MASS SPECTRA AND PHOTODETACHMENT OF SODIUM FLUORIDE NEGATIVE ION CLUSTERS

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ABSTRACT

A flowing afterglow discharge ion source with NaF vaporized into the flow produces the expected stable anions $F^-(NaF)_n$, as well as the unusual species $Na(NaF)_n^-$ and $(NaF)_n^-$ ($n \leqslant 17$). The dominance of $(NaF)_6^-$ suggests that it has a particularly stable structure. A fixed-frequency laser has been used to photodetach electrons from mass-selected ion beams extracted from the flowing afterglow. Photoelectron energy spectra, vertical detachment energies and estimates of adiabatic electron affinities are reported for the $(NaF)_n^-$ and $Na(NaF)_n^-$ ions. The $F(NaF)_n^-$ ions are found to be too stable for photodetachment at 488 nm.

INTRODUCTION

In recent years there have been a number of studies of gas-phase alkali halide cluster ions produced in secondary-ion sources [1–10]. Ion bombardment of crystalline alkali halides (MX) in secondary-ion mass spectrometers produces ions predominantly of the type $M(MX)_n^+$ or $X(MX)_n^-$, with n as large as 300 having been reported for the positive ions [2], and $n = 80$ for negative ions [3]. Much of the recent research in this area has been aimed at understanding the cluster-ion formation process in these sputter-ion sources [3,4] and unimolecular decomposition in flight [5–8]. Campana et al. [9] reported that there are certain favored clusters evident in the mass spectra, i.e. there are "magic numbers" for cluster masses which are apparently particularly stable. Further evidence for very stable cluster structures has been given by Barlak et al. [5,10], Campana and Dunlap [3], and Honda et al. [1]. The current view of these secondary-ion clusters is that metastable ionic clusters are formed by ion bombardment of an alkali halide surface, and that these clusters undergo

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unimolecular dissociation predominantly into the more stable structures [5–8].

In the present experiments we have observed negative ion clusters of sodium fluoride up to about $n = 17$. These clusters are the first negative ion clusters observed for NaF and are interesting in the context of the above discussion, partly because we have produced the clusters in an entirely different manner than previously [1–10]. Here, the NaF cluster ions have been made by heating NaF salt in a flowing afterglow ion source. Several cluster types have been observed here [$(NaF)_n^-$, $Na(NaF)_n^-$, and $F(NaF)_n^-$], in contrast to previous reports which found only ions of the form $X(MX)_n^-$, and there is evidence that the clusters have low internal energy. These NaF clusters were observed in the course of photodetachment experiments in which the electron affinities of ten alkali halide monomers were determined [11]. In this report we describe photodetachment results for many of the NaF negative ion clusters.

A number of theoretical investigations have been carried out to determine possible structures for the neutral and ionic alkali halide clusters [9,10,12–21]. Some of these studies include calculations of vibrational frequencies. The theoretical results indeed show that there are certain cluster masses that are more stable than others in terms of the energy required to remove one molecule from the crystal. However, for a given cluster size there is frequently little energy difference between several quite distinct isomers, typically 0.3 eV or less [16].

In a series of papers [17–22 and references therein] a Georgia Tech and Tel Aviv collaborative effort has yielded fascinating theoretical results for electron attachment to alkali halide clusters, using a "quantum path integral molecular dynamics" method. Although this group has not studied NaF clusters specifically, their overall picture for NaCl is likely applicable to any of the alkali halide clusters: (a) In both the neutral and ionic clusters, phase transitions are seen between isomeric structures in the temperature range 50–1200 K. At some temperatures, several forms may coexist. (b) Attachment of an electron to neutral clusters may cause major structural modifications, including the appearance of structural forms which have no counterpart in the neutral. Two sources of major configurational change were identified. In the first, the excess electron plays the role of a pseudo-negative ion in the cluster; in the second, the excess electron partially neutralizes a single cation in the cluster. (c) A large cluster reorganization energy may be associated with electron attachment, even though the total energy of the system with the attached electron may not reflect much change. (d) Both localized and extended states of the excess electron are found in the calculations.

For example, Scharf et al. [17] found that the charge distribution due to the excess electron in $(NaCl)_4^-$ is contained within a cubic configuration of the

Na$^+$ and Cl$^-$ ions at low temperatures (< 500 K); at very low temperatures (~ 50 K), the excess electron is shared among all Na$^+$, but becomes localized as the temperature is raised; at intermediate temperatures (500–750 K), a distorted planar anion resulted with localized electron density at one of the Na$^+$ corners; and at high temperatures (750–1200 K), four isomers prevailed: a boat-like configuration, a bent-chain shape, an elongated chain, and a planar configuration.

