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Photoionization of small sodium-doped acetic acid clusters

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The uptake of sodium and the fragmentation before and after “soft” photoionization with ultraviolet light are investigated for small acetic acid clusters. The acetic acid clusters are generated in a supersonic expansion and ionized with ultraviolet light after doping with sodium in a pick-up chamber. The composition of the bare acetic acid clusters in the molecular beam is determined independently from complementary photoionization experiments using extreme ultraviolet light. The experimental results are analyzed with the help of density functional calculations for energetics and statistical adiabatic channel calculations for fragmentation kinetics. The study demonstrates that the detected ions originate from fragmentation in the neutral as well as in the ionic state, and in particular that the fragmentation pathway strongly depends on the cluster size. © 2011 American Institute of Physics. [doi:10.1063/1.3559464]

I. INTRODUCTION

Numerous studies have been devoted to the interaction of sodium atoms with gas phase clusters consisting of polar molecules, with the primary objective of better understanding the concept of solvation (Refs. 1–21 and references therein). These studies consequently focused on the determination of size specific properties such as ionization energies, structures, vibrational frequencies, and dissociation energies. Most of the reported data pertain to sodium-doped ammonia and sodium-doped water clusters (Refs. 1–17, 19–21, and references therein), with only a few exceptions.^{18,22}

It appears that the issues of sodium doping, collision complex lifetimes, photoionization efficiency, and neutral and ionic fragmentation were addressed in less detail,^{2,6,9,11,23} although understanding these processes is essential for correlating ionization energies with the ionic appearance energies actually measured in photoionization experiments. The general assumption is that only a small number of monomers evaporate from the cluster as a result of sodium doping. Fragmentation following (soft) ionization is also assumed to be of only minor importance. The excess energy after ionization is sometimes used to estimate the number of evaporated monomers without regard to any further details of the processes involved. For the smallest clusters, the loss of any molecules is obviously significant, and in particular it is to be expected that the underlying processes are size dependent, i.e., they depend on the specific energetics.

In the present work, we have tried to address these issues for the case of small acetic acid clusters. A peculiarity of acetic acid is its ability to form a very strongly bound dimer, which has no permanent dipole moment, while the binding of additional monomers is much weaker. This hierarchy of forces makes the acetic acid system particularly interesting to study sodium uptake, collision complex lifetimes, and

fragmentation. The acetic acid clusters were formed by supersonic expansion similar to many other studies on gas phase sodium-doped clusters. Sodium doping happened in a standard sodium oven.^{11,24} Photoionization with ultraviolet (UV) light and subsequent time-of-flight ion detection were employed to study the properties of the sodium-doped clusters at energies in the region of their ionization energies. From UV-photoionization alone, however, it is impossible to determine the original composition of acetic acid clusters in the molecular beam. An essential feature of the present study is the combination of UV photoionization spectroscopy with independent extreme ultraviolet (XUV) photoionization^{25,26} to assess the original composition of the beam. The latter allows direct ionization of bare acetic acid clusters with well known fragmentation patterns.^{27,28} The experiments were complemented by density functional calculations of cluster geometries and energies²⁹ and by theoretical estimates of the pick-up and fragmentation kinetics of the collision complexes using the statistical adiabatic channel model (SACM).^{30,31}

II. EXPERIMENT

The experimental setup used for the present experiments has been reported in detail previously.²⁶ The only modification was the addition of a sodium pick-up oven similar in design to the ones reported in Refs. 24 and 11 (see also Refs. 1, 6, 10, and 15). The setup consisted of an XUV light source, a UV light source, the sample injection chamber, the sodium oven chamber, and the time-of-flight (TOF) chamber (Fig. 1). The acetic acid (HAc) clusters were generated in a pulsed seeded supersonic expansion from a sample reservoir containing 17 mbar HAc (glacial, Fisher Scientific) in helium (Praxair, 5.0) at a total pressure of 1 bar. The molecular beam entered the sodium pick-up chamber through a skimmer. At a sodium oven temperature of 498 K, single sodium pick-up was optimal, while double pick-up was still negligible. The molecular beam intersected the laser beams 80 mm

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FIG. 1. Experimental setup. A: Four-wave mixing chamber, B: monochromator chamber, C: sample injection chamber, D: sodium oven chamber, and E: TOF chamber.

downstream from the oven in the TOF chamber. Photoionization products were extracted using a dc electric field (1 kV applied across the extractor; Wiley-McLaren type), and detected after the linear flight tube by microchannel plates. XUV light with a wavelength of $3\nu_1 = 74.2$ nm ($134\,790$ cm $^{-1}$) was generated by two-photon resonance enhanced four-wave mixing in a xenon gas jet.^{25,26} The frequency tripled output ν_1 of a dye laser (Sirah Cobra Stretch SL) that matches a two-photon resonance in xenon was used for this purpose. Tunable UV light with wavelengths $\nu_2 \geq 223$ nm ($\tilde{\nu} \leq 44\,843$ cm $^{-1}$) was generated from the doubled output of a second identical dye laser. The two laser beams were directed into the ionization region of the TOF chamber by a diffraction grating. This scheme ensured that the molecular beam was probed at the same position by the UV as by the XUV light (*vide infra*). We used very low UV intensities ($\sim 10^{-3}$ mJ mm $^{-2}$ ns $^{-1}$) to minimize electron ionization, which is always an issue with dc extraction fields because free electrons, produced by the primary ionization or by stray UV photons hitting metal surfaces, are quickly accelerated to energies far above molecular ionization energies.

The UV light was used for photoionization of the Na-doped clusters at photon energies close to their ionization energies. The corresponding TOF spectra will be called “UV-TOF spectra” throughout the remainder of the paper. The XUV light was solely used as an independent check to monitor and adjust the composition of the molecular beam (*vide infra*). The energy of the XUV photon is high enough to ionize HAC and (HAC) $_n$ clusters.²⁵ Direct photoionization of (HAC) $_n$ clusters leads to well known fragmentation patterns,^{27,28} which allow us to draw conclusions about the molecular beam composition. The most characteristic fragmentation path of a cluster with n monomer units leads to the formation of a protonated cluster ion with $(n - 1)$ monomer units along with smaller fragments F_j .

