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Near thermal energy collisions with fullerenes: a generally applicable soft ionization method for low IP molecules?

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Abstract

Sodium clusters were derivatized via reaction with SF_6 or O_2 to generate supersonic molecular beams containing Na_xF_y/Na_xSF_y or Na_xO_2/Na_xO ($x \leq 10$), respectively. These mixed clusters were collided with a C_{60} effusive beam at center of mass kinetic energies in the near thermal regime. Under single collision conditions and in the absence of external light sources, strong cation and anion signals were observed—as detected by mass spectroscopy. Signals are due to resonant electron transfer and concomitant ion pair formation in analogy to previous observations for bare sodium cluster beams. Energetic considerations allow the determination of upper bounds to the appearance potentials of various mixed cluster cations. Comparison to photoionization mass spectra, indicates that such collisional ionization can be relatively soft and is associated with large cross sections even for ionically bound rather than "metallic" electron donors—suggesting that the method may be generally applicable for mass spectroscopy of low IP species. (Int J Mass Spectrom 185/186/187 (1999) 497–505) © 1999 Elsevier Science B.V.

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1. Introduction

We have previously shown [1,2] that bare sodium clusters (Na_x) can undergo resonant electron transfer when colliding with C_{60} under crossed beam conditions according to reaction (1) [3]. In the simplest picture, such transfer is energetically allowed at a harpooning separation $R_c = e^2/[\mathrm{IP}(x)\text{-}\mathrm{EA(A)}]$, for which the generally endoergic difference between cluster (=donor) ionization energy [IP(x)] and acceptor electron affinity [EA(A)] is compensated by the coulombic interaction between the resulting cation and anion. For relative velocities (v_{rel}) near 1000 ms^{-1}, the center of mass kinetic energy [CMKE(x, A)] of the collision pair is large enough to allow most $Na_x^+ \ldots A^-$ to subsequently surmount the coulombic potential well. Copious amounts of (parent) cations and anions are detected simply by colliding two neutral molecules.

$$\mathrm{Na_x + A + CMKE(x) \rightarrow Na_x^{+}* + A^{-}* + CMKE} \tag{1}$$

In a systematic study of ion pair formation in collisions between sodium clusters and a variety of moderate to high electron affinity electron acceptors (A = TCNQ (tetracyano-p-quinodimethane), C_{84}, C_{60}, Br_2 and SF_6), we have established that the threshold energetics for (ubiquitous) reaction (1) are

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Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

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influenced not only by IP(x), EA(A) and CMKE(x,A), but also by donor vibrational excitation. Unsurprisingly, hot donors have lower effective ionization energies and require lower CMKE(x,A) to achieve charge separation.

Among acceptors studied were some with electron affinities large enough such that the ground state harpooning radii $R_c(x,A)$ lie beyond 20 Å. For these, electron transfer under our experimental conditions is expected to be highly improbable. Nevertheless high charging yields were also observed. In contrast to acceptors with lower EA, such charging was also accompanied by significant fragmentation of nascent cations. We rationalized this in terms of multistate coupling/curve crossing transit, to first order equivalent to transfer of electrons from lower-lying donor valence levels (at smaller resonance separations), followed by hole relaxation. Consequently, depending on the difference IP(x)-EA(A) as well as the electronic level density in both donor and acceptor, ionization can be either soft or strongly inelastic.

The soft variant is analogous to that long known to occur in collisions of sufficiently fast alkali atoms with various polyatomic reagents [4]. As in the latter, Landau-Zener theory may be used to provide a first order estimate of the integral charging cross sections (Q) [5]. For $Na_{20} + C_{60} \rightarrow Na_{20}^{+} + C_{60}^{-}$ at around $v_{rel} = 1400\ ms^{-1}$, this assessment is consistent with a rough experimental determination of $Q = 2.4 \times 10^{-18}\ m^2$ (to within an order of magnitude) [2]. In fact, for CMKE(x, A) $\gg$ [IP(x)-EA(A)], the integral charging cross sections for reaction 1 were always found to be several orders of magnitude larger than the corresponding near-threshold Na_x photoionization cross sections—indicative of a potentially useful ionization method.