EXPERIMENTAL

Since the negative ion photoelectron spectrometer used in this work has been detailed previously [24,25], only the ion source will be detailed here. The alkali halide negative ions were formed by electron attachment to alkali halide vapor in 0.6 torr of helium gas in a flowing afterglow ion source. The alkali halide vapor was added to the flowing helium plasma from an alumina crucible (3 mm i.d., 15 mm long) loaded with salt and heated (20–40 W) by a current passed through a tungsten helix wrapped around the crucible. To keep the salt from initially being blown out of the crucible by the flowing helium, the salt was melted in the crucible with a torch. The temperature of the crucible in the afterglow was not measured. Relaxation of the internal energy in the clusters can occur in collisions with the alkali halide vapor in the flow tube. Analysis of the NaF$^-$ photoelectron spectrum [11] showed a vibrational temperature of 320 K for that species. For the present experiments the flow tube length was 42 cm, measured from the microwave discharge region to the ion sampling aperture. The alumina crucible was located 12 cm downstream from the microwave cavity. The ion flow time from the crucible to the ion sampling aperture was ~ 2 ms. The 2.45 GHz microwave discharge was typically operated at 30 W power.

Negative ions were extracted through the 1 mm diameter sampling aperture, where they were accelerated and subsequently mass analyzed with crossed electric and magnetic fields. The ion beam crossed a 100 W ArII laser beam inside the optical cavity. Photoelectrons emitted perpendicular to the ion and laser beams were focused into a hemispherical energy analyzer having a resolution of 10 meV. Multichannel electron detection was accomplished with a resistive anode position-sensitive detector.

We note reports on metal atom release from alkali halide crystal surfaces, induced by ground state atoms in a flowing afterglow apparatus [26]. The latter experiments were carried out at ten times the pressure that we used, and no metal atomization was observed when only helium gas was present. Thus, it appears that the above atomization phenomenon is unrelated to the cluster ion production that we observe in the present work.
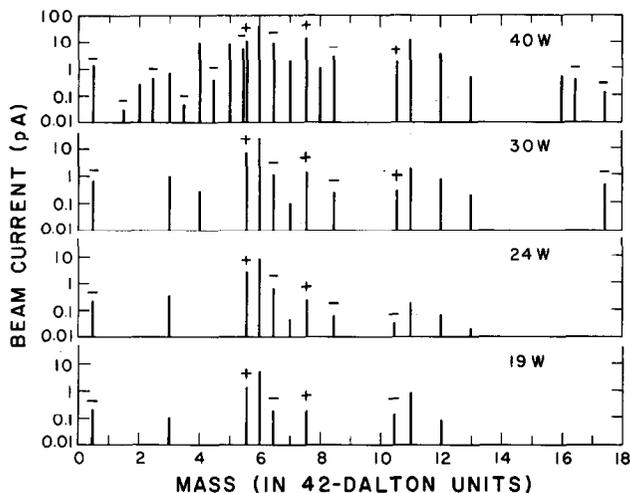
Fig. 1. Negative ion mass spectrum for $Na_n F_m^-$ produced in a flowing afterglow ion source for different crucible heating power levels. The helium pressure was 0.6 torr and the ion flight path in the flow tube was 30 cm. The $(NaF)_n^-$ occur at integer multiples of 42 daltons. The $F(NaF)_n^-$ are marked with a minus sign $(-)$ on this figure, and the $Na(NaF)_n^-$ are denoted by a plus sign $(+)$. Clusters were observed up to about $n = 17$, but the mass resolution does not permit precise identification of the ions above $n = 13$.

MASS SPECTRAL OBSERVATIONS

Mass spectra for different crucible temperatures are shown in Fig. 1. Three types of negative ion were produced from NaF vapor in the flowing afterglow: $(NaF)_n^-$, $F(NaF)_n^-$, and $Na(NaF)_n^-$. The dominant ion is $(NaF)_6^-$, which appears even at fairly low oven power, followed by $(NaF)_4^-$, which requires a higher oven temperature for significant intensity. Other $(NaF)_n^-$ are produced in lesser quantities for $n = 2$–17, though under certain ill-defined conditions the $n = 12$ ion could be prominent. The $(NaF)_8^-$ intensity is almost negligible, and there is a notable lack of $(NaF)_{9,10}^-$ under all conditions examined. This low intensity may be due to a scarcity of the corresponding neutral clusters, as Honea et al. note a near absence of the corresponding size clusters in their studies of photoionization of laser-vaporized NaF [23].

