Negative-Ion Formation on Alkali-Metal Surfaces

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Thermal SF_6 molecules have been observed to decompose and desorb as various atomic and molecular negative ions upon impact with room-temperature alkali-metal surfaces. Many of the negative ions observed have electron affinities which are less than the alkali-metal work function; hence the mechanism for ion formation and desorption is complex. A simple model is proposed to account for some of the observations.

In some recent experiments in which a crossed-beam configuration was employed to study collisions of H^- with various alkali-metal atoms, it was observed[1] that surfaces which became coated with the alkali metal would, under certain conditions, become sources of "noise." It was ultimately realized that this noise was due to those alkali-metal-coated surfaces literally emitting negative ions which, since they came from the region where the crossed beams intersected, competed with the true gas-phase signal coming from charge transfer in, e.g., collisions of $H^- + Na$. Once a rough understanding of the origin of this noise was in hand, the problem was dealt with and the experiments were subsequently completed.[1]

The conditions under which the alkali-metal-coated surfaces became sources of negative ions were rather ordinary; they were at room temperature, free of visible (and more energetic) photons, and were subjected only to electric fields on the order of 10 V/cm. The surface emission was found not to be due to the hydrogen negative-ion beam striking the surface. Rather, it was due to certain neutral, thermal-energy molecules striking the surface, resulting in the desorption of negative ions of unknown mass. The intensity of the desorbed ions was observed to be particularly high for the case of SF_6. It occurred to us that this phenomenon of surface emission of anions was worthy of subsequent investigation; such is the subject of this paper.

The only other example of such a negative-ion–formation mechanism known to the present authors is the generation of UF_6^- when UF_6 strikes a hot platinum or carbon surface, as first reported by Dittner and Datz.[2] The electron affinity (EA) of UF_6 is quite high, exceeding 5 eV, which is larger than the work function, $e\phi$, of the metallic surface. Thus, this process, which was found to occur with unit efficiency, can be viewed as an exothermic reaction. However, not all surfaces with EA $> e\phi$ will convert UF_6 to UF_6^-. This is presumably due to the fact that UF_6 decomposes upon contact with most surfaces and the resulting EA's for the decomposition products are less than the metal's work function. Finally, it should be emphasized that the mechanism responsi-

ble for UF_6^- production ceases as the surface temperature is lowered to 300 K; in that sense it is different from the process discussed herein.

The alkali metals have relatively low work functions[3] $[e\phi_{Na} = 2.75$ eV; $e\phi_K = 2.30$ eV] which are less than the EA of fluorine,[4] viz. 3.4 eV. Consequently, it was thought that F^- was undoubtedly the particular anion produced in collisions of SF_6 with alkali-metal surfaces. As shall be demonstrated, this is not (simply) the case.

A schematic diagram of the experimental arrangement used in this investigation is given in Fig. 1. Either sodium or potassium effuses from an alkali-metal oven and condenses on the room-temperature metallic surface (with an area of a few cm^2) within the interior of a stainless steel cylinder. A weak, positive, extraction voltage is used to accelerate the desorbed ions and focus
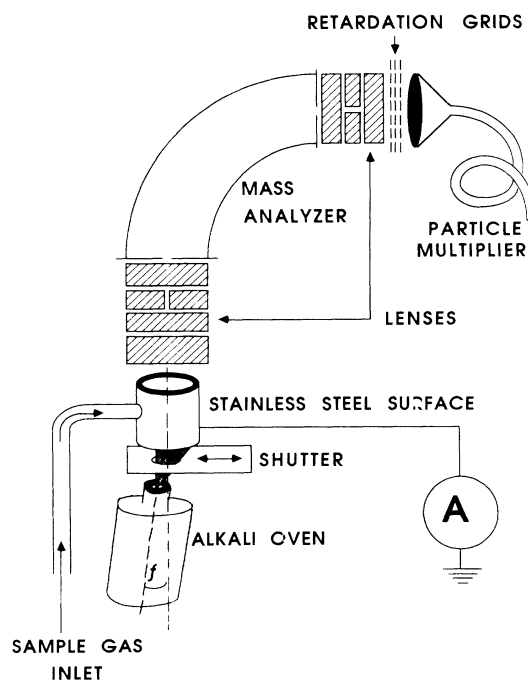

FIG. 1. Schematic diagram of the apparatus.

them into a double-focusing, 90°, magnetic momentum analyzer. The negative ions emerging from the mass spectrometer are focused through a small aperture and detected by a particle multiplier.

The SF_6 gas is admitted into the alkali-metal-coated region by a precision leak valve; the absolute pressure of the gas in that region is determined with a capacitance manometer connected via a short tube, not shown in the diagram. The alkali-metal flow to the surface may be interrupted by means of a mechanical shutter in order to examine the temporal characteristics associated with the surface emission mechanism.

The emitting surface is biased through an electrometer to determine the absolute current leaving the surface. A series of planar parallel grids placed after the momentum analyzer is used in a retardation analysis to measure the kinetic energy of the desorbed anions; such information is necessary to ascertain that the anions are, in fact, created on the surface, and not in gas-phase collisions within the interior of the cylindrical cavity or accelerating lenses. The background pressure within the vacuum chambers is about 10^{-7} Torr; this is not an ultrahigh vacuum normally associated with experiments in surface science.