$(\text{HAC})_{(n-1)}\text{H}^+$ is thus a characteristic for a molecular beam containing (HAC) $_n$. A list of characteristic XUV fragments along with their masses is given in Table I. These TOF spectra are referred to as “XUV-TOF spectra” hereafter.

In a molecular beam, it is not possible to form larger clusters without forming smaller clusters at the same time. The reverse, however, is possible, i.e., to keep the abundance of larger clusters negligible or at least very low, while producing small clusters. To clarify from which Na-doped parent cluster $[\text{Na}(\text{HAC})_n]$ a given Na-doped fragment arises in the UV-TOF spectra, we have recorded spectra under different conditions, systematically increasing the maximum cluster size as monitored by the XUV-TOF spectra. Correlations between individual fragment ions and different maximum cluster sizes become apparent in the accompanying changes in the UV-TOF spectra (Sec. IV). The composition of the molecular beam sampled by the laser was altered primarily by changing the time delay between the sample gas pulse and the trigger of the laser pulse. As this delay is decreased, the part of the sample gas expansion actually probed by the ionizing laser moves from the beginning to the end of the expansion. Moving from the beginning toward the center of the sample gas pulse gradually increases the amount of cooling in the molecular beam, which in turn increases the maximum cluster size that is formed. While optimizing the nozzle timing to enhance the

TABLE I. Upper part: characteristic fragments and masses of HAC and its clusters after XUV ionization. Lower part: masses of Na-doped clusters expected in the UV-TOF spectra.

Masses of fragments after XUV ionization ^a (HAC) $_n + h\nu_{\text{XUV}} \rightarrow (\text{HAC})_n^+ \rightarrow F_i^+ + \Sigma F_j$		
Original ion (HAC) $_n^+$	Fragment ions F_i^+	Mass of F_i^+ (u)
HAC $^+$	CH $_3$ CO $^+$	43
	COOH $^+$	45
	HAC $^+$	60
(HAC) $_2^+$	HAC H^+	61
	(HAC)COOH $^+$	105
(HAC) $_3^+$	HAC H^+	61
	(HAC)CH $_3$ CO $^+$	103
	(HAC) $_2$ H $^+$	121
(HAC) $_4^+$	(HAC) $_3$ H $^+$	181
(HAC) $_n^+$	(HAC) $_{(n-1)}$ H $^+$	$1 + 60(n - 1)$
Masses of Na-doped clusters Na(HAC) $_n^+$ expected after UV ionization		
Ion	Mass (u)	
NaHAC $^+$	83	
Na(HAC) $_2^+$	143	
Na(HAC) $_3^+$	203	
Na(HAC) $_4^+$	263	
Na(HAC) $_5^+$	323	

^aReferences 27 and 28.

TABLE II. B3LYP/6-311++G(3df,2p) calculations for neutral and ionic fragmentation. All energies are counterpoise corrected for the basis set superposition error. From calculated ion energies, 2273 cm^{-1} have been subtracted to match the experimental ionization energy of Na atoms (5.139 eV or $41\,449 \text{ cm}^{-1}$).

Na(HAc) _n	i	→ Na(HAc) _{n-i} + (HAc) _i ^a		→ Na(HAc) _{n-i} ⁽⁺⁾ + (HAc) _i ^a	
		D _e (cm ⁻¹)	D ₀ (cm ⁻¹)	ΔE _{vertical} ^b (hc cm ⁻¹)	ΔE _{adiabatic} ^c (hc cm ⁻¹)
NaHAc	0			34 971 ^d	32 536 ^e
	1	1611	1483	42 932	42 932
Na(HAc) ₂	0			45 658 ^d	30 802 ^e
	1	5199	5569	40 540	38 105
	2	1493	2254	43 703	43 703
Na(HAc) ₃	0			47 596 ^d	32 483 ^e
	1	7646	7210	52 868	38 012
	2	7528	7982	42 953	40 518
	3	6811	7475	48 924	48 924
Na(HAc) ₄	0			47 794 ^d	31 754 ^e
	1	5316	4860	52 456	37 343
	2	7645	7273	52 931	38 075
	3	10 516	10 852	45 823	43 388
	4	8524	9350	50 799	50 799

^aFragment energies relative to the respective neutral parent cluster Na(HAc)_n.

^bΔE_{adiabatic} + ion reorganization energy (vertical ionization energy – adiabatic ionization energy) of Na(HAc)_{n-i}⁽⁺⁾.

^cD₀ of Na(HAc)_n + adiabatic ionization energy of Na(HAc)_{n-i}.

^dVertical ionization energy.

^eAdiabatic ionization energy.

formation of larger clusters can reduce the relative amount of the smallest clusters, this decrease is not very significant.

III. CALCULATIONS

A. *Ab initio* calculations

Ab initio calculations at the B3LYP/6-311++G(3df,2p) level of theory²⁹ were performed for the neutral and ionic

sodium doped acetic acid trimer and for a series of possible fragments thereof. Dissociation energies with (*D*₀) and without (*D*_e) zero-point correction are given in Table II. Figure 2 illustrates these results for the trimer fragmentation process together with the structures of the various clusters. We have chosen this particular level of density functional theory (DFT) since it provides a reasonable description of strongly hydrogen-bonded structures and their energetics. It also yields ionization energies typically within a few 10⁻¹ eV

FIG. 2. Zero point corrected energies [relative to the neutral Na(HAc)₃ ground state] and structures for Na(HAc)₃ and its neutral and ionic fragments from B3LYP calculations. AE₁: adiabatic ionization energy and VE₁: vertical ionization energy.

