm}^3 \text{s}^{-1}$ . The unimolecular decomposition rate constant is described in Eq. (3) for the extreme case in which thermal energy  $kT$  is concentrated in only one oscillator in a molecule with dissociation energy  $D_0$  [19]

$$k^\infty = \nu \cdot \exp(-D_0/kT) \quad (3)$$

where  $\nu$  is the frequency of vibration and is in the order of  $10^{13} \text{ s}^{-1}$ . For the case of  $\text{Fe}(\text{CO})_5 \rightarrow \text{Fe}(\text{CO})_4$ ,  $D_0$  is  $41 \pm 2 \text{ kcal mol}^{-1}$  [20,21] and, if the nozzle temperature ( $T_N$ ) is set to 600 K or lower,  $k^\infty$  is calculated to be  $1.2 \times 10^{-2} \text{ s}^{-1}$  or smaller. This means that after  $1.5 \times 10^{-3}$  s residence in the 600 K region, at most only 0.002% of the  $\text{Fe}(\text{CO})_5$  will be decomposed. Experimentally, the rate constant ( $k$ ) expression for the first bond dissociation of  $\text{Fe}(\text{CO})_5$  was obtained by a pulsed laser pyrolysis experiment, as in Eq. (4)

$$\log(k) = (15.7 \pm 0.8) - ([41.0 \pm 2 \text{ kcal mol}^{-1}]/2.303R)(1/T) \quad (4)$$

giving  $k = 6 \times 10^{-3} \text{ s}^{-1}$  at  $T = 500 \text{ K}$  [21], where  $R$  is the gas constant. In each of the present experiments, the nozzle temperature was set to be lower than 500 K, which corresponds to  $E_k = 4.2 \text{ eV}$  using He as the carrier gas.

### 3.3. Mass spectra of $\text{Fe}(\text{CO})_5$

The spectra from HSIMS of  $\text{Fe}(\text{CO})_5$  are distinctly different from that of surface ionization organic MS (SIOMS; using  $\text{ReO}_2$  without molecular acceleration [22]) (Fig.1). The base peak in SIOMS is  $m/z$  56

( $\text{Fe}^+$ ), due to surface ionization of the final product of the thermal decomposition reactions, and the molecular ion is not observed. Surface chemistry of  $\text{Fe}(\text{CO})_5$  using Pt(1,1,1) show that a small amount of molecular adsorption is observed at 110 K [23], but  $\sim 70\%$  of it decomposes to yield atomic Fe. Adsorption at higher than 275 K results in total decomposition to give a Fe-covered surface layer. This latter case may be the initial process of SIOMS followed by the ionization process to yield  $\text{Fe}^+$ . On the other hand, HSIMS yields large intensities of molecular ions, and no traces at  $m/z$  56 with any kinetic energies examined (Fig. 1). Considering that the energy gap between the IE of Fe (7.9 eV [24]) and  $\phi$  (6.4 eV) is small, these observations support the mechanism described by Amirav et al. [17]; HSI for rather large molecules such as caffeine (M.W. 194) is characterized by a nonthermal equilibrium fast impulsive scattering that incorporates a molecular-surface electron transfer [16]. The molecular ion fragmentation is a secondary process that occurs after intramolecular vibrational energy redistribution, away from the surface. Another mechanism of HSI relevant for small molecules such as piperidine (M.W. 85), described by the same authors [25] as a very fast surface dissociation process, might not be the case for the present  $\text{Fe}(\text{CO})_5$  (M.W. 196) system.

### 3.4. The fraction $\gamma$ for $\text{Fe}(\text{CO})_5$

The value  $\gamma$ , which is defined as the fraction of the kinetic energy effectively used for ionization, is calculated from the slope of the linear regression curve of  $\log(\text{ion current})$  versus  $E_k$  (plotted in Fig. 2). We obtained the value of 0.23 (23%) for  $\gamma$  using Eq. (5),

$$\log(\text{ion current}) = (\gamma \cdot E_k + \phi - \text{IE})/(2.303 kT_s) + \text{constant} \quad (5)$$

where  $T_s$  is surface temperature,  $\phi$  is surface work function, IE is the ionization energy of the molecule, and constant is a proportionality constant that is associated with the instrumental parameters. This estimated  $\gamma$  value for  $\text{Fe}(\text{CO})_5$  is comparable with that of naphthalene, 0.2–0.3 [5]. Naphthalene and