The mass spectra of negative ions which result from collisions of SF_6 with sodium and potassium surfaces are given in Fig. 2. The three dominant peaks correspond unambiguously to the negative ions F^-, S^-, and SF^-. The satellite peaks affiliated with S^- and SF^- correspond to $^{34}S^-$ and $^{34}SF^-$ (the natural abundance of ^{34}S is 4.2%). Peaks corresponding to the desorption of molecular negative ions with larger masses are also identified in Fig. 2 and Table I lists all of the ions which are observed, along with their relative intensities. The mass spectra are obtained by sweeping the magnetic field and the transmission efficiency is taken to be uniform over the mass range shown. The particle multiplier is operated in the pulse mode with a high voltage ($\simeq 700$ V) placed on the input cone. This assures that the negative-ion detection efficiency is mass independent. The spectra observed are stable (for periods as long as days) and reproducible. The pressures of SF_6 and the alkali-metal vapors are in the neighborhood of 10^{-5} Torr. We will return to this later.

Also given in Table I are the electron affinities of the various species observed, where they are known. It is interesting to note that the majority of desorbed negative ions appear to have EA's which fall below the work function of the alkali metal, thus suggesting that some surface-catalyzed chemical reaction must be supplying energy to drive the reaction. Noticeable for its absence from the list in Table I is F_2, whose EA = 3.0 eV.

Many of the molecular negative ions listed in Table I have never been observed before. Moreover, at least one of the neutral parents, NaF_2 and KF_2, has not been observed; indeed, they may not exist as stable neutral molecules.

To ascertain the kinetic energies of the emitted ions, retardation analyses were performed for the F^-, S^-, and SF^- ion beams. First, it was observed that after acceleration through a given electrostatic potential, V, the
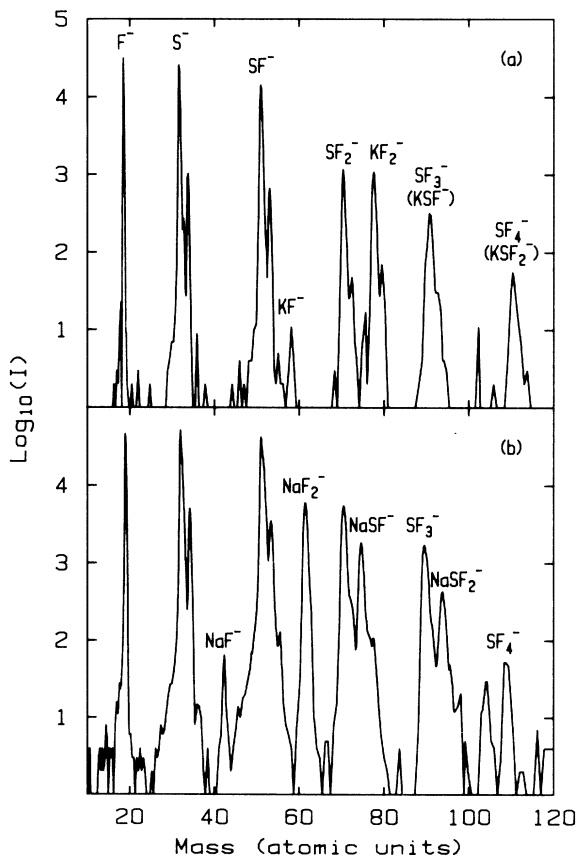

FIG. 2. The logarithm of the relative intensities of negative ions which desorb from (a) potassium surfaces and (b) sodium surfaces, as a function of mass.

TABLE I. Relative intensities of negative ions which desorb from alkali-metal surfaces; taken from Fig. 2.

Species observed	Relative intensities Na surface	Relative intensities K surface	Electron affinity (eV)	Reference
F^-	100	100	3.40	4
S^-	110	80	2.08	4
SF^-	90	45	2.5	5
SF_2^-	12	4	2.1	5
SF_3^-	4	1	3.07	5
SF_4^-	0.1	~0.1	0.8	5
NaF^-, KF^-	0.14	0.04	0.52,0.23	6
NaF_2^-, KF_2^-	13	3.1	$\cdots$	
$NaSF^-$, KSF^-	4	1	$\cdots$	
$NaSF_2^-$, KSF_2^-	1	~0.1	$\cdots$	

most probable kinetic energies of these three ion beams differed by no more than 0.2 eV, the limit of the accuracy of the measurement. Secondly, it was noted that the absolute energy of the ions, E, as determined by retardation, confirmed that the ions were indeed formed on the alkali-metal surface. Specifically, this kinetic energy, E (eV), differed from V by an amount which was less than 0.5 V; the difference is presumably due to contact potentials associated with the alkali-metal surfaces. An additional experiment was performed in which the alkali-metal-coated cylindrical lens was replaced with two planar, electrically isolated grids; the surface normals of the grids were parallel to the cylinder axis. The alkali metal was deposited on these grids and, by varying the voltage between the grids, the ion spectrum could be made to bifurcate in exact accord with the premise that the ions were formed only on the surfaces of the grids. It was clear that no ions were formed in gas-phase collisions in the region between the grids.