of experimental values, which justifies its use for the calculations of acetic acid clusters and their complexes with sodium ions. The use of B3LYP to describe the corresponding neutral complexes resulting from the initial pick-up is more problematic. The long-range interaction is dominated by dispersion (*vide infra*), which semilocal density functionals such as B3LYP usually fail to describe. Therefore, dispersion contributions to the binding energy of Na collision complexes might not be properly described. We have tested the B3LYP results against several density functionals that incorporate empirical atom–atom dispersion corrections (B97D, wB97XD, X3LYP, M062X, see Ref. 29 and references therein). All methods lead to virtually the same equilibrium structures, both for neutral and for ionic complexes. The dispersion-corrected functionals consistently show stronger sodium binding than B3LYP, but the differences vary widely between 10% and more than a factor of 2, depending not only on the cluster size but also on the particular dispersion-corrected functional. In the case of Na-doped HAc-clusters the empirical atom–atom dispersion corrections apparently fail to provide quantitatively reliable predictions, so that we can only consider them as an indication of the uncertainties of the Na-binding energies. Since all DFT calculations largely agree in terms of calculated equilibrium structures and the energetic ordering of fragmentation channels, we conclude that the B3LYP functional provides at least a qualitatively correct picture of the energetics. Calculated ionization energies are expected to be slightly overestimated by the B3LYP/6-311++G(3df,2p) calculations, which yield a value of 5.421 eV for Na, 0.282 eV above the experimental IP of 5.139 eV (Ref. 32). Assuming this error to be approximately constant we have subtracted 2273 cm⁻¹ from all calculated ionization energies.

B. Capture cross sections for Na pick-up

The capture probability is determined by the interaction potentials between sodium atoms and (HAc)_n clusters, by the collision energy, by the densities of the species involved, and by the length of the pick-up cell. We have estimated the thermally averaged cross section $\langle\sigma\rangle$ for the capture of a sodium atom by the various acetic acid clusters using a Langevin model,³³ assuming long-range interaction potentials dominated by isotropic dispersion and induction terms:

$$V_{\text{disp}} = -\frac{C_{\text{disp}}}{R^6} = -\frac{3}{2} \frac{E_1(\text{Na})E_1[(\text{HAc})_n]}{E_1(\text{Na}) + E_1[(\text{HAc})_n]} \frac{\alpha(\text{Na})\alpha[(\text{HAc})_n]}{R^6}, \quad (2)$$

$$V_{\text{ind}} = -\frac{C_{\text{ind}}}{R^6} = -\frac{1}{4\pi\epsilon_0} \frac{\mu[(\text{HAc})_n]^2\alpha(\text{Na})}{R^6}, \quad (3)$$

where R is the interparticle distance. Ionization energies (E_1), polarizability volumes (α), and dipole moments (μ) of the various species are given in Table III. Within the Langevin model, the capture cross section $\sigma(E)$ as a function of collision energy E is given by

$$\sigma(E) = \pi b_{\text{max}}^2 = \pi \left(\frac{27(C_{\text{disp}} + C_{\text{ind}})}{4E} \right)^{1/3}, \quad (4)$$

TABLE III. Properties of different sodium–acetic acid collision complexes: collision energy (E), maximum angular momentum (ℓ_{max}), capture cross section (σ), capture probability p , and decay times τ_j (see Sec. III C for details).

	Collision complex			
	Na–HAc	Na–(HAc) ₂	Na–(HAc) ₃	Na–(HAc) ₄
$\langle E \rangle$ (hc cm ⁻¹)	1070	1243	1313	1350
$\langle \ell_{\text{max}} \rangle$	176	220	250	265
$\langle \sigma \rangle^a$ (Å ²)	102 ^b (100) ^c	120 ^b	136 ^b (135) ^c	146 ^b
p	54%	60%	64%	67%
τ_1^d	2 ps	∞	140 ns	50 ps
τ_2^d		100 ps	7.5 μs	500 ns
τ_3^d			70 μs	∞
τ_4^d				10 s

^aThe thermally averaged capture cross section is derived from Eq. (4) as described in Sec. III B. The Na-oven temperature was $T = 498$ K.

^bParameters used for the calculation of capture cross sections: polarizabilities: $\alpha(\text{Na}) = 24.1$ Å³ (Ref. 34), $\alpha(\text{HAc}) = 4.74$ Å³, $\alpha[(\text{HAc})_2] = 9.78$ Å³, $\alpha[(\text{HAc})_3] = 14.82$ Å³, $\alpha[(\text{HAc})_4] \approx 2\alpha[(\text{HAc})_2]$. Dipole moments: $\mu(\text{HAc}) = 1.67$ D (Ref. 35), $\mu[(\text{HAc})_3] = 1.9$ D, $\mu[(\text{HAc})_2] = \mu[(\text{HAc})_4] = 0$. Ionization energies: $E_1(\text{Na}) = 5.139$ eV (Ref. 32), $E_1(\text{HAc}) = 10.7$ eV (Ref. 25), $E_1[(\text{HAc})_3] = 9.5$ eV, $E_1[(\text{HAc})_4] \approx E_1[(\text{HAc})_3]$. Except where noted, values were calculated in this work at the B3LYP/6-311++G(3df,2p) level.

^cValues in parentheses are the capture cross sections for $\mu[(\text{HAc})_n] = 0$.

^dDecay channel $\text{Na}(\text{HAc})_n \rightarrow \text{Na}(\text{HAc})_{n-j} + (\text{HAc})_j$; $\tau_j = 1/k(E, \langle \ell_{\text{max}} \rangle)$ [Eqs. (10) and (11)].

where b_{max} is an effective capture radius. Averaging over the relative velocities of sodium atoms and acetic acid clusters yields average capture cross sections $\langle\sigma\rangle$. A thermal velocity distribution at a temperature of 498 K is used for the sodium atoms, and a constant and uniform velocity of 1000 m s⁻¹ is assumed for (HAc)_n in the molecular beam. The capture cross section $\langle\sigma\rangle$ together with the Na concentration in the oven ($1.7 \cdot 10^{19}$ m⁻³) and the length of the pick-up region (44 mm), yield the capture probability p .

