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Surface collisions of the acetonitrile molecular ion: evidence for isomerization of $CD_3CN^{\bullet+}$ to the ketenimine cation $CD_2{=}C{=}ND^{\bullet+}$

C. Mair[a], J. Roithová[b], J. Fedor[a,c], M. Lezius[a], Z. Herman[a,b], T.D. Märk[a,c,*]

[a] *Institut für Ionenphysik, Leopold-Franzens Universität, Technikerstrasse 25, A-6020 Innsbruck, Austria*
[b] *V. Čermák Laboratory, J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-182 23 Prague 8, Czech Republic*
[c] *Department of Plasma Physics, Comenius University, Mlynska dolina, SK-842 48 Bratislava, Slovak Republic*

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Abstract

Reactions induced by the impact of acetonitrile and deuterated acetonitrile molecular ions on a hydrocarbon-covered stainless steel surface were investigated using a recently constructed tandem mass spectrometer (BESTOF). Mass spectra of product ions formed were recorded for projectile collision energies in the range of about 5–70 eV. Both, simple dissociations of the projectile ion and chemical reactions involving H-atom transfer from the surface material (followed by subsequent dissociation of the protonated projectile ion formed) were observed. In particular, formation of CD_2H^+ and $CD_3{}^+$ via dissociation of the surface-protonated deuterated acetonitrile ion CD_3CNH^+ and the collision energy dependence of their relative abundance indicate substantial degree of isomerization of the acetonitrile molecular radical cation $CD_3CN^{\bullet+}$ to the ketenimine ion $CD_2{=}C{=}ND^{\bullet+}$. The isomerization seems to take place upon electron impact ionization of the acetonitrile molecule in the ion source preceding the tandem mass spectrometer. (Int J Mass Spectrom 223–224 (2003) 279–290)

Keywords: Acetonitrile cation; Surface reactions; Isomerization; Tandem mass spectrometry

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1. Introduction

In the field of surface scattering experiments, the area of low collision energies (below 100 eV) has attracted in the last years considerable interest since it is characterized by a multitude of physical and chemical processes [1]. Assuming that about 6–10% of the collision energy ends up as internal energy of the projectile ion [2,3], most bond dissociation and activation energies for chemical processes lie within the energy range thus accessible. The surface acts as a mediator to convert the translational energy of the ions into internal excitation of the projectile ion. In addition, chemical reactions of the projectile ion with the surface material have been observed.

In the last years molecular ion/surface interactions have been studied [2,3], especially in order to obtain some structural information about the projectile ions. With the help of tandem mass spectrometry where

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[*] Corresponding author. E-mail: tilmann.maerk@uibk.ac.at

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both the projectile ion and the secondary ions can be identified, it is possible to elucidate the nature of the ion surface interaction. Despite considerable progress, there is still a lack of knowledge regarding the detailed role of the surface beyond that of a hard wall, in particular if the surface is covered with an adsorbate layer. Especially, the formation of protonated parent ions [3] during surface impact suggests that ion surface interactions are highly reactive processes whose energetics and kinetics contain a wealth of information about the mechanisms of different reactions.

Using a recently constructed tandem mass spectrometer apparatus (BESTOF [4–7]), we studied earlier quantitatively surface-induced reactions of the acetone parent ion $CH_3COCH_3{}^+$ and of its most abundant fragment ion CH_3CO^+ as a function of collision energy (from threshold up to 50 eV) [4]. It turned out that secondary ions observed in the case of the projectile ion CH_3CO^+ are either due to dissociative decay of this ion or due to chemical sputtering of surface adsorbates. In the case of the acetone molecular ion $CH_3COCH_3{}^+$ used as a projectile, the corresponding product ions (in particular $m/z = 31$ with the elemental composition CH_3O^+) are also produced by an additional reaction sequence involving in a first step protonation of the parent ion. This has been confirmed using deuterated acetone.

In this communication, we describe results of related studies for acetonitrile and deuterated acetonitrile cations upon interaction with a stainless steel surface covered by a multilayer of hydrocarbons, investigated over the collision energy range of 5–70 eV. Both simple dissociation of the projectile ion and chemical reactions involving H-atom transfer from the surface material (followed by subsequent dissociation of the protonated projectile ion formed) were observed for these projectile ions. Moreover, formation of CD_2H^+ and $CD_3{}^+$ via dissociation of the surface-protonated deuterated acetonitrile projectile ion CD_3CNH^+ and the collision energy dependence of their relative abundance indicate isomerization of the acetonitrile molecular radical cation $CD_3CN^{\bullet +}$ to the ketenimine $CD_2{=}C{=}ND^{\bullet +}$ ion in the ion source preceding the tandem mass spectrometer.

2. Experimental

Experiments were carried out using the tandem mass spectrometer apparatus BESTOF (see Fig. 1) described in detail previously [4–7]. It consists of

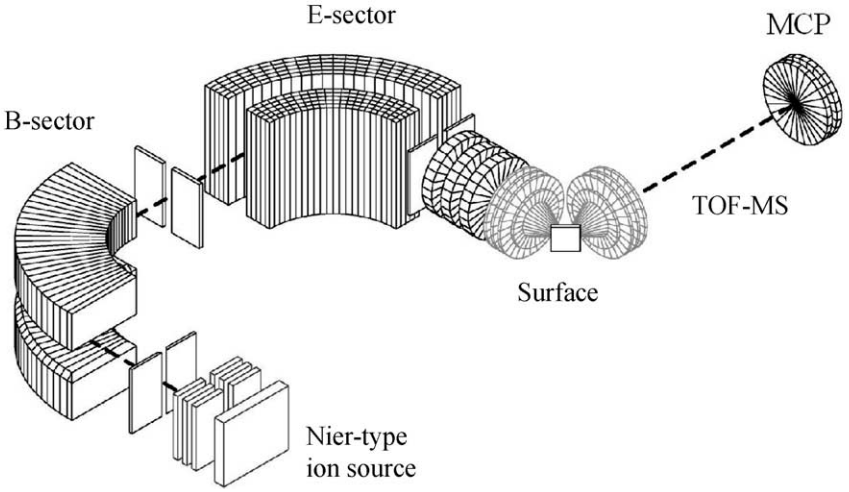

Fig. 1. Schematic view of the experimental setup consisting of a Nier-type ion source, a two-sector-field primary mass spectrometer, a target surface, and a time-of-flight secondary mass spectrometer.