The presence of the $(NaF)_n^-$ and $Na(NaF)_n^-$ ions in these mass spectra is the primary difference between the results reported here and all previous experiments on the negative alkali halide clusters, in which *only* ions of the form $X(MX)_n^-$ were reported [3,27]. The other experiments have all used sputtering of alkali halide surfaces by ion or neutral atom beams at several keV of energy, in contrast with the present work where a more gentle ion production process (evaporation into a flowing afterglow) is utilized.

In the case of the sputter sources, it is found that highly excited clusters are released from the alkali halide surface and that unimolecular decomposition occurs in the ion beam, with certain ion fragment types favored energetically. It has been noted that the masses of these favored structures correspond to the masses of ions in cubic-like lattices, e.g. atomic arrangements $3 \times 3 \times 3$, $3 \times 3 \times 5$, $3 \times 5 \times 5$, and $5 \times 5 \times 5$ [1–10]. The ion formation mechanism in our afterglow is unclear. Tests with shorter flight paths and lower helium pressures indicate that the cluster ions are not the products of successive ion–molecule reactions. Rather, sizeable neutral clusters seem to be boiled off the alkali halide surface in our crucible and are swept up by the flowing helium, with electron attachment taking place downstream in the plasma. (The alkali halide surface in the crucible is not directly exposed to the plasma.) It is quite possible that some dissociation takes place, either due to electron attachment or collisions with metastable helium. The afterglow electrons are not completely thermalized by the time they reach the alkali halide vapor [28]. In addition, hot electrons may be generated in superelastic collisions of electrons with metastable helium [28]. In our work with the alkali halide monomer ions [11], we noted that the monomer ion production was consistent with dissociative electron attachment to neutral dimers. In the case of NaF, however, we were unable to form the monomer ion; instead, direct electron attachment apparently occurred and led to a $(NaF)_2^-$ ion. Non-dissociative electron attachment is common among other perfluoro compounds [29]. The NaF^- photodetachment spectra shown here were obtained using a NaF/NaCl mixture in the source [11].

Welch et al. [13] have carried out calculations for neutral alkali halide structures with $n = 6$ and find that the most stable $(NaX)_6$ form is cubic, except for $(NaF)_6$, where a stacked hexagonal form has the lowest energy. All of the alkali halide trimers are believed to be planar-hexagonal, so the $(NaF)_6$ neutral is essentially two trimers stacked one above the other. $(NaF)_{12}$ could then be expected to be in the form of a four layered stack of trimers, a conclusion which is supported by Martin's calculations for $(NaCl)_{12}$ [16]. The neutral dimer is known to be planar-rhombic, and $(NaF)_4$ is thought to be of similar nature, a slightly skewed cube [13]. The calculations of the Georgia Tech/Tel Aviv group for NaCl clusters [17–21] indicate that at the low temperature (320 K) inferred for our experiment, the anionic clusters have similar structures to those of the corresponding neutrals, with distortion of the lattice in the vicinity of the attached electron.

The other classes of negative ions that we observe, $Na(NaF)_n^-$ and $F(NaF)_n^-$, occur with roughly equal propensity as the $(NaF)_n^-$, although still minor in intensity compared with $(NaF)_6^-$. This result contrasts with the sputtering data [3,27] where the $X(MX)_n^-$ are virtually the only ions present for all values of n. It is appropriate here to note that our nomenclature

$Na(NaF)_n^-$ or $F(NaF)_n^-$ is convenient, but perhaps misleading in implying that there is an "extra" Na or F atom. If n is large enough, the odd atom may be included in the structure in quite a natural way, as in a $3 \times 3 \times 3$ cubic crystal, which has an odd total number of atoms.

Significant clustering has been observed in the present experiments only for NaF, among the ten alkali halides that we studied (the NaX, the MCl, and KBr and KI). The implication is that the strong fluoride bond (due to the small size of the fluoride ion) is conducive to clustering. In the non-fluoride cases, cluster ions were present but constituted roughly 1% of the total beam intensity. The X^- dominated these other mass spectra.