Compared to more conventional polyatomics in their size range, sodium clusters have uncharacteristically low ionization energies [6], large polarizabilities [7], high valence electron derived state densities [8] and extensive valence electron delocalization [9]. In an ongoing study of the phenomenology of ion pair formation in polyatomic neutral–neutral collisions, we are concerned here with the question of whether this peculiar combination of properties is required in at least one of the collision partners, in order for collisional charging to be observable under near-thermal conditions. For this purpose, we have derivatized the primary beam by reacting it with O_2 and SF_6, respectively, *before* colliding it with an electron acceptor. In so doing, we have converted a large fraction of bare metal clusters to mixed cluster species having significant ionic bonding contributions. We have then studied collisional ionization in near-thermal reactions between these species and C_{60} and report the results below.

2. Experimental

The experimental configuration has been described in detail in a previous publication [2]. We have since added a primary “pick-up” reaction region to generate cluster derivatives and briefly describe the present setup below.

Experiments were carried out in a two-stage molecular beam machine comprising a source and a detector chamber as indicated in Fig. 1. The primary supersonic sodium cluster or cluster-derivative beam was generated in the source chamber. This was collided with a secondary (effusive) C_{60} beam in the detector chamber.

Bare sodium clusters were produced by adiabatic expansion of pure sodium vapor from a high temperature cartridge oven. For all experiments reported here, the oven temperature was kept at 1050 K. Derivatives were generated by dosing either O_2 or SF_6 into the sodium cluster beam, 1 cm downstream from the expansion zone in a pick-up region. For this purpose a capillary was mounted at an angle of 45° relative to the primary beam axis with its 1 mm diameter opening offset from the center line by 0.5 cm. This setup facilitated pick-up derivatization without inducing dramatic primary beam turbulence [10,11].

The (effusive) C_{60} beam was generated in the detector chamber using a Knudsen cell mounted underneath the primary beam axis (1 mm diameter orifice, 14 mm underneath the center of the primary beam). Typical cell temperatures were 790 K corresponding to a vapor pressure of 4×10^{-3} Torr [12]. The amount of material evaporated in order to effi-

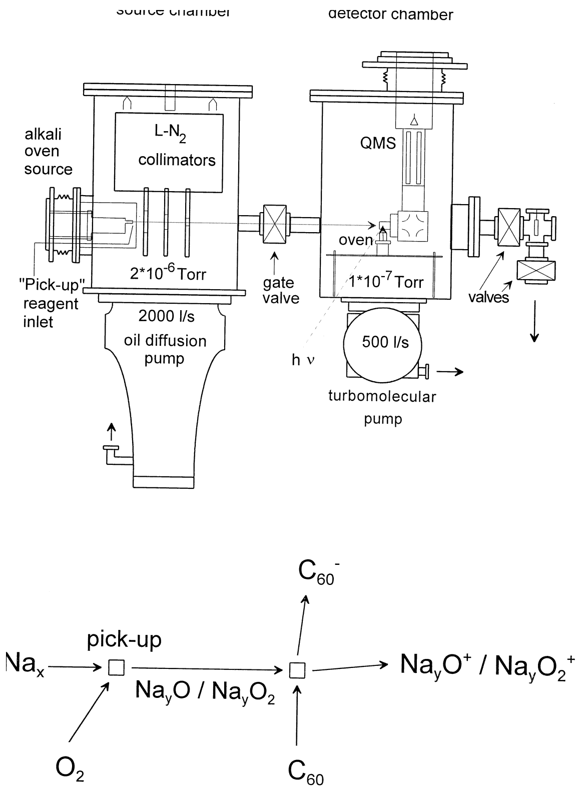

Fig. 1. Schematic of experimental configuration. Sodium clusters are formed by adiabatic expansion of pure sodium vapor. They are then reacted with either O_2 or SF_6 in a pick-up zone. Derivatized clusters travel downstream where they can be characterized by photoionization mass spectroscopy. For studies of collisional ionization, clusters and cluster derivatives instead encounter a C_{60} effusion in a crossed beam arrangement (in the absence of light).

ciently ionize the primary beam under our conditions was on the order of 0.75 mg h^{-1}.

For studies of collisional ionization, the derivatized primary beam was collimated to a diameter of 1 cm and crossed at right angles by an effusive C_{60} beam in turn collimated to a diameter of 0.5 cm. Interaction occurred in a field-free on-axis reaction zone located 52 cm downstream from the pick-up region. Single collision conditions were ensured by performing measurements at a variety of Knudsen cell temperatures.