a double-focusing two-sector-field mass spectrometer (reversed geometry) combined with a linear time-of-flight mass spectrometer. Projectile ions to be used after proper mass and energy analysis (see the following description) may be produced in a variety of ways including a Nier-type electron impact ion source, a supersonic expansion cluster source, a pulsed arc cluster ions source, a Colutron gas discharge source or an electron cyclotron resonance ion source. For the present investigations, we use a direct gas inlet allowing to prepare the projectile ions from the stagnant gas in the Nier-type ion source. Neutral molecules are ionized in this ion source by impact of electrons whose energy can be varied from below the ionization energy up to about 500 eV. Deuteronated deuterated acetonitrile projectile ions $C_2D_4N^+$ have been produced by interacting a cluster beam formed in the supersonic nozzle source with the beam of electrons in the Nier-type ion source.

The ions produced are extracted from the ion source region and accelerated to 3 keV for mass (and energy) analysis by the double-focusing two-sector-field mass spectrometer. After passing the mass spectrometer exit slit, the ions are refocused by an Einzel lens and decelerated to the required collision energy before interacting with the target surface. Shielding the target with conical shield plates minimizes field penetration effects. The incident impact angle of the projectile ions is kept at 45° and the scattering angle (defined as a deflection from the incident beam direction) is fixed at 91°.

The collision energy of ions impacting on the surface, defined by the potential difference between the ion source and the surface, could be varied from about 0 to about 2 keV with a typical resolution of about 200 meV (full-width at half-maximum). The collision energy and a measure of the projectile beam energy spread was obtained by applying to the target surface a retarding potential and then measuring the (reflected) total ion signal as a function of the target potential.

A fraction of the product ions formed at the surface exits the shielded chamber through a 1-mm diameter orifice. The ions are then subjected to a pulsed extraction and acceleration field that initiates the time-of-flight analysis of the ions. The second mass analyzer is a linear time-of-flight mass selector with a flight tube of about 80-cm length. The mass selected ions are detected by a double-stage multichannel-plate, connected to a multichannel scaler (time resolution of 5 ns per channel) and a laboratory computer. The product ion intensities were obtained by integration of the recorded signals.

The surface used was a polished stainless steel surface maintained under ultra high vacuum conditions (10^{-9} Torr) in our bakeable turbo-pump evacuated target collision chamber. However, even these conditions did not exclude deposition of multilayers of hydrocarbon contaminants on the surface whenever the valve between the mass spectrometer and the target collision chamber was opened and the pressure in the target region increased to the 10^{-8} Torr range.

3. Results and discussion

The main process in ion collisions with the surface is neutralization. We estimate from the product ion intensities measured that less than about 1% of the incident ions results in product ion formation. In addition to ions resulting from projectile ion interaction with the surface, there exist also secondary ions sputtered from the surface by the projectile ions and their composition depends strongly on the collision energy. Fig. 2 shows as an example the product ion mass spectra obtained for a collision energy of 35 eV for three projectile ions, the acetonitrile molecular ion ($C_2H_3N^{\bullet+}$)[1] and the deuterated acetonitrile molecular ion ($C_2D_3N^{\bullet+}$), both produced in the Nier-type ion source by impact of 80 eV electrons and the deuteronated deuterated acetonitrile ion ($C_2D_4N^+$) prepared with the help of the cluster source. It can be readily seen that in comparison to the molecular

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[1] As the structure of the acetonitrile molecular ion is the subject of this communication, we are using here the summary chemical formula $C_2H_3N^{\bullet+}$ rather than the usual $CH_3CN^{\bullet+}$. Consistently with this, we are using summary formulas for all ions throughout this paper save for the discussion of the isomeric acetonitrile cations.