Values of $\langle\sigma\rangle$ and p for collisions between sodium and different acetic acid oligomers are listed in Table III. The values are very similar, even though the dimer and the tetramer do not have a permanent dipole moment. The dispersion interaction is evidently much more important for the capture process than the induction interaction, as illustrated by the values of $\langle\sigma\rangle$ for HAc and (HAc)₃ given in parentheses, which were calculated neglecting V_{ind} . Despite the very approximate character of the above calculations, it is clear that even small species without a permanent dipole moment quite readily pick up a sodium atom.

C. Lifetimes of Na(HAc)_n⁺ collision complexes

The capture probabilities derived from the Langevin model indicate a uniformly high pick-up efficiency, but whether the collision complexes formed in the sodium oven chamber enter the ionization chamber intact or not depends on their lifetimes. With a molecular beam velocity on the order of 1000 m s⁻¹ it takes the Na(HAc)_n complexes about 80 μs to travel the distance to the ionization region. The unimolecular decay rates of the collision complexes can be estimated by statistical rate theories. We have chosen the statistical adiabatic channel model of Quack and Troe,³⁰ since it encompasses

practically all other statistical theories as limiting cases.³¹ Assuming barrierless dissociation and fast intramolecular energy redistribution, we determined the decay rates of all possible fragmentation channels of the neutral collision complexes to estimate their lifetimes, and to elucidate the product distribution and energy disposal of the fragmentation.

Within SACM the unimolecular decay rate as a function of energy E and angular momentum quantum number J is given by

$$k(E, J) = \frac{W(E, J)}{h\rho(E, J)}, \quad (5)$$

where h is Planck's constant, ρ is the density of reactant states, and W is the number of open decay channels, which are defined in terms of the reactant (E_r) and product (E_p) levels they connect. The associated channel potentials $V_{rp}(q)$ describe the adiabatic change of the corresponding energy levels along the reaction coordinate q from the reactant state, $V_{rp}(q)$, to the product state, $V_{rp}(\infty) = E_p$. At energy E a channel is open if

$$\max_q(V_{rp}) \leq E. \quad (6)$$

In correlating reactant and product levels any exact or approximate symmetries (conservation laws) are accounted for either in detail, i.e., level by level, or on average by appropriate symmetry numbers. For simplicity the channel potentials are formulated for a dissociating Morse oscillator with a single interpolating function between reactant and product energy levels:

$$V_{rp}(q) = D_e(1 - e^{-\beta q})^2 + (E_p - D_e)(1 - f) + (E_r - E_{Zq})f + V_{\text{cent}}(q). \quad (7)$$

All energies are referred to a common energy zero, in this case the reactant zero-point level. E_{Zq} is the vibrational zero-point energy in the reaction coordinate q . For the interpolation of the channel potential, we use the simple exponential damping originally suggested in Ref. 30:

$$f(q) = \exp\{-\beta q\}. \quad (8)$$

The centrifugal potential $V_{\text{cent}}(q)$ is approximated for two separating point masses:

$$V_{\text{cent}}(q) = B_e \left[\left(\frac{r_e}{r_e + q} \right)^2 - f \right] \times [f(J - \ell) + \ell][f(J - \ell) + \ell + 1], \quad (9)$$

where ℓ is the orbital angular momentum of the separating fragments and q is taken as the change of the distance between their centers of mass, from its equilibrium value r_e with corresponding rotational constant B_e . The Morse parameter β was determined from the dissociation energy D_e and the harmonic wavenumber of the oscillator assigned to the reaction coordinate, all calculated at the B3LYP/6-311++G(3df,2p) level of DFT. We set the universal damping parameter in $f(q)$ equal to β , which is consistent with the loose transition state assumption implicit in the Langevin model for the capture process.

Densities of state were determined by direct count assuming harmonic oscillators and rigid asymmetric tops. We have tested the effect of anharmonicities in the case of NaHAc, by explicitly treating the dissociating Morse oscillator and the tunneling CH_3 -rotor (with the appropriate symmetry number three). At the relevant energies, the anharmonic count yields $k(E, J)$ values 10%–20% above those obtained in the harmonic approximation (mostly because of CH_3 torsion), which is negligible for the purposes of the present study. For the determination of $W(E, J)$ the energy levels of conserved and disappearing oscillators were treated separately. The former correlate with the internal vibrations of the fragments, while the latter correlate with fragment rotation and orbital motion. Detailed angular momentum conservation was observed. Collision complex lifetimes were determined for the average collision energy $\langle E \rangle$ and $J = \langle \ell_{\text{max}} \rangle$ (see Table III).

$$\tau = \frac{1}{k(\langle E \rangle, \langle \ell_{\text{max}} \rangle)}. \quad (10)$$

We assume that the initial angular momentum of the $(\text{HAc})_n$ in the beam is negligible, compared with the maximum orbital angular momentum for successful capture, $\langle \ell_{\text{max}} \rangle$, given by the Langevin model:

$$\hbar^2 \langle \ell_{\text{max}} \rangle^2 \approx 2\mu \langle E \rangle \frac{\langle \sigma \rangle}{\pi}, \quad (11)$$

where μ is the reduced mass of the fragments.

IV. RESULTS

A. Monomer and dimer

As explained in Sec. II, photoionization with XUV light was used to probe the cluster composition in the molecular beam. XUV-TOF mass spectra recorded at different times in the supersonic expansion are presented in Fig. 3. Trace (a) depicts the spectrum for conditions under which only the monomer (HAc) and the dimer $[(\text{HAc})_2]$ are present in the part of the molecular beam that is sampled. This is demonstrated by the fact that only fragments characteristic of the monomer and dimer are observed (Table I). Under these conditions, no signals of sodium doped species of the monomer or the dimer, or any fragments thereof, were observed in the UV-TOF spectra (not shown) recorded at photoionization wavelengths ranging from 223 to 302 nm. $\text{Na}(\text{HAc})$ and $\text{Na}(\text{HAc})_2$ are either not formed in the pick-up chamber, they dissociate in the neutral state while traveling from the pick-up oven to the ionization region, or they are not ionized efficiently enough by the UV laser to be recorded. This is further discussed in Sec. V A.