PHOTOELECTRON SPECTRA

The photodetachment results may be briefly summarized by noting that (a) none of the $F(NaF)_n^-$ ions could be photodetached with 2.540 eV photons, while (b) the $(NaF)_n^-$ and $Na(NaF)_n^-$ did detach. The $F(NaF)_n^-$ do not have an "extra" electron in the sense usually intended; the $F(NaF)_n^-$ are a conglomeration of Na^+ and F^- ions and end up with a net negative charge due to the odd number of F^- ions. Since the electron affinity of an isolated F^- ion is 3.399 eV [30], it is understandable that we could not photodetach the $F(NaF)_n^-$ at 488 nm. On the other hand, it is likely [17–22] that the charge distribution attributed to the extra electron for the $(NaF)_n^-$ and $Na(NaF)_n^-$ is concentrated near a Na^+ ion, as in NaF^- [11].

Photoelectron energy spectra for the $(NaF)_n^-$ ions are shown in Fig. 2. The beam intensities for clusters not represented in Fig. 2 ($n = 8$–11) were too weak to permit photoelectron data to be obtained readily. Data for $Na(NaF)_n^-$ ions are shown in Fig. 3. The diffuse structure evident in these photoelectron spectra is due to congestion of vibrational progressions. In a few cases two broad peaks are seen, and may either be due to electronic excitation or to the presence of isomers.