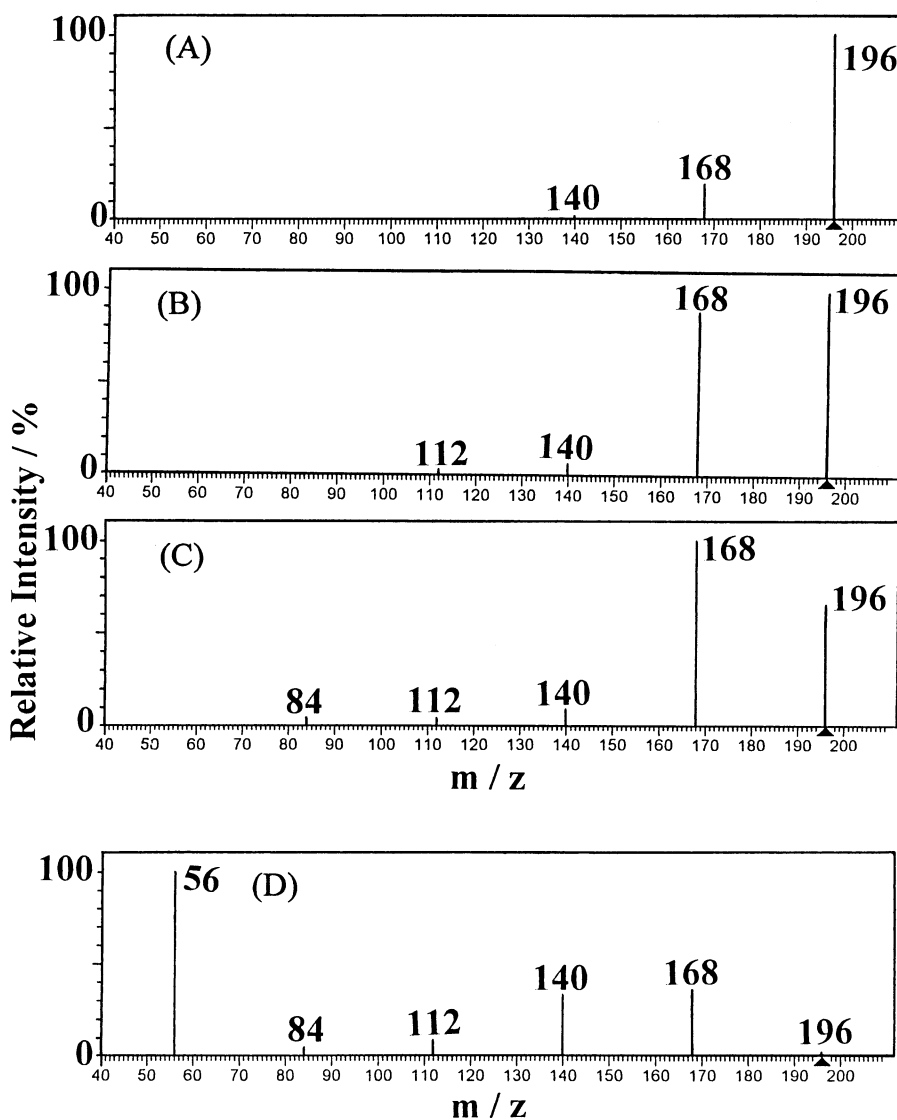


Fig. 1. Hyperthermal surface ionization mass spectra of  $\text{Fe}(\text{CO})_5$  [(A)–(C)] at constant surface temperature ( $T_s = 975$  K). Molecular kinetic energies ( $E_k$ ) are (A) 2.46 eV, (B) 3.37 eV, and (C) 4.15 eV. The surface ionization organic mass spectrum (D) of thermal energy molecules at  $T_s = 1650$  K [21] is also shown. The triangle indicates the molecular mass in each spectrum.

$\text{Fe}(\text{CO})_5$  have similar ionization energies, 8.14 and 8.00 eV, respectively [24].