B. Trimer

When the expansion is optimized for clusters up to the trimer with only very minor amounts of tetramer present, a strong signal at $m/z = 83$ corresponding to $\text{Na}(\text{HAc})^+$ (Table I) is observed in the UV-TOF spectrum at ionization wavelengths between 223 and 300 nm [Fig. 4(a)]. While a weak signal at $m/z = 143$ in the spectrum shown in Fig. 4(a) indicates the presence of small amounts of $\text{Na}(\text{HAc})_2^+$, the

FIG. 3. XUV-TOF spectra recorded under different conditions: Molecular beam contains (a) monomer HAC and dimer $(\text{HAc})_2$; (b) monomer HAC, dimer $(\text{HAc})_2$, and trimer $(\text{HAc})_3$ (amount of tetramer is very small); (c) monomer HAC, dimer $(\text{HAc})_2$, trimer $(\text{HAc})_3$, and tetramer $(\text{HAc})_4$; (d) large clusters. The species are identified by their characteristic fragments given in Table I. Note that the signals in traces (a)–(d) are scaled by different factors for masses above 70 u. Also note that the m/z scale in trace (d) differs from traces (a) to (c).

absence of any signal at $m/z = 203$ means that no $\text{Na}(\text{HAc})_3^+$ is formed from $\text{Na}(\text{HAc})_3$. Figure 3(b) depicts the corresponding XUV-TOF spectrum recorded under the same conditions. The characteristic dimer and trimer fragment ions (Table I) show up strongly, which proves the predominance of clusters up to the trimer under these conditions in the molecular beam. The very weak fragment peak at $m/z = 181$, which is a characteristic of the tetramer, shows that the abundance of $(\text{HAc})_4$ in the beam is only minor.

As mentioned in Sec. IV A, the UV-TOF spectra of the monomer and dimer do not exhibit any sodium-doped fragments, so that neither of the species can be at the origin of the $m/z = 83$ fragment in Fig. 4(a). Furthermore, the XUV-TOF spectrum in Fig. 3(b) clearly shows that the tetramer content is minor and that no larger clusters are present under these conditions. Therefore, the $m/z = 83$ fragment must definitely originate from $\text{Na}(\text{HAc})_3$. From the ion yield as a function of the UV photon energy shown in Fig. 5(a), we estimate an approximate value for the appearance energy of the $m/z = 83$ fragment of 4.13 ± 0.05 eV ($33\,333 \pm 450$ cm^{-1}). By appearance energy we mean the onset of a particular ion signal as a function of the UV excitation wavelength.

The origin of $\text{Na}(\text{HAc})_2^+$ ($m/z = 143$) is less obvious. As shown in Sec. IV C, the $m/z = 143$ fragment is characteristic of the Na-doped tetramer $\text{Na}(\text{HAc})_4$. It thus seems likely that the small $m/z = 143$ contribution in the UV-TOF spectrum arises from the small amount of $\text{Na}(\text{HAc})_4$ and hence is unrelated to $\text{Na}(\text{HAc})_3$. We have tried to confirm this hypothesis by systematically increasing the amount of tetramer

FIG. 4. UV-TOF spectra of Na-doped HAC clusters recorded under different molecular beam conditions as specified in Fig. 3: (a) same conditions as in Fig. 3(b) (up to the trimer); (b) same conditions as in Fig. 3(c) (up to the tetramer); (c) same conditions as in Fig. 3(d) (including large clusters). The masses of the various Na-doped HAC clusters are given in Table I.

in the molecular beam, while still avoiding the formation of larger clusters. The $m/z = 143$ signal intensity observed in the UV-TOF spectrum was indeed found to scale linearly with the tetramer concentration, as determined from the $m/z = 181$ signal in the XUV-TOF spectra. The uncertainty of this method is rather large, but we can still conclude that the dominant contribution to the $\text{Na}(\text{HAc})_2^+$ signal comes from $\text{Na}(\text{HAc})_4$ and not from $\text{Na}(\text{HAc})_3$.

How the $\text{Na}(\text{HAc})^+$ fragment forms from $\text{Na}(\text{HAc})_3$ and why $\text{Na}(\text{HAc})_2^+$ does not (or only in extremely small amounts) is further discussed in Sec. V B, where we also explain the absence of $\text{Na}(\text{HAc})_3^+$.

FIG. 5. Ion yield curve (scaled with UV light intensity) as a function of the UV excitation wavelength of (a) NaHAc^+ and (b) $\text{Na}(\text{HAc})_2^+$.

C. Tetramer

Figure 3(c) depicts the XUV-TOF spectrum under conditions when clusters up to the tetramer are present in the molecular beam. The $m/z = 181$ fragment signal (Table I) proves the increased abundance of $\text{Na}(\text{HAc})_4$ compared with Fig. 3(b), where almost no tetramer was formed. Figure 4(b) shows the UV-TOF spectrum recorded under these conditions. With the significantly increased amounts of $(\text{HAc})_4$ in the beam, the $\text{Na}-(\text{HAc})_2^+$ fragment at $m/z = 143$ now appears as a strong signal at photoionization wavelengths between 223 and 300 nm. It is clear that this fragment must have been formed from $\text{Na}(\text{HAc})_4$. For the appearance energy of $\text{Na}(\text{HAc})_2^+$ in the tetramer UV-TOF, determined in the same way as described above for the $\text{Na}(\text{HAc})^+$ fragment, we find a value of 4.13 ± 0.05 eV ($33\,333 \pm 450$ cm⁻¹) [see Fig. 5(b)]. Within experimental uncertainties this is the same value as found for $\text{Na}(\text{HAc})^+$ in the trimer UV-TOF. No ion signals are observed at higher m/z values in the tetramer UV-TOF of Fig. 4(b), specifically proving the absence of any parent ions $\text{Na}(\text{HAc})_3^+$ ($m/z = 203$) or $\text{Na}(\text{HAc})_4^+$ ($m/z = 263$) under tetramer conditions.

