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HYPERTHERMAL ENERGY COLLISIONS OF CF_3^+ IONS WITH MODIFIED SURFACES: SURFACE-INDUCED DISSOCIATION

TALAYEH REZAYAT, ANIL SHUKLA

ABSTRACT

Collisions of low-energy ions, especially polyatomic ions, with surfaces have become an active area of research due to their numerous applications in chemistry, physics and material sciences. An interesting aspect of such collisions is the dissociation of ions which has been successfully exploited for the characterization of colliding ions, especially high mass ions from biological molecules. However, detailed studies of the energy transfer and dissociation have been performed only for a few simple systems and hence the mechanism(s) of ions' excitation and dissociation are not as well understood even for small ions. We have therefore undertaken a study of the dissociation of a small polyatomic ion, CF3+, at several collision energies between 28.8 eV and 159 eV in collision with fluorinated alkyl thiol on gold 111 crystal and a LiF surface. These experiments were performed using a custom built tandem mass spectrometer where the energy and intensity distributions of the scattered fragment ions were measured as a function of the fragment ion mass and scattering angle. In contrast with the previous studies of the dissociation of ethanol and acetone cations where the inelastically scattered primary ions dominated the collision process (up to ~50 eV maximum energy used in those experiments), we did not observe a measurable abundance of inelastically scattered undissociated CF3+ ions at all energies studied here. We observed all fragment ions, CF2+, CF+, F+ and C+ at all energies studied with the relative intensity of the highest energy pathway, C+, increasing with collision energy. Also, the dissociation efficiency decreased significantly as the collision energy was increased from to 159 eV. The energy distributions of nearly all the fragment ions showed two distinct components, one corresponding to the loss of nearly all of the kinetic energy and scattered over a broad angular range while the other corresponding to smaller kinetic energy losses and scattered closer to the surface parallel. The latter process is due to delayed dissociation of excited ions after they have passed the collision region.

INTRODUCTION

Interaction of low-energy ions with surfaces is an important area of research in science and technology [1] ranging from plasma-wall interactions in fusion devices, etching reactions in semiconductor industry, chemical reactions at surfaces, catalysis and microelectronics, and recently extended to tandem mass spectrometry [2]. Both areas of research have been combined in recent studies on the fragmentation of "small"

polyatomic ions which are scattered off metal and adsorbate covered surfaces [1].

Most Ion-surface collisions studies have included monatomic or diatomic ions with a variety of pure metals, oxide surfaces and adsorbate covered surfaces over a very broad range of kinetic energies [3]. Recently these studies have included polyatomic ions, complex biological molecular ions and ion clusters with emphasis on their internal excitations and subsequent dissociation [3] for analytical applications.

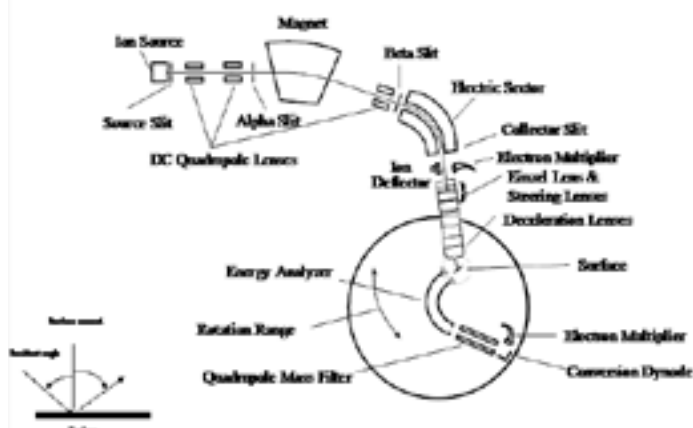## Ion-Surface Collision Instrument

Figure 1. Schematics of the crossed-beam scattering instrument used for SID experiments.

When low energy polyatomic ions interact with surfaces, a variety of processes may occur [4], including elastic scattering, inelastic scattering [possibly followed by dissociation, a process known as surface-induced dissociation (SID)], charge exchange, particle deposition (soft landing), and chemical reactions (surface induced reactions (SIR)) [5]. SID is especially useful for the study of ions from large molecules because the better-defined and higher energy transfers in the ion-surface collisions can lead to specific fragment ions and hence more structural information concerning the parent ions [2,3,6,7].