### 3.5. Internal energy distribution versus $E_k$

The threshold energies  $\varepsilon(i)$  used to estimate the internal energy through the collision process are

shown in Table 1 [24,26,27]. By using these values, the internal energy distributions can be estimated for  $\text{Fe}(\text{CO})_5$  with kinetic energies ranging from 0–5 eV. From the internal energy distributions at five different values of  $E_k$  at a constant surface temperature (Fig. 3), we can estimate the following: (1) the average internal energy (the average of the internal energy weighted

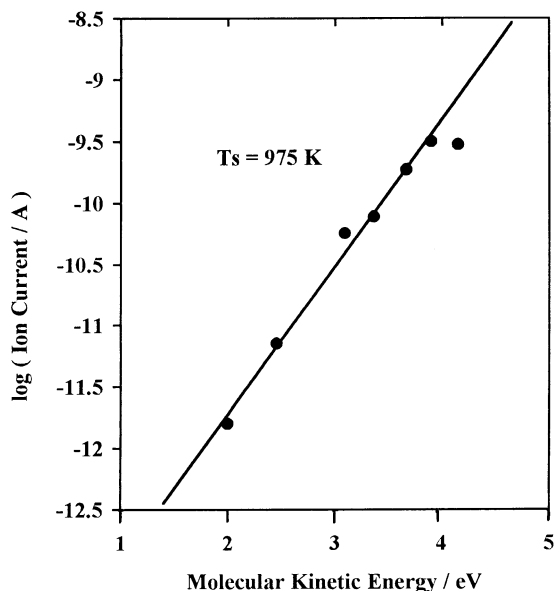


Fig. 2. Dependence of the molecular ion current (A) of  $\text{Fe}(\text{CO})_5$  on the kinetic energy at a constant surface temperature ( $T_s = 975 \text{ K}$ ). From the slope of this linear regression curve, the ratio of the kinetic energy effectively used for ionization ( $\gamma$  factor) is estimated to be 0.23 (23%).

Table 2

Average internal energy, conversion rate, and FWHM at constant surface temperature of  $T_s = 975 \text{ K}$

$E_k$ (eV)	Average internal energy (eV)	Conversion rate (%)	FWHM (eV)
2.46	0.73	30	1.0
3.10	0.86	28	1.3
3.37	1.06	31	1.6
3.67	1.12	30	1.5
4.15	1.23	30	1.6

by the abundance), (2) the conversion rate (the ratio of the average internal energy to the molecular kinetic energy,  $E_k$ ), and (3) the distribution width [FWHM (full width at half maximum) of the distribution curve]. These estimations are tabulated in Table 2. The average internal energy was plotted against  $E_k$  (Fig. 4) with the regression curve giving a straight line within the energy range tested. The line seems to pass near the origin (0,0), but the small intercept remains unexplained.

The results reveal that (1) the average internal energy increases with the increase in  $E_k$ , (2) the conversion rate is almost constant and amounts to

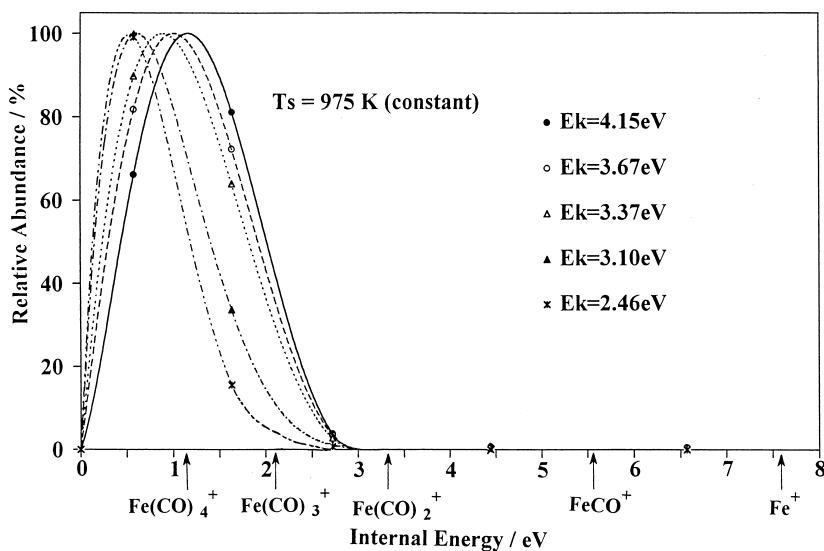


Fig. 3. Dependence of the internal energy distribution functions on kinetic energy ( $E_k$ ) at a constant surface temperature ( $T_s = 975 \text{ K}$ ). Molecular kinetic energies were 4.15 eV (closed circle); 3.67 eV (open circle); 3.37 eV (open triangle); 3.10 eV (closed triangle); 2.46 eV (asterisk). The values on the horizontal axis indicated by arrows are threshold energies for each ion.