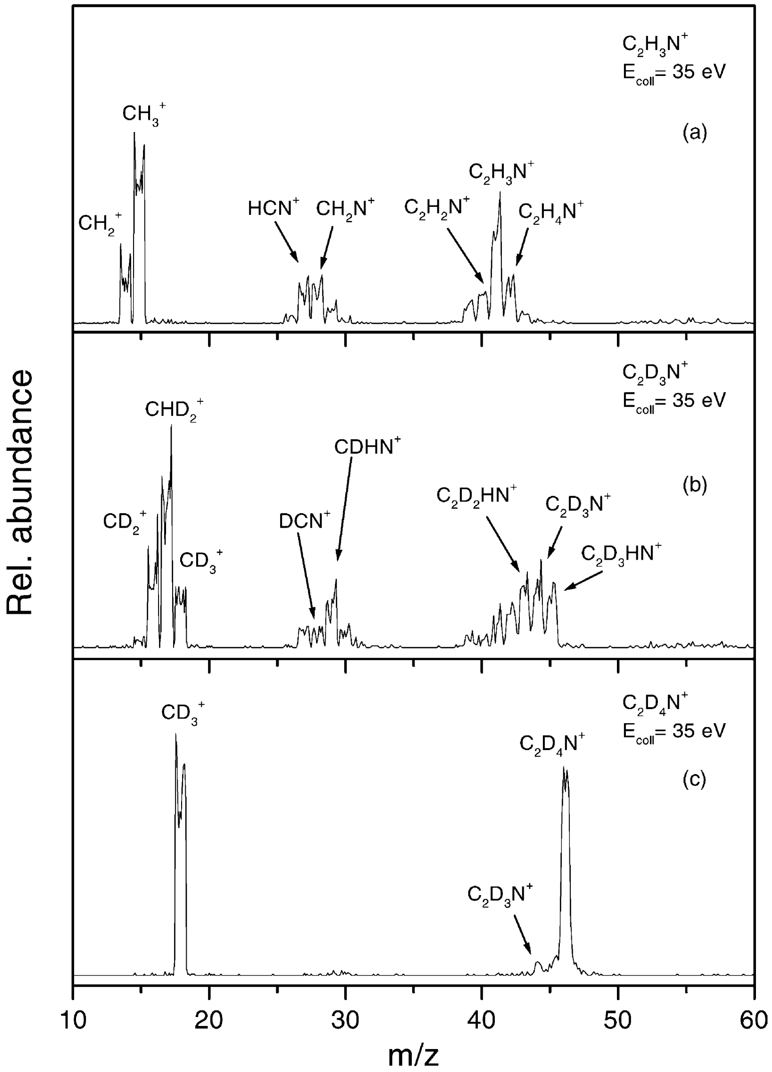

Fig. 2. Product ion mass spectra from surface interactions of (a) $C_2H_3N^{\bullet+}$, (b) $C_2D_3N^{\bullet+}$, and (c) $C_2D_4N^+$ at the collision energy of 35 eV.

ions the surface-induced dissociation pattern of the deuteronated ion $C_2D_4N^+$ (CD_3CND^+) is very simple, the main decomposition channels being (in parenthesis the respective *m*/*z* values)

$$C_2D_4N^+ (46) + \text{surface} \rightarrow CD_3^+ (18) + DCN \quad (1)$$

$$C_2D_4N^+ (46) + \text{surface} \rightarrow C_2D_3N^{\bullet+} (44) + D^{\bullet} \quad (2)$$

$$C_2D_4N^+ (46) + \text{surface} \rightarrow DCN^{\bullet+} (28) + CD_3^{\bullet} \quad (3)$$

Reaction (1) is the main decomposition channel, reaction (2) is a minor channel (see Fig. 3c), reaction (3) is only visible at collision energies of about 40–50 eV.

On the other hand, the product ion mass spectra obtained for the interaction of the acetonitrile molecular ions $C_2H_3N^{\bullet+}$ (and $C_2D_3N^{\bullet+}$) with the surface