SID is similar to collision-induced dissociation (CID) of ions with neutral gases in that they both involve the activation of ion, followed by the unimolecular decomposition [3, 8]. In SID where metal surfaces with low work functions are used majority of the colliding ions are neutralized with only a small fraction of them (‹ 1%) scattering off the surface and being detected as fragment ions [9]. To overcome this problem and obtain better yields self-assembled monolayers (SAM) have been used- alkyl thiols and fluorinated alkyl thiols are among the more commonly used SAMs [10-12]. The SAM surfaces reduce the ion neutralization by blocking the ions from direct contact with the metal substrate by means of tightly packed monolayer molecules [13]. Several recent studies have demonstrated that ions do not collide with the bulk surface or the whole SAM molecules on the surface but with the end group or a small chain length at the end of it [7, 14]. Also, a significant fraction of the ions kinetic energy is transferred into surface modes and only a small fraction is transformed from kinetic energy to internal modes of the projectile ion [3]. Hase and coworkers showed from trajectory simulations that the nature of the surface plays an important role in energy transfer and dissociation of ions [15, 16].

In the present study a recently constructed ion beam scattering instrument has been used to study the energetics and mechanism(s) of the SID processes of the CF3+ ions by measuring the energy and intensity distributions of scattered primary and fragment ions as a function of collision energy and scattering angle [17]. First studies on the SID of acetone and ethanol molecular ions with a SAM surface of fluorinated alkyl thiol on Au (111) demonstrated that SID precedes via several energetically and angularly distinct dissociation pathways depending on the ion energy. An interesting result from these studies was that the collisions involved only a fraction of the SAM molecular chain, such as the end group(s) (i.e. CF3 and CF2CF3), rather than the whole SAM molecule or the bulk surface [3]. Thus the interaction between the ion and the surface is not just a physical interaction and requires additional exploration to achieve a deeper understanding of the ion excitation and dissociation phenomena associated with SID.

There have been several SID studies of the CF3+ ion from different surfaces. Previous studies performed by Cooks and co-workers [8] on the interactions of CF3+ ions with a hydrocarbon covered stainless steel surface showed that at lower collision energy the major secondary ion is the intact CF3+ projectile ion.. In later studies of the collision of 50 eV and higher energy CF3+ ions with several surfaces, viz., graphite, perfluoro polyether, Al, Ag and Ba/Ag, it was shown that extensive fragmentation of the projectile ion occurs simultaneously to CF2+, CF+, F+ and C+ along with negatively charged fragment ions, CF3-, CF2-, and F-.

Interestingly, we haven't found a similar study of the collision-induced dissociation of CF3+ in collision with gaseous neutrals. Only Peko et al. [18] have recently measured CID cross sections for this ion in collision with CHF3 neutrals as a part of their study of the cross section measurements of the ion-molecule reactions occurring in CHF3 discharges. We have

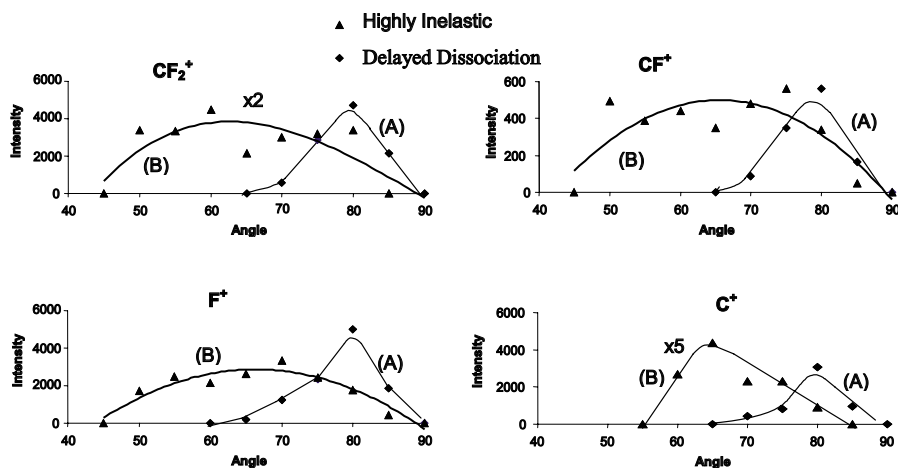**Angular Distributions of Scattered Fragment**

Figure 2. Angular distributions of CF2+, CF+, F+ and C+ fragment ions from SID of CF3+ ions in collision with the SAM surface at 28.8 eV energy.