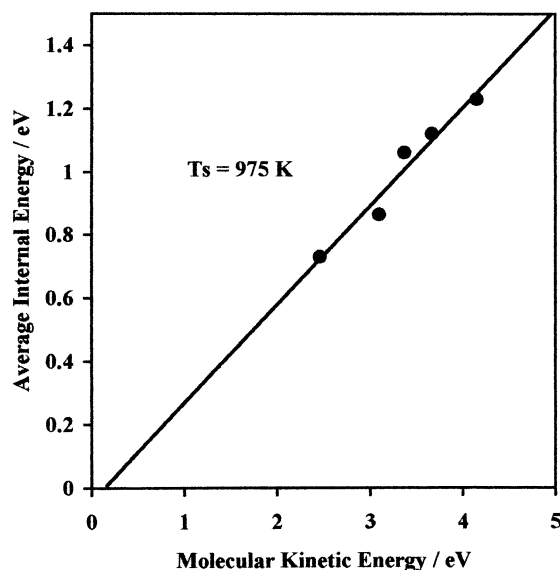


Fig. 4. Average internal energy plotted against the molecular kinetic energy at constant surface temperature,  $T_s = 975$  K.

some 30%, and (3) the distribution width is in the range of 1–1.6 eV. The HSI process with the present experimental setup has a high conversion rate and narrow distribution width, and can be compared with the results of the other groups.

The QET-based procedure of Danon et al. [6] for 1-iodopropane/diamond at 450 °C gave a transfer rate of 8% (0.52 eV rotational–vibrational energy from 7.0 eV kinetic energy) and 18% for cholesterol/ReO<sub>2</sub> [7]. The slightly larger discrepancy in transfer rate from the present article, especially in the latter case where the same surface is used and the molecular weight is comparable, may be attributed to the nature of the molecule included, or to the estimation method used. An analogous method of the SID process by Cooks et al., covering the energy range 20–130 eV of incident beam with various surfaces, gave a transfer rate of 8–20% [9]. Compared with these results, our estimates are again high and remain to be explained.

A useful criterion for discussing the inelastic collision process of a molecule with a surface is the Massey parameter [28]. It is defined as:

$$\text{Massey parameter} = \frac{t_c}{\tau} \quad (6)$$

where  $t_c$  is the time taken for the collision interaction and  $\tau$  is the period of the internal motion. When the vibrational degrees of freedom are excited through the collision process,  $\tau$  is around  $10^{-13}$  s, because most vibrational frequencies are in the order of  $10^{13}$  s<sup>-1</sup>. Assuming the length of the interaction region is  $\sim 0.2$  nm ( $2 \times 10^{-10}$  m),  $t_c$  is around  $10^{-13}$  s when the particle velocity is 2200 m/s ( $E_k = 5.0$  eV). The Massey parameter comes close to unity for the present case and the resonant transfer of energy upon collision is likely to take place. This may be a plausible explanation for the high conversion rate in the HSI process.

### 3.6. Dependence of the internal energy on surface temperature

The dependence of the internal energy distribution on the surface temperature ( $T_s$ ) at a constant kinetic energy of 2.4 eV is shown in Fig. 5. The average internal energy plotted against the surface temperature at a constant kinetic energy of 2.4 eV is shown in Fig. 6. A kinetic energy of 2.4 eV contributes around 0.7 eV to the internal energy using the 30% conversion rate. Despite the large difference in surface temperature ( $\sim 300$  K), the 759 K and the 1038 K distribution curves shown in Fig. 5 come close to each other, and their average internal energies are calculated to be from around 0.6–0.7 eV. This indicates the very small probability of thermal energy transfer from the surface to the vibrational degrees of freedom. At higher surface temperatures, average internal energies increase slightly with an increase in  $T_s$  (Fig. 6). If we assume that the  $3n-6$  vibrational degrees of freedom are all in equilibrium with  $kT_s$  (where  $n$  is the number of atoms in a molecule), a molecule may have a large internal energy. Fe(CO)<sub>5</sub> has 27 degrees of freedom ( $n = 11$ ), and if they are in equilibrium with the thermal energy of  $T_s = 1300$  K, the molecule has an internal energy of 3.0 eV. From the internal energy distribution curve for  $T_s = 1287$  K (Fig. 5) we can estimate the average internal energy to be 1.2 eV. Because 0.7 eV comes from the  $E_k$  contribution, only 0.5 eV is taken from the surface thermal energy. This suggests that the molecule is in a state far from