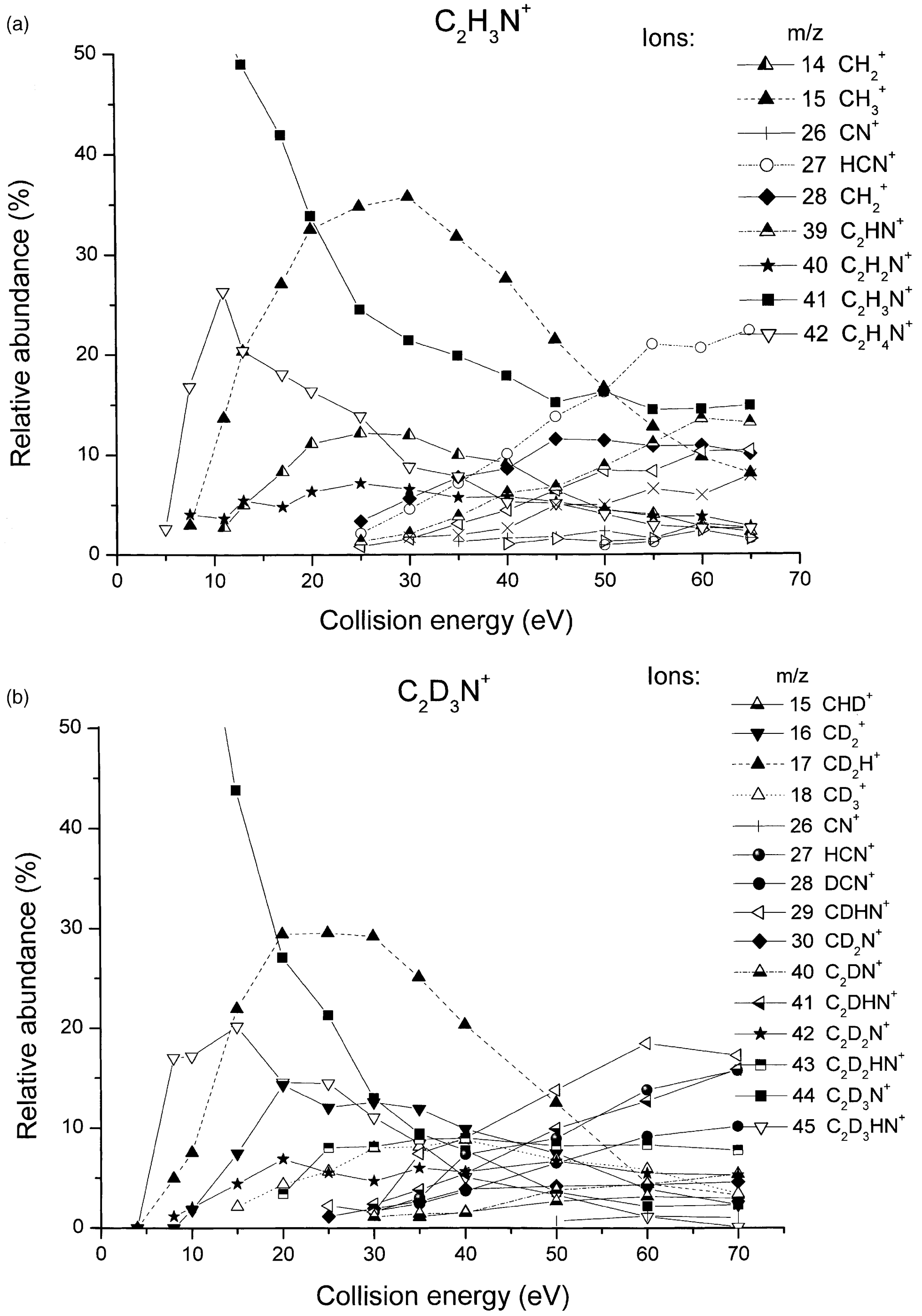

Fig. 3. Dependence of the relative abundance of product ions on the collision energy from surface interactions of projectile ion (a) $C_2H_3N^{\bullet +}$, (b) $C_2D_3N^{\bullet +}$, and (c) $C_2D_4N^+$.

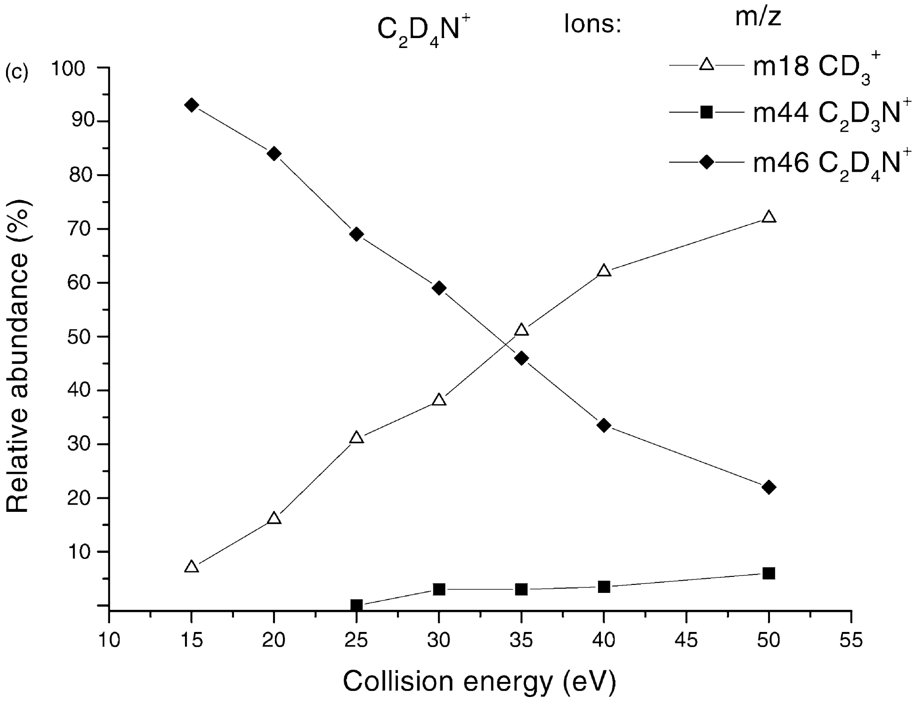

Fig. 3. (*Continued*).

(Fig. 2a and b) consist of ions originating evidently from two different formation routes:

A. Ions formed by direct surface-induced dissociation of the acetonitrile molecular ion $C_2H_3N^{\bullet+}$ (41), including the fragment ions $C_2H_2N^+$ (40), $C_2HN^{\bullet+}$ (39), and $CH_2^{\bullet+}$ (14), and
B. Ions formed in H-transfer reactions with surface hydrogen leading to the formation of the protonated acetonitrile ion, $C_2H_4N^+$ (42), followed by subsequent dissociation of this protonated ion to $C_2H_3N^{\bullet+}$ (41), $CH_2N^{\bullet+}$ (28), $HCN^{\bullet+}$ (27), and $CH_3^{\bullet+}$ (15) (see also reactions (1)–(3) discussed earlier for the case of surface-induced dissociation of the deuteronated deuterated acetonitrile ion $C_2D_4N^+$).

The collision energy dependence (in the range of 5–70 eV) of all major product ions for the three projectile ions, $C_2H_3N^+$, $C_2D_3N^+$, and $C_2D_4N^+$, is summarized in Fig. 3. Here we have plotted product ion intensities, normalized to the sum of all product ion intensities, as a function of the collision energy (sometimes referred to as energy-resolved mass spectrum (ERMS)). Ions of abundance below 5% of the total ion yield were for simplicity not included into this figure.

Table 1 summarizes thermochemical data [8–10] on the ions and neutrals pertinent to this study and Fig. 4 shows the energetics of the dissociation processes involved in both dissociation of the molecular projectile ion and dissociation of the surface-protonated product ion.