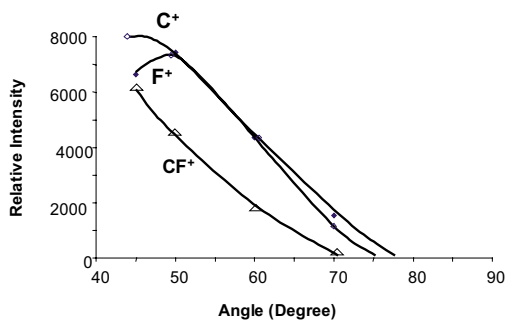**Angular Distribution of Scattered Ions at 159 eV from SAM Surface**

Figure 3. Angular distribution of various fragment ions from SID of CF3+ ions in collision with SAM surface at 159 eV ion energy.

therefore studied the SID of CF3+ in collisions with a SAM surface of fluorinated alkyl thiol on gold substrate and a LiF surface on titanium at low kinetic energies.

EXPERIMENTAL

The SID experiments were performed using a tandem hybrid mass spectrometer designed and constructed specifically to study the dynamics of ion-surface collisions [17]. This instrument is shown schematically in Figure 1. The primary ions, CF3+, were created by 70 eV electron ionization of CF4 neutrals in the ion source. These ions were accelerated to ~1250 eV for mass and energy analysis by the first stage double focusing reverse geometry mass spectrometer (JEOL- GCMate.) The mass and energy selected primary ions were transported into a collision chamber where they were decelerated to desired ion energy by a series of tube lenses and collided with the surface at 45° [17]. The energy and mass of the secondary ions were analyzed by a 160° hemispherical energy analyzer and a quadrupole mass filter, respectively and detected by a channel electron multiplier. The detector assembly is rotated between the specular angle and surface parallel to measure intensity and energy distributions of the fragment ions as a function of scattering angle

The collision region surrounded by the final deceleration lens, entrance lens to the energy analyzer and the surface were all maintained at the same potential to minimize field penetration effects that may interfere with their scattering distributions. The energy analyzer and quadrupole mass filter were floated with respect to the ion source potential to reduce the energy of ions passing through the analyzers and to increase and maintain sufficient energy and mass resolutions. The energy analyzer was operated in constant transmission and resolution mode to avoid any discrimination of low energy ions. All the secondary ions were therefore accelerated to 100 eV for their transmission through the energy analyzer.

We used two different surfaces, a 600 nm thick LiF on titanium substrate and a self assembled monolayer (SAM) surface of fluorinated alkyl thiol (FC12), CF3(CF2)9(CH2)2SH, on gold 111 crystal. The SAM surface was prepared by immersing the UV cleaned gold crystal in 1 mM ethanol solution of the SAM material for 48 hours and removing excess SAM material by ultrasonic cleaning of the crystal in ethanol for 10 minutes before transferring the surface into vacuum. The mass spectrometer and the collision chamber were all pumped by turbomolecular pumps and the pressure in the collision chamber was ~ 3 x 10 -7 Torr during experiments. We performed SID experiments at several ion energies ranging from 28.8 eV to 159 eV to develop a better understanding of the energy transfer on surface collisions.

The primary CF3+ ions were formed by 70 eV electron ionization of CF4 in the ion source, which resulted in the dissociative ionization and produced predominantly CF3+ ions. It is well established that the ground and the electronically excited A and B states of CF4+ dissociate to CF3+ while the excited C and D states fragment to CF3+ and CF2+ ions. Thus the CF3+ ions formed in the ion source are most likely vibrationally excited. Since previous SID studies were also done with vibrationally hot ions no attempts were made to relax them by ion-neutral collisions inside the ionization chamber or to form them by alternate ionization techniques.

RESULTS AND DISCUSSION

We did not observe any significant quantities of inelastically scattered CF3+ primary ions even at the lowest energy (28.8 eV) used in our experiments for both surfaces. This was in contrast with all previously studied ions by us where the inelastically scattered primary ions dominated the collision process. However, all fragmentation processes reported for CF3+, e.g. CF2+, CF+, F+ and C+, were observed at all energies with intensities of the lowest energy dissociation pathway decreasing with increasing ion energy.