It is possible to estimate the efficiency for negative ion production by the observation of the total negative-ion emission current for a given SF_6 pressure. For example, at an SF_6 pressure of 7×10^{-6} Torr, the emission current is about 12 nA. The assumption of an effective surface area of 1 cm^2 yields a conversion efficiency of 2×10^{-5}. This is the probability that an SF_6 molecule strikes the surface and results in the emission of a negative ion. This figure could be in error (primarily because of an uncertainty in the effective area of the converting surface) by as much as a factor of 3.

As discussed earlier, the temporal characteristics of the process can be examined by our abruptly terminating either the SF_6 or alkali-metal flow to the surface. If the SF_6 is terminated, the emission ceases immediately, in a time comparable to that required to pump the SF_6 from the region (a few seconds).

However, if the SF_6 pressure is maintained as the alkali metal flow is abruptly terminated the ion emission decays in an exponential manner with a decay time found to vary inversely with the SF_6 pressure. For example, an SF_6 pressure of 10^{-5} Torr yields a time constant $\tau = 63$ sec.

Let us assume that the effective area, A, for conversion decreases with time as

$$dA/dt = -a\phi A\eta,$$

where η is the probability that an incident SF_6 molecule sticks to the surface rendering an area, a, incapable of subsequent conversion and ϕ is the incident SF_6 flux determined by the temperature and pressure of the SF_6. Since

$$dA/A = -dt/\tau = -a\phi\eta \, dt,$$

$$\eta = 1/\tau a\phi.$$

If we assume that $a = 10$ Å^2 and use the above condi-

tions for ϕ and τ, then we find that

$$\eta \simeq 3 \times 10^{-3}.$$

Hence the probability that an SF_6 molecule poisons the surface is about 100 times larger than the negative-ion conversion probability.

The details of just how the desorption of negative ions from these room-temperature alkali-metal surfaces occurs are far from understood. However, there is one feature of the mass spectra of Fig. 2 which may provide some insight into the desorption mechanism. Specifically, the intensity of SF_i^- ($i = 0, 1, \ldots, 5$) increases in an approximately exponential manner as i decreases. This observation suggests that the "remaining" $6 - i$ fluorine atoms may provide the energy necessary for SF_i^- to escape from the surface since the average fluorine bond strength in SF_6 is 3.4 eV (Ref. 5) whereas the bond strengths for NaF and KF are 5.3 and 5.1 eV, respectively. Of course, in order to leave the surface, SF_i^- must possess translational energy in excess of the image potential which binds it to the surface. This binding potential is given by[7]

$$E_0 \simeq e^2/4(z + R_s),$$

where z is the distance of the ion from the surface and R_s is a "screening length" of about $2a_0$. For $z \simeq 4a_0$ (the mean radius of SF_6 is about $3.5a_0$), $E_0 \simeq 1$ eV. It is not clear how the SF_i^- ions acquire at least this amount of translational energy.

In summary, it has been observed that products of surface reactions which are exothermic apparently can acquire sufficient energy to escape the surface as negative ions. The detailed mechanisms responsible for this transfer of chemical energy into translational energy sufficient for ions to desorb from the surface are not known. Further investigations of interest include a study of surface negative-ion production as a function of the temperature of the alkali-metal-surface and a detailed study of the temporal characteristics of the process. The latter study can possibly be accomplished by our employing a pulsed source of SF_6 with time resolution on the order of a few tens of microseconds. Such studies are in progress.

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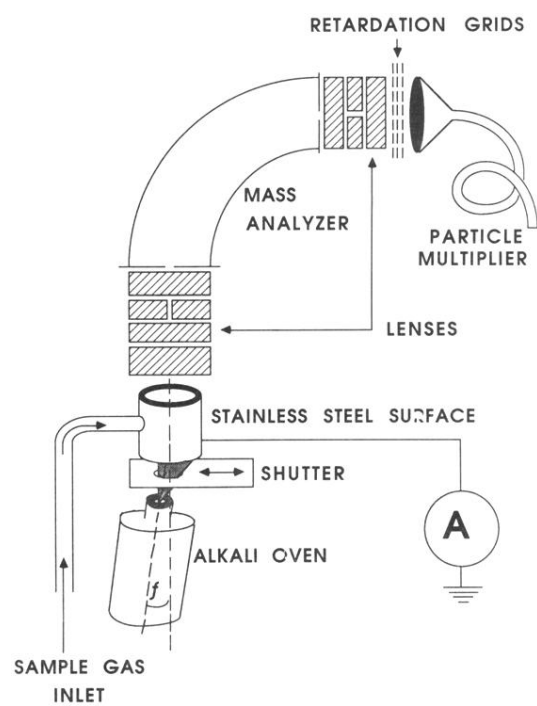[7]R. Gomer and L. W. Swanson, J. Chem. Phys. **38**, 1613 (1963).

FIG. 1. Schematic diagram of the apparatus.