The main dissociation pathways of the acetonitrile molecular ion $C_2H_3N^{\bullet+}$ (see earlier discussed A) are analogous to those reported in electron or photon impact ionization [8] studies of acetonitrile, i.e.,

$$CH_3CN + e\,(h\nu) \rightarrow C_2H_3N^{\bullet+}\,(41) \rightarrow C_2H_2N^+\,(40) + H^\bullet \qquad (4)$$

$$CH_3CN + e\,(h\nu) \rightarrow C_2H_3N^{\bullet+}\,(41) \rightarrow C_2HN^{\bullet+}\,(39) + H_2 \qquad (5)$$

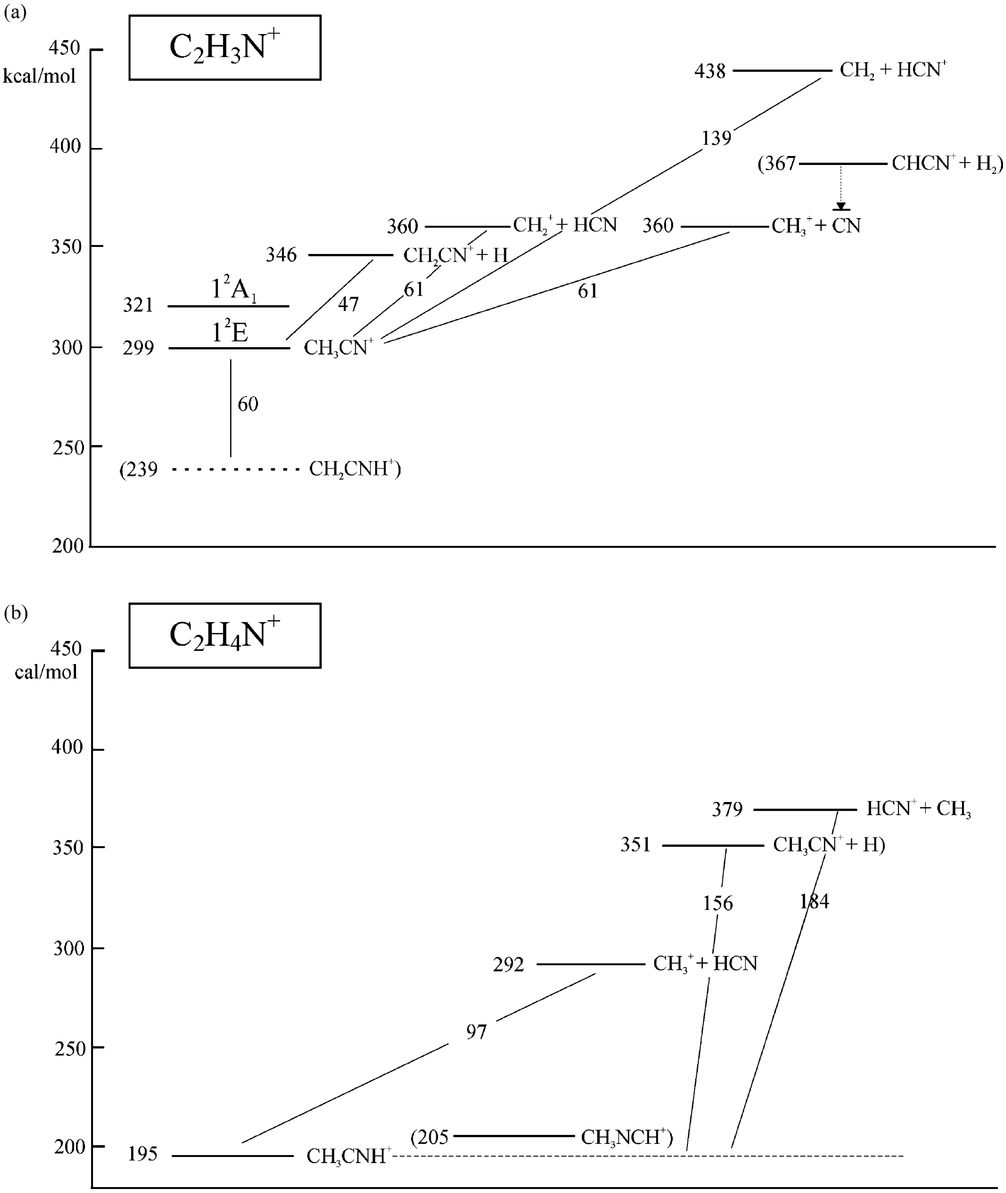

Fig. 4. Energetics of dissociation processes of (a) the acetonitrile molecular ion $C_2H_3N^{\bullet+}$ and (b) the protonated acetonitrile ion $C_2H_4N^+$ [12]. Two heats of formation of the acetonitrile cation correspond to the formation of the ground and first excited state of the molecular cation. The value of 60 kcal/mol for the $CH_3CN^{\bullet+} \rightarrow CH_2{=}C{=}NH^{\bullet+}$ isomerization is from Ref. [11].

$$CH_3CN + e\,(h\nu) \rightarrow C_2H_3N^{\bullet+}\,(41) \rightarrow CH_2^{\bullet+}\,(14) + (HCN) \qquad (6)$$

Formation of CH_3^+ (15) + $CN^\bullet$, though energetically very similar to reaction (6), was only observed in considerably smaller amounts (three to four times) than $CH_2^{\bullet+}$ + (HCN) both in electron impact and in photoionization studies and thus it was not included here. The dissociation pathways of the molecular ion projectile $C_2H_3N^{\bullet+}$ (41) yielding $C_2H_2N^+$ (40), $C_2HN^{\bullet+}$

Table 1
Thermochemical data of various ions and neutrals after Ref. [9]

	$\Delta H_f^\circ(\mathrm{M}^+)$[a] (kcal/mol)	$\Delta H_f^\circ(\mathrm{M})$[a] (kcal/mol)	IE (eV)
CH_3CNH^+	195	–	
CH_3NCH^+	205		
CH_3CN^+	299	17.7	12.20
CH_2CN^+	294[a]	58–59.7	
$CHCN^+$	(367)[b]		
HCN^+	345.7	32.3	13.59
CH_3^+	260	33.2	
CH_2^+	328	92.4	
CH^+	(399)	(142)	
H^+	366	52.1	

[a] From Ref. [10].
[b] From Ref. [8].