A. Collision with the FC12 SAM Surface:

Angular Distribution of Fragment Ions: The intensities of all the fragment ions were measured at several ion energies as a function of scattering angle (with reference to surface normal). The energy distributions of the majority of fragment ions contained two peaks distinct in energy and angle, as shown in Fig. 2 for 28.8 eV collisions, suggesting two different excitation/dissociation processes contributing to these dissociations. As ion energy was increased from 28.8 eV to 55 eV and higher, one peak (marked B in Fig.2) decreased in intensity and completely disappeared at higher energies, in the energy distributions of CF2+ fragment ions. This is not unexpected since fragmentation to CF2+ ions is the lowest energy dissociation process and with increase in kinetic energy of the primary ions, energy transferred into internal modes increases leading to the opening of higher energy dissociation channels, such as CF+, F+ and C+. We presented intensity distributions of the two processes separately to clearly demonstrate the distinctive nature of the two dissociation processes associated with SID that will otherwise be lost in the integrated intensity distributions as in the measured mass spectra reported by other SID studies.

U.S. Department of Energy Journal of Undergraduate Research

We will discuss the nature of the two peaks in Fig. 2 later. For the present discussion we have designated them as delayed (A) and highly inelastic (B) dissociations, corresponding to a sharp peak centered closer to the surface parallel and a peak with a broad distribution covering the whole scattering region and centered around the middle of the scattering region. As the ion energy is increased, maximum of (B) remains nearly the same and that of (A) shifts even closer to the surface parallel. At the lowest energy, 28.8 eV, all four fragment ions are observed with total intensities varying in the order CF+ > CF2+ > F+ > C+. Thermochemical thresholds for these fragmentation processes are in the order: 6.2 eV for CF2+, 7.4 eV for CF+, 12.3 eV for F+ and 15.1 eV for C+ [18]. Since the lowest energy dissociation would dominate until the threshold for the next higher energy dissociation is reached, these results suggest that dissociating CF3+ ions have more than 7.4 eV energy into internal modes.

Figure 4. Kinetic energy lost by primary CF3+ ions for their dissociation to various fragment ions at 28.8 eV ion energy in collision with the SAM surface.

The relative intensity of the fragment ions first increases for both dissociation processes as the kinetic energy of the ions is increased and then begins to decline. At 159 eV energy, very little fragmentation is observed and the second peak corresponding to the delayed dissociation process has disappeared for all fragment ions, as shown in Fig. 3, indicating loss of the majority of primary ions by neutralization on the surface. Also, CF2+ fragments from the lowest energy pathway are not present at this energy, as expected with increase in the internal energy of the dissociating ions.