Ions generated within about 10 μs of secondary collisions were collected, transported out of the primary beam with a quadrupole deflector and then injected into an orthogonally mounted quadrupole mass spectrometer. The corresponding ion collection and deflection optics was designed to optimize extraction of charged species moving on the primary beam axis [1,2]. Ions generated with significant off-axis kinetic energy components were therefore discriminated against. Everything else being equal, cation sensitivity was about an order of magnitude larger than for anions due to the conversion dynode detector used. In order to optimize signal-to-noise ratios, mass spectra were typically acquired at a resolution ($m/\Delta m$) of ~100.

Under our conditions, pick-up reaction of Na_x with either O_2 or SF_6 leads not only to the formation of neutral but also charged products [1,2]. Measurements and ion trajectory calculations show that any charged products carried on primary-beam axis towards the secondary reaction zone are fully deflected prior to reaching it and therefore do not contribute to the collisional ionization signals reported below.

Beam velocity distributions were not accurately determined in this study. However, on the basis of the deflection potentials required for optimum ion detection as well as from velocity measurements previously carried out for bare cluster beams analogously generated [13,14] the primary beam velocity was estimated to be 1400 ± 200 ms^{-1} [full width at half maximum (FWHM)] with negligible mass dependent velocity slip. The C_{60} effusive beam velocity average was calculated to be 153 ms^{-1} at $T = 790$ K. For right angle collisions, this corresponded to center of mass kinetic energies (calculated as: $\{[m(Na_x)*m(C_{60})]/[m(Na_x) + m(C_{60})]\}*[w(Na_x)^2 + w(C_{60})^2]/2$, where w_i are the velocities of primary and secondary beams, respectively), from 0.2–5.6 eV for primary beam component mass from 23–2300 [u].

Photoionization measurements were performed with the Knudsen cell off by irradiating the primary beam with an IR-filtered, focused 1 kW Xe/Hg arc lamp which generates photons with up to about 5.5 eV [11]. Chemicals were from commercial sources.

3. Results

The mass spectra presented below are to be regarded as typical but qualitative. Various experimen-

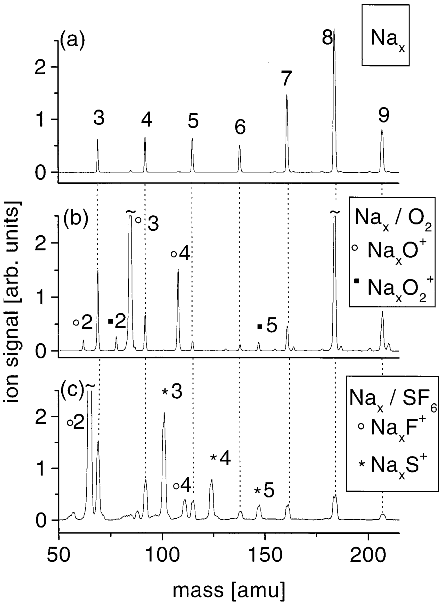

Fig. 2. Partial photoionization mass spectra recorded for a pure sodium cluster beam (a), and sodium cluster beams which have been pick-up derivatized with O_2 (b) and SF_6 (c), respectively (see text for details).

tal limitations, notably variations in sodium oven nozzle geometry and therefore beam alignment prevent quantitative comparison of data from one experiment to the next [2].

3.1. Photoionization

Fig. 2(a) shows a partial photoionization mass spectrum of a typical underivatized Na_x primary beam [15,16]. Such beams (containing clusters up to $x >$ 90 as indicated in Fig. 3) were reacted with either SF_6 or O_2. Fig. 2(b) shows a partial photoionization mass spectrum of neutral products (and remaining reagents) obtained upon O_2 pick-up derivatization. The formation of Na_xO and Na_xO_2 can be inferred from the observation of Na_yO^+ and $Na_yO_2^+$—consistent with previous work [17]. Relative intensities of these neutral products are however unknown in the absence of photoionization cross section determinations and detailed studies of photoionization induced fragmentation. Near-threshold photoionization efficiency curves determined for Na_3O [10,11,18], Na_4O [10,11] and Na_5O_2 [10,11] indicate that these species are generated/probed with significant internal excitation.