(39), and $CH_2^{\bullet+}$ (14) (designated earlier as formation route A) and $C_2D_3N^{\bullet+}$ (44) yielding $C_2D_2N^+$ (42), $C_2DN^{\bullet+}$ (40), and $CD_2^{\bullet+}$ (16) are analogous to reactions (4)–(6).

The decomposition pathways of the protonated acetonitrile ions, $C_2H_4N^+$ (42) or $C_2D_3HN^+$ (45), both formed by H-atom transfer reactions of the respective acetonitrile molecular ion with the surface hydrogen, can be inferred from the dissociation pathways of the deuteronated deuterated $C_2D_4N^+$ projectile ion, formed already in the ion source (see Fig. 2c and reactions (1)–(3)). Thus, in the case of the molecular projectile ion $C_2H_3N^{\bullet+}$ (41) reaction with surface hydrogen leads to protonated ion $C_2H_4N^{\bullet+}$ (42), and to its dissociation products $C_2H_3N^+$ (41) (reaction (2)), $HCN^{\bullet+}$ (27) (reaction (3)), and CH_3^+ (15) (reaction (1)). In addition, formation of CH_2N^+ (28), presumably in reaction

$$C_2H_4N^{\bullet+} \rightarrow CH_2N^{\bullet+} + CH_2 \qquad (7)$$

takes place. The higher extent of fragmentation and the occurrence of reaction (7) in the spectra in Fig. 2a and b, in comparison with the spectrum in Fig. 2c, may be ascribed to the fact that the protonated ion formed in an exoergic surface-induced H-transfer reaction has a higher internal energy content than a protonated acetonitrile ion (in the present case the deuteronated deuterated acetonitrile ion) formed in the ion source.

In contrast, the series of decomposition of the protonated deuterated acetonitrile ion, $C_2D_3HN^+$, formed via surface H-atom transfer reactions of the deuterated acetonitrile projectile ion, gives pairs of analogous product ions (see Fig. 3b), of a different H/D content, namely the ion pairs (8)–(12) (written by sum formulas):

$$C_2D_3N^{\bullet+}\,(44) \quad \text{and} \quad C_2D_2HN^{\bullet+}\,(43) \qquad (8)$$

$$C_2D_2N^{+}\,(42) \quad \text{and} \quad C_2DHN^{+}\,(41) \qquad (9)$$

$$CD_2N^{\bullet+}\,(30) \quad \text{and} \quad CDHN^{\bullet+}\,(29) \qquad (10)$$

$$DCN^{\bullet+}\,(28) \quad \text{and} \quad HCN^{\bullet+}\,(27) \qquad (11)$$

$$CD_3^{+}\,(18) \quad \text{and} \quad CD_2H^{+}\,(17) \qquad (12)$$

The data shown in Fig. 3a and b were re-normalized to show separately: (i) the normalized intensities of product ions formed by dissociation of surface-excited projectiles $C_2H_3N^{\bullet+}$ (Fig. 5a) and $C_2D_3N^{\bullet+}$ (Fig. 5b), and (ii) the normalized intensities of product ions formed by decomposition of the surface-protonated acetonitrile cation $C_2H_4N^+$ (Fig. 6a) and $C_2D_3HN^+$ (Fig. 6b).

The collision energy dependence of the normalized intensities of products of simple dissociation of surface-excited molecular ions $C_2H_3N^{\bullet+}$ (Fig. 5a) and $C_2D_3N^{\bullet+}$ (Fig. 5b) is in mutual agreement and it is consistent with the impact ionization dissociation pathways (4)–(6). The intensity of the molecular ion $C_2H_3N^{\bullet+}$, shown in Fig. 5a, had to be corrected, of course, for the contribution of the dissociation from the protonated product ion, reaction (2), and the corrected intensities are designated by open squares.

A very interesting result represents the decomposition of $C_2D_3HN^+$, formed in H-atom transfer reaction between the projectile deuterated acetonitrile ion projectile and surface hydrogen. The spectra of the reaction products show ion pairs which contain or do not contain the H-atom abstracted from the surface (see ion pairs (8)–(12)). Sums of the relative intensities of these ion pairs add well to the relative intensities of the respective ion decomposition of the surface-protonated acetonitrile ion, $C_2H_4N^+$

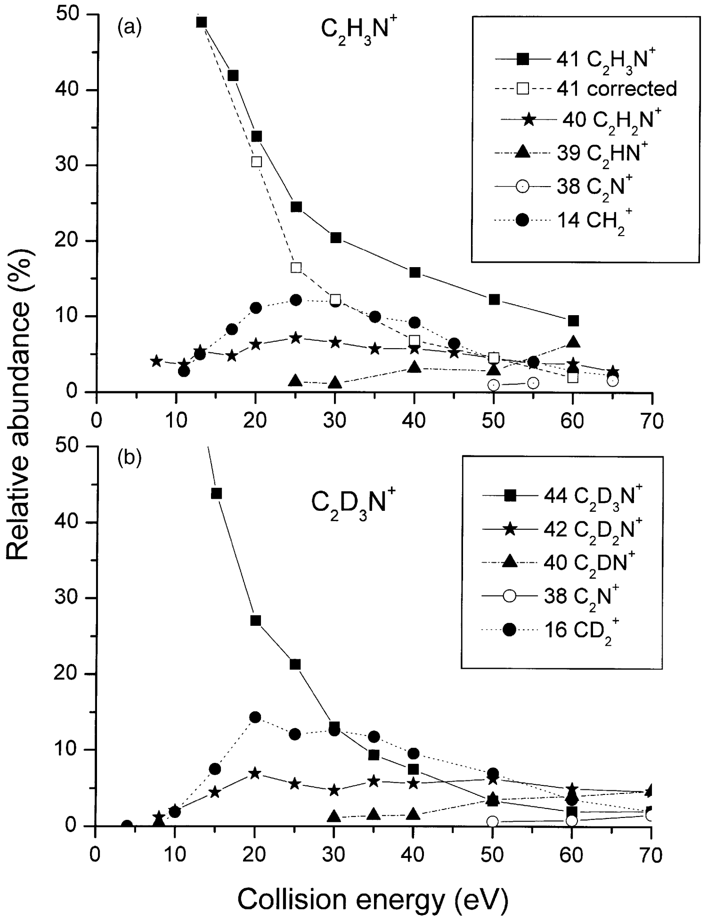

Fig. 5. Dependence on the collision energy of the relative abundance of product ions from surface interactions of (a) $C_2H_3N^{\bullet +}$ and (b) $C_2D_3N^{\bullet +}$, dissociation pathways pertinent to direct dissociation of the molecular ion.