b. Kinetic Energy Losses: We determine the kinetic energy lost by the parent ions (dissociating ions) for each dissociation process from the measured kinetic energies (most probable) of the fragment ions multiplied by the mass ratio of the primary ion and the fragment ion (giving kinetic energy of primary ions that dissociated into respective fragment ions) and subtracting it from the initial kinetic energy of the primary ions. The broad peaks designated as highly inelastic are due to the loss of very large amounts of energy, approaching the initial kinetic energy of the primary ions, irrespective of the initial kinetic energy. However, the second peak analyzed in the same manner results in very large negative losses (i.e., very large energy gains) which theoretically and/or experimentally is not possible and cannot be justified. Similar results obtained for ethanol and acetone SID were earlier rationalized [3, 19] by suggesting that these ions are excited to long-lived electronic states that dissociate after the excited ion has passed through the collision region and the energy analyzer. In this case, energy analyzed ions dissociate and pass through the quadrupoles as fragment ions even though their energy was measured as primary ions. This is further supported by the fact that intensity distributions of these fragment ions are not as broad as those of the highly inelastic process. We estimate the energy lost for the delayed dissociation process by subtracting the measured kinetic energy of the fragment ions from the initial kinetic energy of the primary ions.
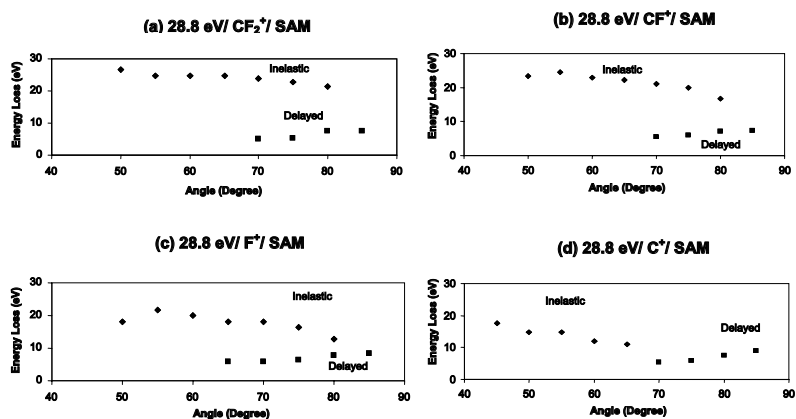
Figure 4 shows kinetic energy losses for the SID of CF3+ to various fragment ions at 28.8 eV kinetic energy, for the two types of dissociation processes calculated as described above. The kinetic energy lost for the highly inelastic process is very large approaching the initial kinetic energy in some cases. However, the same for the delayed dissociation process varies only between 6 and 10 eV for all processes and at all collision energies. Very similar kinetic energy losses were observed for these processes at higher energies as well. It is rather surprising that energetics of both dissociation processes leading to several different fragment ions and significantly different thermochemical thresholds do not change significantly, even though the primary ion energy has been changed by a factor of more than four. The only explanation for this phenomenon, specifically for the delayed dissociation process is that we are producing vibrationally hot parent ions from dissociative ionization of CF4 by 70 eV energy electron impact. These results also demonstrate that there are no energetically competing processes taking place for this dissociation process.

The highly inelastic process leading to all fragment ions at all energies has the common feature that a very large fraction of it is lost by the dissociating ions. Certainly, all this energy is not transferred into internal modes of the ions alone but partitioned between the ion and surface's degrees of freedom. Since the surface has a long fluorocarbon chain, it has a sufficiently large number of degree-of-freedoms to absorb energy into its internal modes. There are no a priori rules that will dictate how energy is partitioned between the colliding ion and neutral, however, the fact that the same trend is observed at all collision energies is a strong indication of a similar energy transfer mechanism(s) operative at all energies. This also suggests that majority of the energy lost is transferred into surface vibrations.

It has been suggested from theoretical modeling using Rice, Ramsperger, Kassel and Marcus (RRKM) theory [20] and binary collision model [21] of ion-surface collisions that ions do not collide with the bulk surface or the whole SAM molecule. Instead, an end group or a fraction of the SAM molecule participates in the collisional excitation process.

Estimated neutral mass for a number of ions colliding with the same FC12 surface, have been found to vary between F/CF3/CF2CF3 groups of the SAM chain for different ion collisions. By assuming collision with the full SAM molecular chain (mass 579) and with only an F atom in the SAM chain, we can set the upper and lower limits of energy losses as 25.0 and 6.2 eV, respectively for 28.8 eV collisions of CF3+ ions. Since the upper limit for the energy losses for the highly inelastic process leading to all fragment ions approach 25 eV, we suggest that the dissociation of this ion via highly inelastic process results from the collision of CF3+ ions with nearly the whole SAM molecular chain. Similar arguments can be made for the SID at higher energies as the energy loss increases correspondingly. It is difficult to state if the bulk surface plays any part in the interaction process.

The delayed dissociation observed here is similar to that observed for ethanol and acetone molecular ions [3, 19]. We may explain these results in the same way. However, it seems very fortuitous that all the ions studies so far behave in this similar manner. There are no known long-lived excited states for ethanol and CF3 + cations that can be the intermediate step for these dissociations after surface collisions, just as there are none associated with the ethanol cations. There must be an alternative mechanism to explain this phenomenon. More studies are needed in order to understand this. However, it is certain that these are not very highly inelastic dissociation processes
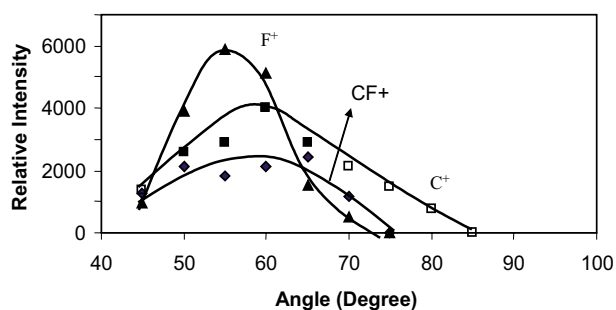