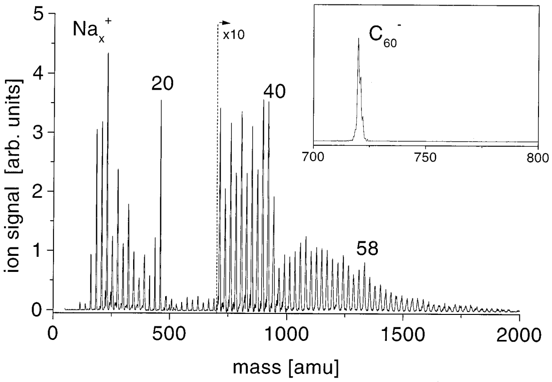

Fig. 3. Full positive ion and partial negative ion mass spectra obtained upon crossing a pure sodium cluster beam with an C_{60} effusion under single collision conditions *in the dark*. Note the occurrence of a threshold size range for detection of Na_x^+.

Fig. 2(c) shows an analogous partial photoionization mass spectrum obtained for SF_6 pickup. Observation of $Na_xF_y^+$ *and* $Na_xSF_y^+$ indicates the presence of corresponding neutrals. The same boundary conditions apply to this statement as for the O_2 reaction system. Note that for both O_2 and SF_6 we have chosen pick-up reagent fluxes, such that surviving $Na_x^{(+)}$ intensities are small—indicative of extensive derivatization.

3.2. Collisional ionization

Fig. 3 shows a full cation and partial anion (insert) mass spectrum obtained upon colliding an underivatized Na_x beam with C_{60} *in the dark*. We observe exclusively Na_x^+ and C_{60}^-. Na_x^+ relative intensities and threshold size for cation formation (near $x = 5$), have been extensively discussed previously [2]. The measurements document efficient electron transfer/ion pair formation according to reaction (1). In particular, the observation of mass spectral structure attributable to neutral jellium shell closings, indicates that the internal excitation associated with ionization [* in reaction (1)] is not large enough to induce significant fragmentation on the experimental time scale.

Figs. 4 and 5 show partial mass spectra of cations

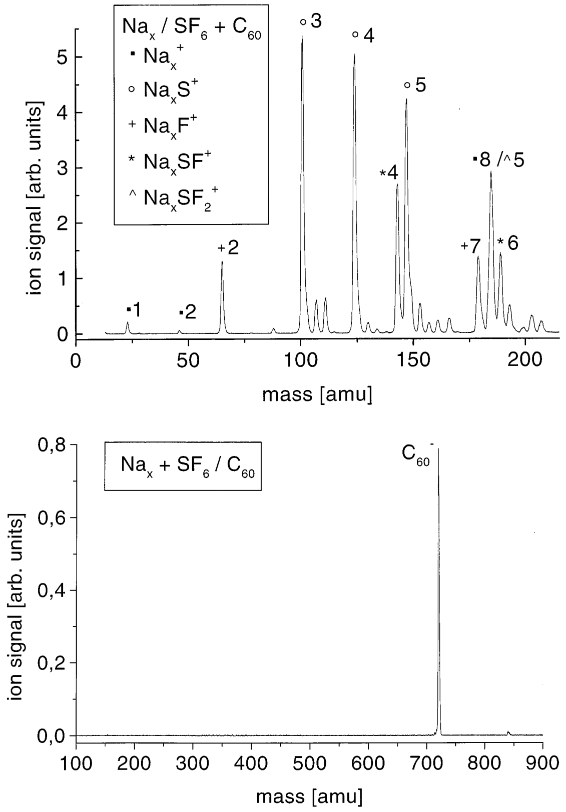

Fig. 4. Partial cation and anion mass spectra resulting upon colliding an Na_xSF_6-pickup primary beam with a C_{60} effusion.

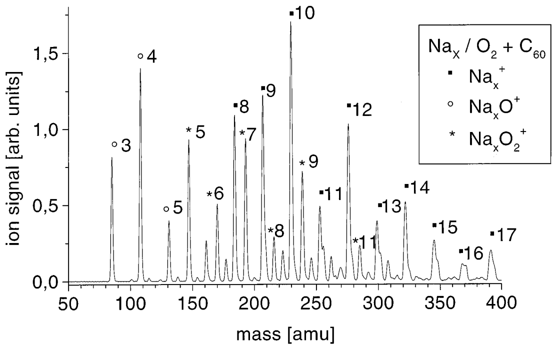

Fig. 5. Partial cation mass spectrum obtained upon colliding an Na_x/O_2-pickup primary beam with an C_{60} effusion.