($C_2H_3N^+$, $C_2H_2N^+$, CH_2N^+, HCN^+, and CH_3^+). The formation of these ion pairs could possibly be ascribed to H/D scrambling in the protonated acetonitrile ion $C_2D_3HN^+$ produced upon impact of the deuterated $C_2D_3N^{\bullet +}$ ion on the hydrocarbon-covered surface.

However, the abundance of the ion pairs (8)–(12) in the spectra (Figs. 3b and 6b) does not correspond to that expected from statistical scrambling and it changes with collision energy. For instance, Fig. 7 shows the ratio of intensities of the products of the most prominent dissociation channel, reaction (12), yielding either CD_2H^+ or CD_3^+, i.e., $[CD_2H^+]/[CD_3^+]$, as a function of the collision energy. The intensity ratio varies from about 9 to less than 1 over the collision energy range from 15 to 70 eV, while for statistical scrambling a constant ratio of 3.0 would be expected. Analogously, the ratio of the products of the high-energy dissociation process (11), (DNC^+/HNC^+), decreases with increasing collision energy. This indicates that other mechanism(s) than simple statistical hydrogen scrambling are responsible for this behavior.

It was suggested earlier [11,12] that an isomeric form of the acetonitrile cation, the ketenimine cation $CH_2{=}C{=}NH^{\bullet +}$, may be by as much as about 60 kcal/mol more stable than $CH_3CN^{\bullet +}$. The occurrence of

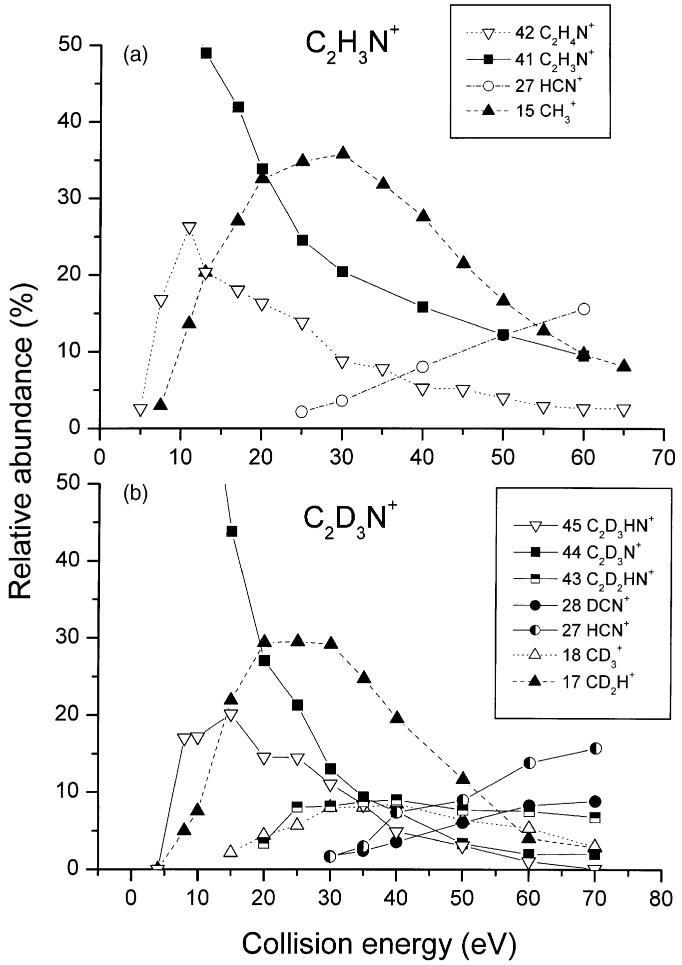

Fig. 6. Dependence on the collision energy of the relative abundance of product ions from surface interactions of (a) $C_2H_3N^{\bullet +}$ and (b) $C_2D_3N^{\bullet +}$, dissociation pathways pertinent to dissociation of the *surface-protonated* molecular ions $C_2H_4N^+$ and $C_2D_3HN^+$, respectively.

two isomeric forms of the acetonitrile cation was used to explain two different reaction rates of formation of the acetonitrile ion from charge transfer between O^+ or Kr^+ and acetonitrile and difference in further reactivity with COS [11]. One may expect that two isomers of the acetonitrile cation would behave differently in a surface-induced reaction of H-atom transfer with surface hydrogen. The reaction of the deutero-ketenimine cation $CD_2{=}C{=}ND^{\bullet +}$ would result in the formation of $CD_2H{-}C{=}ND^+$ and lead to the formation of the fragment ion CD_2H^+ and also DCN^+. On the other hand, surface-protonation of $CD_3CN^{\bullet +}$ would lead to the formation of CD_3CNH^+ and corresponding dissociation products CD_3^+ and HCN^+.