Figure 5. Angular distribution of various fragment ions from SID of CF3+ ions in collision with the LiF surface at 74 eV ion energy

with energy losses varying between 5 and 10 eV at all collision energies. The delayed dissociation is therefore not strongly dependent on the collision energy, at least in the energy range used for the present study.

B. Collisions with LiF Surface:

Kinetic energy distributions of fragment ions from collision of CF3+ with the LiF surface are significantly different from those measured for the SAM surface. We observe only one peak that corresponds to the delayed dissociation, except that its scattering characteristics are different from similar process with the SAM surface. Figure 5 shows the angular
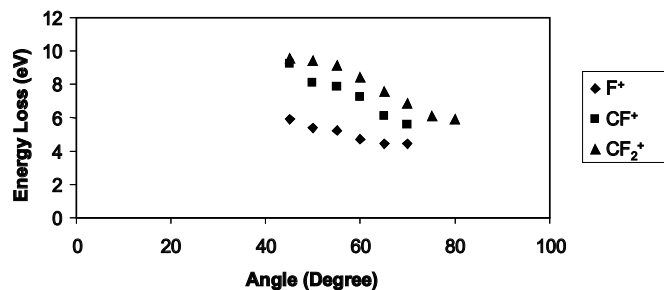

Figure 6. Kinetic energy lost by primary CF3+ ions for their dissociation to various fragment ions at 74 eV ion energy collisions with a LiF surface.

distributions for the CF+, F+ and C+ fragment ions at 74 eV ion energy. Inelastically scattered undissociated CF3+ ions were not observed in LiF collisions either. All three distributions are nearly the same, suggesting a common mechanism for ion activation and dissociation for these dissociation processes. Figure 6 shows the kinetic energy lost by the primary ions for these dissociations, which are of the same magnitude as those for the SAM surface collisions at the same ion energy. Thus a common mechanism of delayed dissociation of projectile ions from surface collisions is observed for both the SAM surface and the LiF surface, here presented at 74 eV collision energy. Further experiments are required to explore if highly inelastic dissociation channel or some other pathways become competitive at higher/lower collision energies when LiF surface is used for collisions.

The difference in the kinetic energy distributions of fragment ions from SAM and LiF surfaces can be easily rationalized to the different nature of the SAM surface. LiF is a harder surface compared to the SAM surface due to extending hydrocarbon chains that act as a soft spring. Hase and coworkers [22] have recently shown from their trajectory simulations that "hard" diamond surface and "soft" SAM surface interact differently with incoming ions, diamond being significantly more effective in inducing higher energy transfer into internal modes. Another difference in the two surfaces is that LiF surface is a dipole and hence ion-surface interaction in this case may be different from the SAM surface. Further studies are necessary in order to understand these processes completely.

CONCLUSIONS

1. No significant amounts of inelastically scattered primary ions are observed in the collision of CF3+ ions with the fluorinated SAM and LiF surfaces at all the energies from 29 eV to 109 eV, unlike all other ions previously studied under similar experimental conditions.

2. There are two energetically and angularly distinct dissociation pathways for the dissociation of CF3+ ions to all its fragment ions. One process corresponds to very large energy losses approaching full kinetic energy of the projectile ions and scattered over a wide angle. The second dissociation process is due to delayed dissociation of excited projectile ions after

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they have passed through the collision region and the energy analyzer. These two processes are collision energy dependent with the delayed dissociation process disappearing at higher collision energy.

3. Collisional excitation of CF3+ ions from LiF surface is very different in comparison with excitation from the SAM surface. Only the delayed dissociation process is observed at 74 eV ion energy used in the present study and there is no contribution from the highly inelastic dissociation process in collision with LiF surface. The energetics of the delayed dissociation is similar to that from the SAM surface except the scattering of fragment ions is broader and centered between the specular angle and the surface parallel.

ACKNOWLEDGEMENTS

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