Only in the case of NaF^- is the photoelectron spectrum readily interpreted [11]. The NaF^- ion may be thought of as a F^- ion near to and strongly polarizing a neutral Na atom; it is the Na valence electron that is photodetached [11,19,31]. As the electron is detached, the restoration of ionic forces results in vibrational excitation of the NaF molecule, reflected in the extended electron kinetic energies distribution. It is possible to identify the peak corresponding to the transition between the ground vibrational state of NaF^- and the ground vibrational state of NaF [11], so that the adiabatic electron affinity of NaF may be specified accurately (0.52 ± 0.01 eV). In the photoelectron spectra shown in Figs. 2 and 3, threshold vibrational structure is not resolved, except for NaF^-, and consequently only estimates of the electron affinity may be given in each case. Where peaks in the electron energy
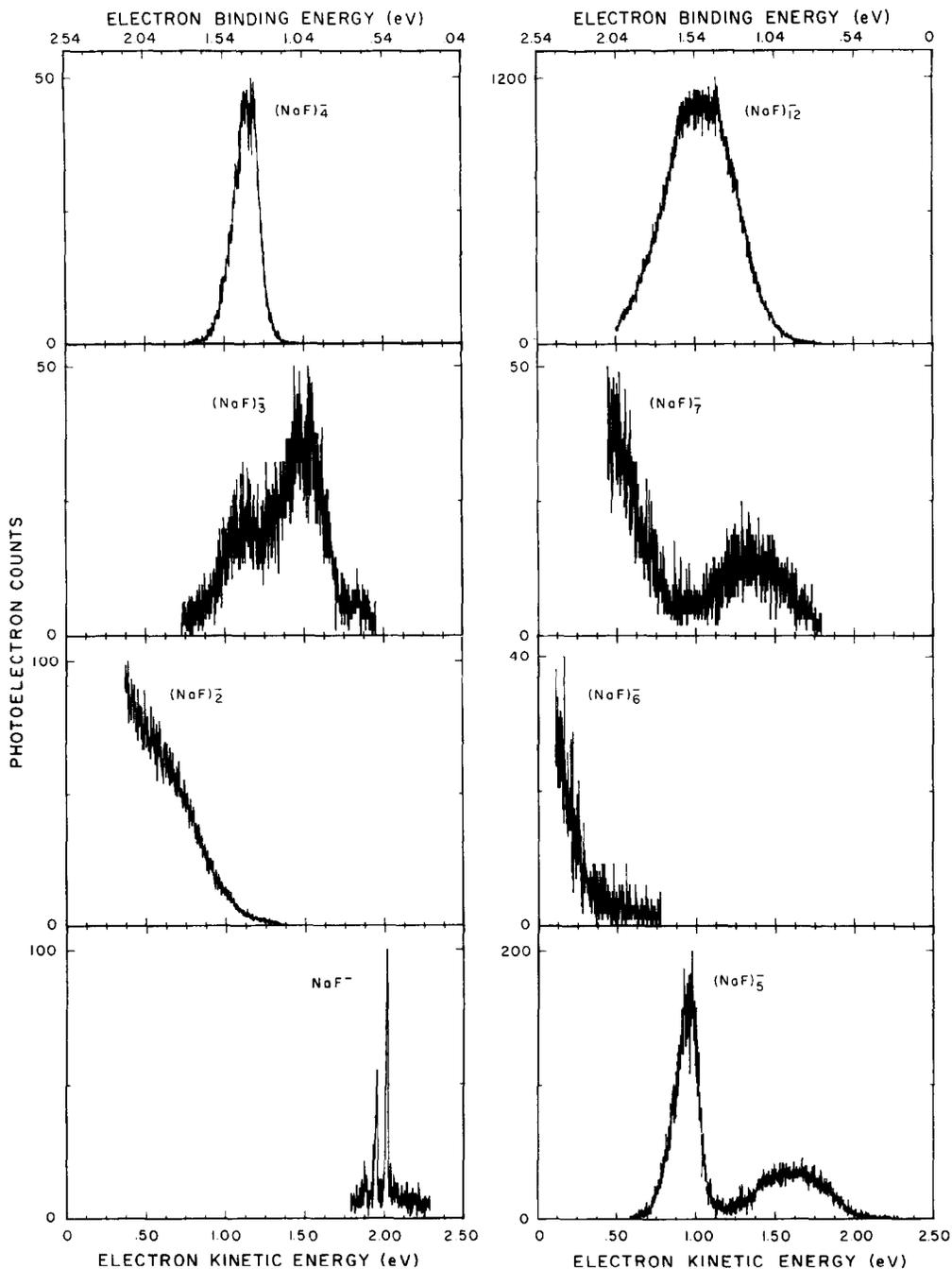
Fig. 2. Photoelectron spectra for $(NaF)_n^-$ ions at 488 nm. [The $(NaF)_6^-$ data were actually obtained at 454 nm because of the high electron binding energy in this case, and the electron energy scale was shifted by 0.070 eV to facilitate comparisons with the other spectra.]
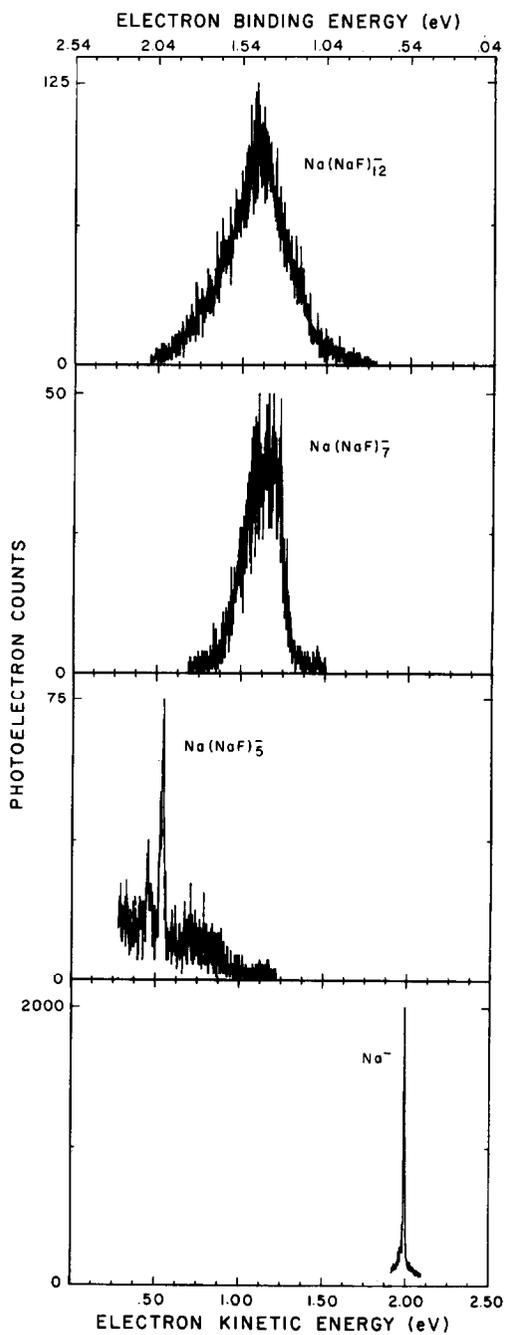
Fig. 3. Photoelectron spectra for Na(NaF)$_n^-$ ions at 488 nm.