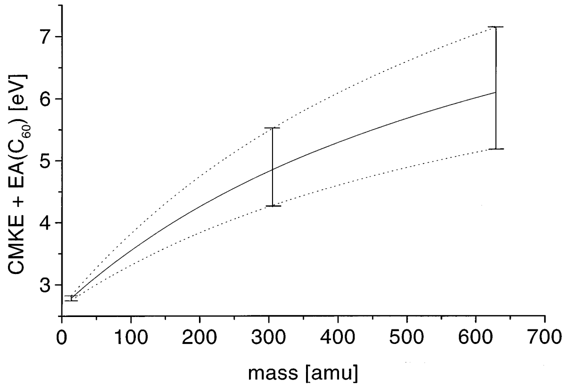

Fig. 6. Onset energies (center of mass kinetic energies [CMKE(m,A)] plus electron affinity EA(C_{60})) versus donor mass (m) for the present experimental conditions. CMKE(m,A) values for crossed beam collision with C_{60} are calculated under the assumption that the primary beam velocity distribution is not affected by pick-up derivatization (see text for details). Error bars correspond to CMKE(m,A) width as determined essentially by primary beam velocity distribution.

generated in analogous collisions of pick-up derivatized primary beams with C_{60}. Strong signals were observed for both Na_x/O_2 and $Na_x/SF_6 + C_{60}$. For Na_x/SF_6-pickup beams, we also studied anions [Fig. 4(b)]. The only species detected was C_{60}^-, suggesting that as in the case of Na_x/C_{60}, an electron transfer/ion pair separation sequence is occurring. We therefore tentatively extend reaction (1), where A now also corresponds to those Na_xO,Na_xO_2,Na_xF_y and Na_xSF_y observed as cations (see sec. 4.1.).

Interestingly, the C_{60}^- yield observed in colliding bare Na_x with C_{60} rises by more than an order of magnitude upon admitting SF_6 to the pick-up reaction zone—under otherwise identical conditions. We shall return to this point below.

4. Discussion

4.1. Appearance potentials (AP)

For a given EA, charged products resulting from electron transfer are energetically possible if the (effective) donor IP is less than CMKE + EA. Fig. 6 plots this threshold energy versus mass for our experimental conditions (assuming mass independent relative velocity). Together with Figs. 4 and 5, the latter can be used to provide rough upper limits to the appearance potentials (=effective ionization energies)

Table 1
Upper limits to cation appearance potentials vs. literature [a]

A	AP(A^+)	IP_{exp}	Ref.	IP^{b}_{calc}	Ref.
Na_3O	<3.4	3.80 (3) [c]	[11,18]	3.86	[19]
		3.90 (15)	[25]	3.58	[26]
				3.3	[18]
				3.48	[27]
				3.13	[28]
Na_4O	<3.6	3.80 (5)	[11]	4.16	[19]
		3.95 (15)	[25]	3.60	[28]
Na_5O	<3.8	—	—	3.84	[19]
Na_5O_2	<3.9	3.29 (5)	[11]	3.43	[19]
Na_2F	<3.3	3.5 (2)	[20]	3.72	[29]
		4.0 (1)	[21]		
Na_3S	<3.6			3.31	[27]
Na_4S	<3.8				
Na_4SF	<3.9				
Na_5S	<3.9				

[a] All values in eV.
[b] Adiabatic ionization energies.
[c] Brackets correspond to exp. errors (e.g. 3.80 (3) = 3.80 ± 0.03 eV).

of specific mixed cluster cations. For a given A^+ to be observable, its appearance potential must lie *below* the threshold energy shown for that mass in Fig. 6. Of course, such numbers, while formally correct, become increasingly meaningless the larger CMKE and therefore the larger the AP limit. Nevertheless, several species are here experimentally observed for the first time such that even rough AP upper limits are of potential interest.