When optimizing the conditions for the tetramer, it is impossible to avoid the presence of trimer in the molecular beam. Therefore, the $\text{Na}(\text{HAc})^+$ fragment ($m/z = 83$) observed in Fig. 4(b) can in principle arise from $\text{Na}(\text{HAc})_4$ as well as from $\text{Na}(\text{HAc})_3$, which was clearly identified as the source of $\text{Na}(\text{HAc})^+$ in the trimer UV-TOF [Fig. 4(a), see Sec. IV B]. From the UV-TOF spectrum in Fig. 4(b) it is thus not possible to decide whether the $\text{Na}(\text{HAc})^+$ arises solely from $\text{Na}(\text{HAc})_3$ or whether $\text{Na}(\text{HAc})_4$ also contributes to the $m/z = 83$ signal. Again, we have tried to identify the clusters with which this fragment correlates by systematically changing the cluster composition of the molecular beam. Although the results confirm the Na-doped trimer as the major source of the $m/z = 83$ fragment, we cannot exclude a contribution from the Na-doped tetramer because of the large uncertainty of this method.

D. Larger clusters

Finally, we changed the expansion conditions to include oligomers larger than the tetramer. The corresponding XUV-TOF spectrum is shown in Fig. 3(d). Albeit in very low abundance, clusters up to $(\text{HAc})_8$ are present in the beam, as can be seen from the occurrence of their characteristic fragments [Eq. (1)]. The UV-TOF spectrum in Fig. 4(c) shows that the presence of larger clusters leads to an additional signal at $m/z = 263$ due to $\text{Na}(\text{HAc})_4^+$. For larger clusters it becomes increasingly difficult to draw a line between successive oligomers being present in the molecular beam. As a consequence, it is more difficult to trace the $\text{Na}(\text{HAc})_4^+$ fragment back to a particular acetic acid oligomer. From our experiments, the $m/z = 263$ signal seems to correlate with the presence of the pentamer. Apart from this fragment, no other Na-doped clusters were observed under these conditions, presumably a consequence of limited sensitivity combined with the low abundance of larger clusters. Note also that the

$m/z = 203$ [$\text{Na}(\text{HAc})_3^+$] fragment is still not observed, even in the presence of larger clusters (see Sec. V C for a brief discussion).

V. DISCUSSION

Four distinct processes determine which Na-doped species can be observed in the UV-TOF spectra. The first of these is the sodium pick-up itself, the probability of which is estimated here from the calculations of the capture cross section described in Sec. III B. The second is the lifetime of the $\text{Na}-(\text{HAc})_n$ collision complex and its fragmentation kinetics, which depends on the collision energy and on the angular momentum. SACM calculations described in Sec. III C provide, at least, an order of magnitude for the lifetimes of the different clusters studied here, together with the product distribution and energy disposal of the fragmentation process. The third and the fourth factors are the photoionization efficiency and the fragmentation pattern of the ionic Na-acetic acid clusters. The absence of a particular ionic fragment cluster in the UV-TOF spectrum thus does not necessarily prove the absence of the corresponding neutral species in the molecular beam, but might simply indicate a particularly small photoionization cross section.

A. Monomer and dimer

The calculated cross sections for Na pick-up by HAc and $(\text{HAc})_2$ are comparable to those of the trimer and tetramer (Table III), but no Na-containing fragments are observed in the UV-TOF spectra under conditions when $(\text{HAc})_3$ and higher oligomers are practically absent in the part of the beam sampled (Sec. IV A). Given that the trimer clearly does pick up Na atoms (Sec. IV B), the monomer and the dimer probably do so just as efficiently. In particular it is worth noting that the missing permanent dipole moment of $(\text{HAc})_2$ does not significantly affect the collision cross section, which is dominated by dispersion interactions.

If it is not the low Na uptake, it must be the lifetimes of the NaHAc and $\text{Na}(\text{HAc})_2$ collision complexes that explain why no ion peaks are observed in the UV-TOF spectra of HAc and $(\text{HAc})_2$. The results from SACM calculations in Table III clearly demonstrate that NaHAc^* and $\text{Na}(\text{HAc})_2^*$ dissociate by breaking the Na-cluster bond shortly after Na pick-up. (The asterisk emphasizes that the collision complexes are formed in an excited state.) Figure 6 shows the corresponding unimolecular decay rates as a function of energy for $J = 0, 100, \langle \ell_{\text{max}} \rangle$. The curves illustrate the increase of the threshold energy with J due to the centrifugal potential, but even at threshold the Na-HAc collision complex barely survives a few hundred nanoseconds. For the dimer complex threshold lifetimes of almost 1 ms seem to suggest that $\text{Na}(\text{HAc})_2$ could reach the ionization region intact, but very small excess energies of 50–100 cm⁻¹ suffice to reduce the lifetimes of both complexes by about 5 orders of magnitude. At the average collision energy of 1070 cm⁻¹ the Na-doped monomer loses its sodium atom

within 2 ps after its formation—far too quickly for any He-atom collisions to stabilize it. The situation for the dimer is similar. The loss of Na happens within 100 ps for this cluster. In principle, the collision complex could stabilize by evaporating a HAc monomer, which is the main stabilization mechanism for larger clusters (*vide infra*), but the unusually high dissociation energy of (HAc)₂ (4797 cm⁻¹ or about 57 kJ/mol) makes this channel inaccessible at the collision energy of 1243 cm⁻¹. It would require at least an additional 2027 cm⁻¹ to evaporate a monomer from the collision complex (Table II). As a consequence, both the Na-doped monomer and the Na-doped dimer already fragment in the oven and never reach the ionization region (the flight time from the oven to the ionization region amounts to about 80 μs). The effects are sufficiently large (many orders of magnitude) that our conclusions are not affected by the uncertainties of the calculated dissociation energies (see Sec. III A), which translate into uncertainties in calculated lifetimes of about an order of magnitude.