TABLE 1

Vertical detachment energies and adiabatic electron affinities of the sodium fluoride clusters from photoelectron spectroscopy of negative ions

Only for NaF was vibrational structure resolved which permitted unambiguous assignment of the adiabatic electron affinity. For $(NaF)_2$, $(NaF)_6$ and $Na(NaF)_5$, the photon energy was inadequate to allow observation of the entire Franck–Condon distribution of transition energies. In these cases, only an estimate of the vertical detachment energy was possible. Similarly, the shape of the $(NaF)_2^-$ photoelectron spectrum is suggestive that the adiabatic EA may be yet lower in energy

Neutral molecule	Adiabatic EA (eV)	Vertical detachment energy (eV)	Neutral molecule	Adiabatic EA (eV)	Vertical detachment energy (eV)
NaF	0.52 ± 0.01	0.52	Na	0.548	—
$(NaF)_2$	< 1.3	> 2.3			
$(NaF)_3$	0.7	1.05			
$(NaF)_4$	1.25	1.4			
$(NaF)_5$	0.60	0.9	$Na(NAF)_5$	~ 1.8	?
$(NaF)_6$	2.1	> 2.5			
$(NaF)_7$	0.9	1.2	$Na(NaF)_7$	1.25	1.4
$(NaF)_{12}$	1.1	1.5	$Na(NaF)_{12}$	1.1	1.45

distribution can be observed, it is possible to give reasonably accurate estimates of the *vertical detachment energy*. These estimates, as well as the less accurate estimates of the *adiabatic electron affinity*, are tabulated in Table 1. No specific tests have been made to rule out the possibility of two-photon transitions. Doubly charged ions are also a possibility, but no unexplained mass peaks have been observed. Among our results we note the following:

(a) The observation that the electron binding energy in $(NaF)_2^-$ is over twice that for NaF^- is particularly interesting. Experience would lead us to expect a smaller electron affinity for the dimer, because the neutral dimer is planar-rhombic with no dipole moment. Further, an extra electron attached to a Na^+ in the rhombic dimer would have two F^- ions polarizing it. Indeed, Jordan and Kurtz [32] have found theoretically that the planar-rhombic dimer will not bind an electron, and they suggest that the dimer negative ion is linear. The linear dimer would have a larger dipole moment than in the monomer. Thus, our estimated ~ 1.3 eV adiabatic electron affinity for $(NaF)_2$ supports the notion of a linear dimer negative ion. It is relevant to note that the calculations of Welch et al. [12] yield a metastable linear form of neutral $(NaF)_2$, located 0.78 eV above the planar-rhombic structure. They found a small (0.004 eV) barrier stabilizing the neutral linear dimer. Only for $(NaF)_2$ and $(LiCl)_2$ did the metastable linear dimers correspond to a local minimum [12].

(b) For the $(NaF)_n^-$ with odd values of n, the apparent electron affinity is small (< 1 eV) but increases with n. It is possible that the increase in electron binding energy is due to the increase in the number of Na^+ sites in the complex odd-n structures. The even-n neutral structures are calculated to be more regular, i.e. cubic or hexagonal [13,15]. For the $(NaF)_n^-$ with even values of n, the apparent electron affinities are larger (1–2 eV) but show no systematic trends. Neutral $(NaF)_6$ is predicted to be particularly stable [13]. Interestingly, we find the largest electron binding energy for $(NaF)_6^-$, and the greatest intensity in the mass spectrum.

(c) The electron binding energies for the $Na(NaF)_n^-$ decrease with increasing n. Surprisingly, sharp features are observed in the photoelectron spectrum for $Na(NaF)_5^-$, including a strong $700\,cm^{-1}$ mode of $Na(NaF)_5$. There is weak diffuse structure underneath the sharp features.

CONCLUSIONS

We have observed negative ion clusters formed by vaporizing NaF salt in a flowing afterglow ion source. $(NaF)_n^-$ ions dominate the mass spectrum, which extends up to about $n = 17$. The $(NaF)_6^-$ beam intensity is especially strong under all conditions studied. $F(NaF)_n^-$ and $Na(NaF)_n^-$ ions are also observed. The ion mass spectra contrast markedly with those obtained with sputter sources. Photodetachment data support the speculation of a linear $(NaF)_2^-$ ion. The $F(NaF)_n^-$ ions cannot be photodetached with 2.54 eV photons.

ACKNOWLEDGEMENTS

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