Determination of upper AP limits as described above is subject to the assumption that collisional ionization induced fragmentation is insignificant. There are three possible such fragmentation mechanisms: (i) head-on collisions leading to conversion of CMKE-(IP-EA) into internal excitation followed by "scattering" and dissociation of hot cations, (ii) chemiionization (bond rearrangement followed by charged fragment emission—see [1]) and (iii) inner-valence electron transfer followed by hole relaxation/fragmentation [2]. On the basis of our previous observations for $Na_x + C_{60}/C_{84}$/TCNQ it appears that mechanism (iii) is only relevant for systems with large ground state R_c (i.e. IP's close to EA(C_{60}) = 2.65 eV). Even then, the proposed electron transfer at smaller R_c may take place only if donor level structure allows for this *and* CMKE suffices for subsequent charge separation. Both conditions are not likely to be met for small mixed cluster species (in particular for those with large ionic bonding contributions). For small = light species, CMKE is similarly not large enough for (i) to be relevant. The anion mass spectrum observed for $Na_x/SF_6 + C_{60}$ shows no indication of mixed products such as NaC_{60}^-, which would be expected for processes along the lines of (ii). Similarly, we have no direct indication of exoelectron emission in the present reaction systems [1]. *Therefore we infer fragmentation to be insignificant for light A and concentrate on this size range below.*

Table 1 lists upper limits to appearance potentials for selected A^+ resulting from an analysis of Figs. 4–6. Values are shown only for the most abundant <8-at. species observed. Note that in all cases, primary beam velocity distribution leads to CMKE broadening which increases with donor mass. Typical CMKE widths at various masses are shown in Fig. 6. Table 1 also compares AP's to literature IP's from experiment and theory—where available. A number of entries deserve specific comment.

4.1.1. $Na_x/O_2 + C_{60}$

Four strong cation signals are observed in the relevant size range: Na_xO^+ ($x = 3 - 5$) and $Na_5O_2^+$.

The ionization energy of Na_5O has not yet been experimentally determined. Our limit is consistent with a recent density functional calculation [19]. Upper limits to the appearance potentials of Na_4O^+ and $Na_5O_2^+$ agree with the experimentally determined ionization energies [11]. The AP limit obtained for Na_3O^+ is about 0.4 eV *smaller* than the adiabatic ionization energy derived from photoionization efficiency measurements under analogous beam conditions [18]. However, the latter measurement comprises a signal onset at about 3.2 eV indicative of a population with significant internally excited fraction.

Such extensive thermal "tailing" is plausible given the large exoergicities associated with sodium cluster oxidation [19]. The binding energies released would lead to extensive fragmentation of hot nascent pick-up products. In particular, for small $Na_xO^*/Na_xO_2^*$ excited to above their respective dissociation energies, one would expect such fragmentation to occur on a time scale faster than pick-up → secondary reaction zone transit. The lowest dissociation energy of $Na_3O \rightarrow Na_2O + Na$ (=1.70 eV), then provides an upper limit to the internal excitation remaining in Na_3O^* prior to electron transfer [18,19]. As in the case of bare Na_x, it appears that a significant fraction of this (vibrational) excitation can couple into the electron transfer energetics.

Note that on the basis of photoionization efficiency measurements and of a rough estimate of absolute near-threshold photoionization cross sections [11,18], the overall beam abundance of Na_3O is significantly larger than that of either Na_4O, Na_5O or Na_5O_2. Interestingly, this is not reflected by the collisional ionization yield (Na_3O^+, Na_4O^+, Na_5O^+ and $Na_5O_2^+$ signals are comparable within a factor of 3–4). Consistent with the AP inference above, it appears that only the "hottest" members of the Na_3O ensemble are collisionally ionizable.

4.1.2. $Na_x/SF_6 + C_{60}$

Thermal excitation of donors is likely also significant for this reaction system. In particular the Na_2F^+ appearance potential at 3.27 eV is about 0.2 eV *lower* than the most recent (photo)ionization energy determination (3.5 ± 0.15 eV [20]). Note that the latter measurement was carried out on Na_2F^* generated by pulsed coexpansion of Na vapor and SF_6. This IP value is in turn significantly lower than an older IP bracket (4.0 ± 0.1 eV) determined for Na_2F generated by coexpansion of Na and NaF vapors from a thermal oven source [21]. Kappes et al. [21] also accessed the (lowest) Na_2F dissociation energy [$D(\text{NaF-Na}) = 1.5 \pm 0.25$ eV], which provides an upper limit to the amount of vibrational excitation which could conceivably be stored in Na_2F^* prior to electron transfer.