B. Trimer

The UV-TOF spectrum of the Na-doped trimer shows a strong signal only from Na(HAc)⁺ (*m/z* = 83), while the weak signal at *m/z* = 143 most likely originates from residual Na(HAc)₄ in the beam and not from Na(HAc)₃ (see Sec. IV B). The following scheme illustrates the most likely formation channel of the *m/z* = 83 fragment ion and explains why *m/z* = 143 is unlikely to be formed from Na(HAc)₃.

SCHEME 1.

In the case of the acetic acid trimer, sodium pick-up (Step 1) is obviously successful in line with the calculated pick-up probability of 64% (Table III). The resulting Na(HAc)₃^{*} collision complex has an internal energy of 8788 cm⁻¹ (binding energy + collision energy; Fig. 2 and Tables II–III). According to Fig. 2, three neutral dissociation channels Na(HAc)₃^{*} → Na(HAc)_{3-i} + (HAc)_i are open for the excited complex, corresponding to the evaporation of a monomer (*i* = 1) or a dimer (*i* = 2), or the dissociation back into a sodium atom and a trimer (*i* = 3). All three channels are close in energy, which is mainly a consequence of the formation of strongly bound acid dimer units (Fig. 2). Note that multiple evaporation, e.g., of two monomers, is energetically not possible. SACM calculations (Table III) predict the stabilization by evaporation ($\tau_1 = 140$ ns, $\tau_2 = 7.5$ μs) to be much faster than the loss of the sodium atom ($\tau_3 = 70$ μs). Therefore, NaHAc and Na(HAc)₂ are formed quickly (Step 2) and constitute the two major species that reach the ionization region. UV ionization of NaHAc forms Na(HAc)⁺, which

FIG. 6. Unimolecular decay rates as a function of energy for the Na collision complexes of the acetic acid monomer, NaHAc, and the dimer, Na(HAc)₂. $D_0 = V_{00}(\infty) - V_{00}(0) - E_{\text{ZP}}$ is the Na + (HAc)_n dissociation limit including zero-point corrections [see (7)].

is observed as a strong peak at $m/z = 83$. The photoionization cross section of this process is expected to be high because the relatively small difference between the vertical ($34\,971\text{ cm}^{-1}$) and the adiabatic ionization energy ($32\,536\text{ cm}^{-1}$) of 2435 cm^{-1} (ion reorganization energy, see Table II) indicates only minor geometry changes upon ionization and hence favorable Franck–Condon factors. Furthermore, the calculated ionization energies nicely bracket the observed appearance energy of the $m/z = 83$ fragment ($33\,333 \pm 450\text{ cm}^{-1}$, Sec. IV B), which confirms the mechanism of Scheme 1. According to the SACM calculations the NaHAc fragment is formed with an average vibrational excitation of $E_{\text{vib}} = 270\text{ cm}^{-1}$ yielding a lower bound to the appearance energy of $\Delta E_{\text{adiabatic}} - E_{\text{vib}} = 32\,266\text{ cm}^{-1}$ (see Table II). Figure 2 also illustrates why $\text{Na}(\text{HAc})_2^+$ ($m/z = 143$) is not likely to be observed when formed from $\text{Na}(\text{HAc})_3$, even though it is expected to be the major decay fragment arriving at the ionization region. The corresponding adiabatic and vertical ionization energies are almost 2 eV apart, a large reorganization energy resulting from major geometry changes, which in turn implies extremely unfavorable Franck–Condon factors and hence a small photoionization cross section, even high above the adiabatic ionization energy. Evaporation leaves the remaining $\text{Na}(\text{HAc})_2$ with only modest vibrational excitation of 1150 cm^{-1} , so that low Franck–Condon factors are the most plausible reason why $\text{Na}(\text{HAc})_2^+$ is not observed in the UV-TOF spectrum following sodium pickup by $(\text{HAc})_3$.

We stress again that the uncertainties of the calculated energetics discussed in Sec. III A do not affect the above conclusion, since the arguments are based on order of magnitude considerations and the calculated energetic ordering of different fragmentation channels is quite reliable. Let us assume for a moment that a significant fraction of $\text{Na}(\text{HAc})_3^*$ could reach the ionization region, even though this is not in agreement with the SACM results discussed above. In this case, the fragmentation would have happened after UV photoionization of $\text{Na}(\text{HAc})_3^*$. The energetics as well as the observed appearance energies for $\text{Na}(\text{HAc})^+$ and $\text{Na}(\text{HAc})_2^+$ would be consistent with this (Fig. 2). At photoionization energies above $33\,333\text{ cm}^{-1}$ (in between the adiabatic and vertical ionization energies of $\text{Na}(\text{HAc})_3$), the photoionization efficiency might be high enough to form $\text{Na}(\text{HAc})_3^+$, which would then immediately decay into $\text{NaHAc}^+ + (\text{HAc})_2$ and $\text{Na}(\text{HAc})_2^+ + \text{HAc}$. The fact, however, that $\text{Na}(\text{HAc})_2^+$ ($m/z = 143$) is not observed (or only in very small amounts) clearly speaks against this scenario, as do of course the SACM results. Whenever NaHAc^+ is observed in the UV-TOF spectrum, $\text{Na}(\text{HAc})_2^+$ should also be observed, if the fragments were to originate from ionic dissociation of $\text{Na}(\text{HAc})_3^+$ (Fig. 2). Furthermore, in this case the $\text{Na}(\text{HAc})_2^+$ yield should be even higher than that of NaHAc^+ because the latter lies significantly higher in energy (about 2500 cm^{-1}). Again, the experimental spectrum of Fig. 4(a) clearly contradicts such a scenario. While the UV-TOF of the trimer cannot be convincingly explained in this way, an analogous scenario provides the most likely explanation in the tetramer case.