The isomerization $CD_3CN^{\bullet +} \rightarrow CD_2{=}C{=}ND^{\bullet +}$ could in principle occur via surface collision which would supply the energy to overcome the isomerization barrier. Then one can expect that the ratio $[CD_2H^+]/[CD_3^+]$ should be small at low collision energies and *increase* with increasing collision energy, as there will be more and more energy available for overcoming the barrier. Analogous behavior could be expected for the ratio (DNC^+/HNC^+). However, the results in Fig. 7 indicate just the opposite behavior.

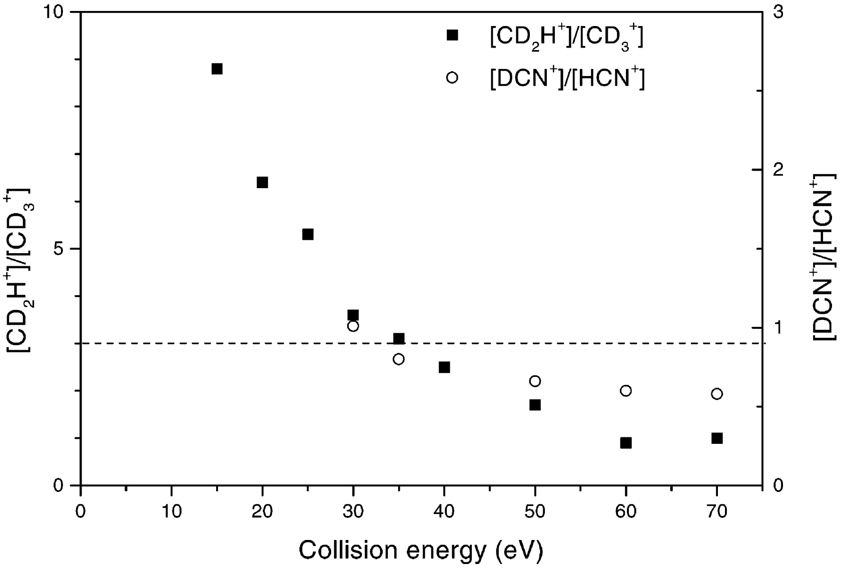

Fig. 7. Dependence on the collision energy of the ratio of relative abundances of product ions CD_2H^+ and $CD_3{}^+$, $[CD_2H^+]/[CD_3{}^+]$ from Fig. 3b (full points); dashed line indicates the $[CD_2H^+]/[CD_3{}^+]$ value assuming statistical D/H scrambling in the methyl cation. Open points, analogous dependence of the ratio of the products $[DCN^+]/[HCN^+]$ (right ordinate).

Therefore, it appears that in fact substantial isomerization $CD_3CN^{\bullet+} \rightarrow CD_2{=}C{=}ND^{\bullet+}$ occurs as early as upon the electron impact ionization and the incident projectile beam is composed of both isomers of the molecular ion.

Our preliminary DFT calculations (B3LYP/6-31G**) of the energetics of the isomerization process $CH_3CN^{\bullet+} \rightarrow CH_2{=}C{=}NH^{\bullet+}$ show that the height of the isomerization barrier is less than 22 kcal/mol and that the ketenimine cation is by about 49 kcal/mol more stable with respect to $CH_3CN^{\bullet+}$. Natural bond orbital (NBO) analysis leads to a Lewis structure of the β-distonic ion $^{\bullet}CH_2CNH^+$. The unpaired electron is partly localized on the carbon of the CH_2– group (0.8) and the charge appears to be delocalized over the (CNH) group. However, due to the interaction of π-orbitals over the C–C–N entity, the ketenimine structure of the cation, $CH_2{=}C{=}NH^{\bullet+}$ is plausible, too. There is sufficient energy available as the excitation energy of the molecular ion formed by photon [13] or electron impact ionization of the acetonitrile molecule (see also the position of ground and first excited states of the acetonitrile cation in Fig. 4) to make isomerization of a substantial fraction of molecular ions possible. Also, electron impact mass spectra of acetonitrile show a higher abundance of the $CH_2{}^+$ in comparison with $CH_3{}^+$, though the energetics of the dissociation processes to $CH_2^+ + HCN$ and $CH_3^+ + CN$ is very similar. A dissociation process leading to $CH_2^+ + CNH$ is even by about 16 kcal/mol more endoergic than $CH_3^+ + CN$ (with $\Delta H_f\ (CNH) = 48$ kcal/mol [9,14]). This suggests that $CH_2{}^+$ ions are formed by a cleavage of the acetonitrile cation isomerized to ketenimine $CH_2{=}C{=}NH^{\bullet+}$.

All these observations are consistent with the hypothesis that during the ionization process a substantial fraction of the acetonitrile molecular ion formed isomerizes to the ketenimine cation. In surface collisions, this isomerized cation interacts with the surface hydrogen and accepts a H-atom into the CH_2-group to form protonated acetonitrile. In collisions of deuterated acetonitrile cation with the surface, this shows as prevailing formation of the dissociation product CD_2H^+ in comparison with $CD_3{}^+$, the latter resulting from dissociation of the non-isomerized acetonitrile cation CD_3CN^+. The decreasing ratio $[CD_2H^+]/[CD_3^+]$ with increasing collision energy suggests an increase of the backward, endoergic, surface-induced isomerization of the ketenimine cation to the acetonitrile cation.

In conclusion, the results of studies of surface reactions of the acetonitrile cation and their interpretation seems to provide further evidence for the existence of the two isomeric forms of the acetonitrile molecular ion formed in ionization processes. The existence of these two isomeric forms is in agreement with earlier suggested evidence on the basis of the observation of two different reaction rates of the acetonitrile ion in reactive and charge transfer processes [11,12]. The present results provide yet another example of how surface collisions and surface reactions can be used to elucidate structure of gaseous ions.

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