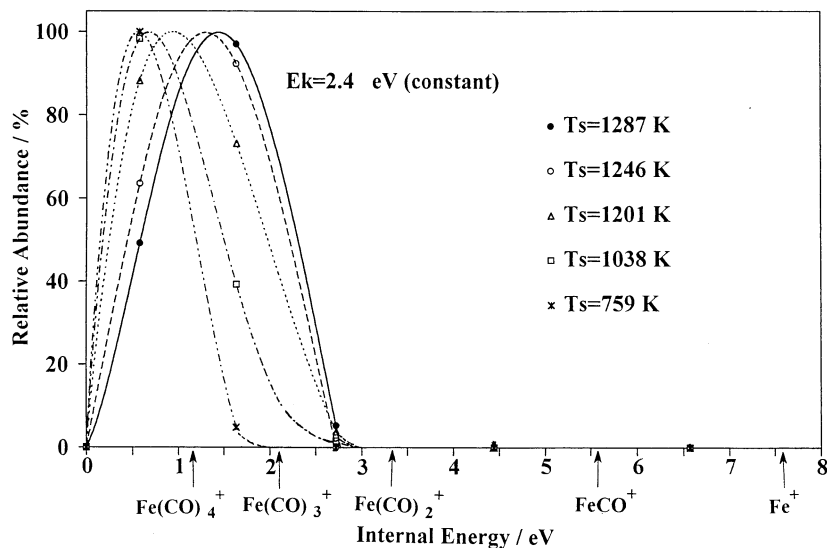


Fig. 5. Dependence of the internal energy distributions on surface temperature ( $T_s$ ) at constant kinetic energy ( $E_k = 2.4$  eV). Surface temperatures were 1287 K (closed circle); 1246 K (open circle); 1201 K (open triangle); 1038 K (open square); 759 K (asterisk). The values on the horizontal axis indicated by arrows are threshold energies for each ion.

thermal equilibrium with the solid surface. This observation is consistent with the discussion by Dagan et al. [7] that the surface temperature does not affect the

mass spectra obtained in the temperature range 500–1300 K, concluding that the ionization and energy transfer process were unaffected by adsorption.

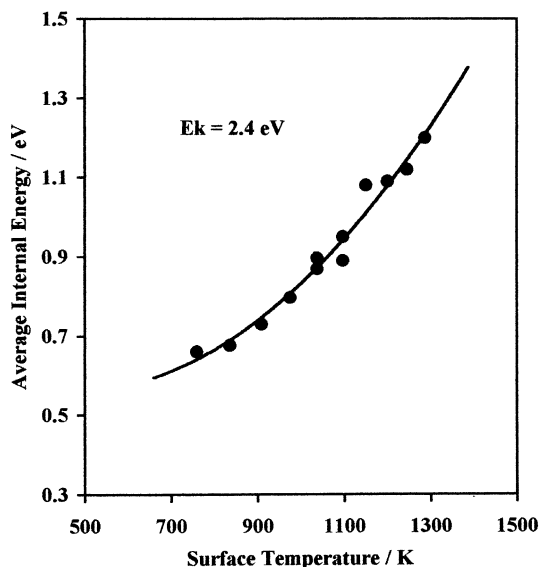


Fig. 6. Average internal energy plotted against the surface temperature at constant kinetic energy,  $E_k = 2.4$  eV.

#### 4. Conclusions

To the best of our knowledge, this is the first study to apply the method of Cooks et al. to elucidate the energy transfer of kinetic energy to vibrational degrees of freedom by collisions of neutral molecular beams with a solid surface. The scattering of molecules from the surface results in molecular and/or fragment ions, their relative intensities depending on both the kinetic energies of the molecules and on the surface temperature. The data were acquired within a limited range of  $E_k$  to avoid thermal decomposition reactions at the heated part of the nozzle.

We conclude that the kinetic energies are partially used for the excitation of vibrational degrees of freedom in a molecule; the conversion rate amounts to some 30% for  $\text{Fe}(\text{CO})_5$ . The conversion efficiency of translational energy used for ionization ( $\gamma$  fraction) for the same molecule is deduced to be 23%. There is



only a very small probability of surface thermal energy being transferred to the internal energy of the molecule, suggesting that the process is far from being at thermal equilibrium with the surface. This is consistent with the impulsive mechanism postulated to explain the HSIMS patterns [3,17].

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