C. Tetramer and larger clusters

For the tetramer and larger clusters, it is much more difficult to determine the major formation channels of the ions observed in the UV-TOF spectra. The interpretation of the experimental data is less clear in this case, since the spectra of larger clusters always contain contributions from smaller clusters. Furthermore, fragmentation patterns of larger systems are likely to be more complex due to the increased number of possible fragments. Here the combination of experimental results with the theoretical prediction of energetics and fragmentation kinetics proves instrumental in drawing a consistent picture of the processes underlying the observed UV-TOF spectrum.

The Na uptake probability of $\text{Na}(\text{HAc})_4$ in the Na oven is similar to that of the smaller clusters (Table III), and its fragmentation kinetics bear strong analogies to those of $\text{Na}(\text{HAc})_3$. The SACM calculations confirm the increasing dominance of monomer evaporation stabilizing the original collision complex $\text{Na}(\text{HAc})_4^*$ (Step 1 in Scheme 2).

SCHEME 2.

The loss of HAc monomer is many orders of magnitude faster than any of the other possible dissociation channels. According to the B3LYP calculations, the available energy ($D_0 + \langle E \rangle = 10\,700\text{ cm}^{-1}$) is just not enough to evaporate a trimer (Table II), so that the production of NaHAc is expected to be insignificant. While the evaporation of a dimer is possible, evaporation of a single monomer is much faster than any of the other decay channels, since it is strongly favored energetically. According to the SACM calculations, on an average 86% of the excess energy stays with the remaining $\text{Na}(\text{HAc})_3$ in the form of vibrational excitation $E_{\text{vib}} = 5022\text{ cm}^{-1}$, so that the evaporation of a second monomer would be energetically possible, but the corresponding lifetime is on the order of 10 ms. Of all the possible sodium containing fragments of the tetramer that could reach the ionization region (Step 2), $\text{Na}(\text{HAc})_3$ is by far the dominant one, and it will carry significant internal excitation. The energy disposal predicted by SACM (86% of total available energy as vibrational excitation) accords with previous observations for $\text{Na}(\text{H}_2\text{O})_n$ clusters.⁹ The ionization of $\text{Na}(\text{HAc})_3$ (Step 2a) and subsequent fragmentation in the ionic state (Step 3) is the only path that forms both the $m/z = 83$ and the $m/z = 143$ fragment observed in Fig. 3(c). In other words, this path must contribute to the UV spectrum if Step 1 is the dissociation in the neutral state as suggested in Scheme 2. This path is

consistent with the energetics in Fig. 2 and with the fact that no $m/z = 203$ $[\text{Na}(\text{HAc})_3]^+$ is visible in the UV spectrum. The observed appearance energy of $\text{Na}(\text{HAc})_2^+$ ($33\,333 \pm 450\text{ cm}^{-1}$) also fits perfectly into the scheme, which predicts a value of $32\,990\text{ cm}^{-1}$ ($\Delta E_{\text{adiabatic}} - E_{\text{vib}}$, see Table II). The appearance energy for the monomer fragment ion NaHAc^+ formed via Scheme 2 would lie 2500 cm^{-1} higher, a further independent hint that the $m/z = 83$ signal in the UV-TOF arises from $\text{Na}(\text{HAc})_3$ rather than from $\text{Na}(\text{HAc})_4$. The fact that the observed values for the $m/z = 83$ and $m/z = 143$ appearance energies are the same (within experimental uncertainties) must be considered a mere coincidence. We note again that direct photoionization of the Na-doped dimer (Step 2b) is unlikely to contribute to the $m/z = 143$ signal in the UV-TOF spectrum not only by kinetic arguments, but also because of the large ion reorganization energy (Fig. 2). Finally, photoionization of the Na-doped monomer (Step 2c), if formed, could in principle contribute to the $m/z = 83$, but obviously not to the $m/z = 143$ signal.

VI. CONCLUSION

The determination of ionization energies of sodium doped molecular clusters from UV photoionization spectroscopy is a standard approach to investigate size-dependent properties of these clusters. In the present study, we have combined this method with XUV photoionization and with modeling of cluster energetics and fragmentation kinetics to obtain information on the cluster composition in the molecular beam prior to ionization. The example of small sodium doped acetic acid clusters demonstrates how crucial such independent information is for the proper interpretation of the ultraviolet photoionization spectra (Fig. 4). Only the combination with XUV spectra (Fig. 3) and the prior knowledge of characteristic fragmentation patterns made an unambiguous assignment of the UV-TOF spectra possible.

No ion signals are observed in the UV-TOF spectra if only $\text{Na}(\text{HAc})$ and $\text{Na}(\text{HAc})_2$ are present in the molecular beam because of fast dissociation of the collision complexes into their original components. For the sodium doped dimer, this is a consequence of the strong $(\text{HAc})_2$ bond, which makes evaporation of an acetic acid monomer impossible. It is worth noting that the sodium capture itself is not the limiting step, since it is dominated by the dispersion interaction, which is quite similar for all the clusters studied here. The major UV ion signals of $\text{Na}(\text{HAc})_3$ and $\text{Na}(\text{HAc})_4$ are NaHAc^+ ($m/z = 83$) and $\text{Na}(\text{HAc})_2^+$ ($m/z = 143$), respectively. NaHAc^+ originates from dissociation of $\text{Na}(\text{HAc})_3$ in the neutral state and subsequent photoionization of NaHAc . In this case, the appearance energy of $m/z = 83$ roughly corresponds to the ionization energy of NaHAc . $\text{Na}(\text{HAc})_2^+$, by contrast, is formed from $\text{Na}(\text{HAc})_4$ in a sequential fragmentation in the neutral and in the ionic state. The measured appearance energy of $m/z = 143$ provides absolutely no measure for the ionization energy of $\text{Na}(\text{HAc})_2$. The fact that both appearance energies have the same value is purely coincidental.

Without the additional information from XUV experiments and from modeling, the interpretation of the UV spectra and of the observed appearance energies would

probably have been rather different from the scenario unraveled in the present study. Statements about fragmentation and the assignment of ionization energies based on standard UV photoionization experiments alone can be uncertain and make further conclusions tenuous, in particular for small clusters.

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