The large Na_2F^* signals observed in photoionization compared to the comparatively modest Na_2F^+ signals obtained upon C_{60} collisional ionization (together with the energetic argument above), again suggest that only a small "hot" fraction of the Na_2F population is collisionally ionizable.

4.2. Applicability

While not quantified in this study, the robust cation/anion signals observed, indicate that the underlying integral charging cross sections are roughly comparable to those observed for analogous Na_x/C_{60} reactions. The enhancement in C_{60}^- yield observed upon collision with Na_x/SF_6 pick-up beams, relative to bare Na_x, can be understood in terms of a reduction in "average" IP of the donor beam constituents upon SF_6 derivatization. Consequently, there appears to be no fundamental difference in the phenomenology observed for donors having delocalized "metallic" valence electrons (such as Na_8) and those with more localized "F-center" like HOMOs (such as Na_2F—at least for the internal excitation levels and cluster size range experimentally realized in this study [22]).

Is such a simple, low cost ionization method generally applicable for mass spectroscopic characterization of low IP polyatomics under near-thermal or even thermal energy collision conditions? For our setup, the procedure is of analytical use if its ion yield and IP range is comparable to that of broad band photoionization. Furthermore, the sum of cross sections for all other competing charged particle formation channels (e.g. chemiionization) must ideally be significantly smaller than that of soft collisional ionization.

From these points of view, C_{60} is a near perfect electron acceptor. As our experiments with Na_x show, the large EA(C_{60}) $= 2.65$ eV is associated with favorable electron transfer probabilities for donors having IP < 4.5 eV [2]. This can be rationalized in terms of Landau-Zener theory, which for around $v_{rel} = 1400\ ms^{-1}$ predicts an optimum donor IP range of about 1 eV width centered at approximately 4.0 eV [2]—for ground state transfer to C_{60}. For most *A* within this IP range, the high molecular weight of C_{60} ensures sufficient CMKE for subsequent charge separation ("fly-by" transfer) under our conditions. For (rarer) "head-on" impact parameters, the high chemical stability of the carbon cage precludes measurable bond breaking and chemiionization on the experimental time scale. Finally, the low cohesive energy and high thermal stability of $C_{60}(s)$ allows the preparation of intense enough effusive beams for collisional charging signals to be competitive with broad band photoionization yields.

On the basis of our previous work [2], we would expect (electronically) inelastic electron transfer to C_{60} and associated fragmentation to become possible for large *A* having IP < 3.5 eV. For these, softer collisional ionization could be achieved by going to lower EA acceptors. At the other extreme (and likely to be more commonly encountered), efficient electron transfer from donors with IP > 4.5 eV requires higher EA acceptors. Note that in general, fullerene EA's increase with increasing cage size [EA(C_{84}) $= 3.14$ eV and EA(C_{104}) $= 3.42$ eV [23]] such that the IP range may be correspondingly extended if sufficiently intense effusive beams can be made. Feasibility has already been demonstrated for C_{84} [2]. Sublimable fullerene derivatives such as endohedrally metal doped Gd@C_{82} (EA $= 3.3$ eV) are more readily accessible than C_{104} and provide another possible approach to larger EAs [24].

5. Conclusion

Near-thermal energy collision with (neutral) fullerenes provides a low cost, efficient, comparatively soft and generally applicable method of ionizing neutral polyatomics having ionization energy below about 5 eV. This includes many bare and chemically derivatized metal clusters.

Many elemental clusters [e.g. small C_x, M_x (where M = transition metal)] have EA(x) > 4.0 eV. At the same time IP(x) can be quite moderate. Consequently, collisional charging is expected to be a common feature of cluster–cluster collisions. Among the specific implications of this is the feasibility of reaction (2) for a wide range of M_x.

$$M_x + M_x + CMKE \rightarrow M_x^+ + M_x^- + CMKE' \qquad (2)$$

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[22] Clearly, harpooning electron transfer probability must depend not only on IP-EA but also on the relative orientation (and state symmetries/degeneracies) of donor and acceptor. Larger ionic clusters having low ionization energies and at the same time "surface-localized" HOMOs (e.g. $Na_{18}F_{17}$) would be interesting cases in point for further study. One might expect relative orientation to have an extreme influence on transfer probability compared to compact metallic clusters with the same IP.

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