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Jarvis, Gary; Seccombe, Dominic; Tuckett, Richard

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The effects of isotopomers in the state-selected photofragmentation of BCl_3^+ , PCl_3^+ and PBr_3^+

Gary K. Jarvis^a, Dominic P. Seccombe^b, Richard P. Tuckett^{b,*}

^a School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

^b School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

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Abstract

Analysis of the shapes of time-of-flight (TOF) peaks of singly-charged polyatomic cations produced in photoelectron-photoion coincidence spectra allows a determination of the total mean kinetic energy released into translational motion of the fragment species, $\langle \text{KE} \rangle_t$. In turn, this value can indicate the mechanism of unimolecular photofragmentation. We show that in cases where the daughter ion has more than one isotopomer, allowance must be made for them in analysing the TOF distributions. Otherwise, values for $\langle \text{KE} \rangle_t$ are obtained which are too large. Examples are given from recent work by us on state-selected $(\text{BCl}_3^+)^* \rightarrow \text{BCl}_2^+ + \text{Cl}$ and $(\text{PX}_3^+)^* \rightarrow \text{PX}_2^+ + \text{X}$ ($\text{X} = \text{Cl}, \text{Br}$). © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Since their discovery over twenty years ago, coincidence experiments have offered powerful techniques to determine the decay dynamics of excited electronic states of positively-charged molecular ions in the gas phase. In particular, the use of tunable vacuum-UV radiation from a synchrotron allows the threshold photoelectron-photoion coincidence (TPEPICO) technique to be applied to the study of the dissociation of electronic states of polyatomic ions. Here, threshold electrons (i.e., those with zero and near-zero kinetic energy) are detected in time-delayed coincidence with parent or fragment ions which have been separated by their different times-

of-flight (TOF) through a linear mass spectrometer. Fragment ions are often formed with substantial amounts of translational kinetic energy. For unimolecular reactions involving the simple cleavage of one bond (e.g., $(\text{BCl}_3^+)^* \rightarrow \text{BCl}_2^+ + \text{Cl}$), the total mean translational kinetic energy, $\langle \text{KE} \rangle_t$, released into these channels can indicate the mechanism of the dissociation. In particular, the fraction of the available energy channelled into translational motion of the two fragments, $\langle f \rangle_t = \langle \text{KE} \rangle_t / E_{\text{avail}}$, can suggest whether the excited state of the parent ion dissociates by a statistical [1] or an impulsive [2,3] mechanism.

Three years ago at the UK synchrotron source at Daresbury, we recorded high-resolution TOF distributions of BCl_2^+ formed from photofragmentation of the $\tilde{\text{C}}^2\text{A}'_2$, $\tilde{\text{D}}^2\text{E}'$ and $\tilde{\text{E}}^2\text{A}'_1$ excited states of BCl_3^+ [4]. More recently, we recorded similar spectra for PCl_2^+ and PBr_2^+ produced from state-selected

* Corresponding author. Tel.: +44-121-414-4425; Fax: +44-121-414-4426; E-mail: r.p.tuckett@bham.ac.uk

(PCl_3^+)^{*} and (PBr_3^+)^{*} [5]. The time resolution of the experiment was not sufficient to resolve ions differing in mass by less than 2 u. The purpose of this Letter is to state a fairly obvious fact. That is, in these three situations where the fragment ions do not have a unique mass-to-charge ratio due to the different isotopes of naturally-occurring B, Cl and Br (¹⁰B 20%, ¹¹B 80%; ³⁵Cl 75%, ³⁷Cl 25%; ⁷⁹Br 50%, ⁸¹Br 50%), the wrong answer is obtained for $\langle \text{KE} \rangle_t$ unless allowance is made in the fitting procedure for isotopic broadening. In turn, this may lead to the wrong conclusions being drawn about the unimolecular reaction mechanism. Isotopic effects were allowed for in the analysis of the PCl_2^+ and PBr_2^+ peaks [5], but were ignored in the earlier project on BCl_2^+ [4] because the fitting procedure used then could not accommodate many different isotopic combinations. In this Letter, we describe our new fitting procedure for fragment ions in more detail, and we correct the earlier BCl_2^+ data.

2. Fitting procedure for TOF distributions of fragment ions

Analysis of the shapes of the TOF peaks allows a determination of the kinetic energy release distribution (KERD), and hence $\langle \text{KE} \rangle_t$. Our new method of analysis follows closely that of Powis et al. [6]. A basis set of TOF peaks, each with a discrete energy release ε_i , is computed and assigned a probability. The discrete energies are obtained by $\varepsilon_i(n) = [(2n - 1)^2 \Delta E]$ where $n = 1, 2, 3, 4, \dots$. ΔE depends primarily on the statistical quality of the data; in theory, the higher the signal-to-noise ratio of the spectrum, the lower ΔE and the higher n can be set to obtain the best fit. Each computed peak in the KERD is assumed to span the range $4(n - 1)^2 \Delta E$ to $4n^2 \Delta E$, with a band centre at $\varepsilon_i(n) + \Delta E$. The reduced probability of each discrete energy, $P(\varepsilon_i)$, is varied by linear regression to minimise the least-squared errors between the simulated and the experimental TOF peaks. ($P(\varepsilon_i)$ has units of $(\text{energy})^{-1}$, and is defined as the probability of that energy release divided by the span of energies; the probabilities obviously sum to unity). Unlike that of Powis et al., our programme can allow for the full range of isotopes of the daughter ion to be accommodated.

Thus for BCl_2^+ , six daughter ions (with masses 10,35,35 11.25%; 10,35,37 7.5%; 10,37,37 1.25%; 11,35,35 45%; 11,35,37 30%; 11,37,37 5%), all with different masses and hence peak centres, are accommodated in the fitting procedure. Only three isotopic combinations are needed for PCl_2^+ and PBr_2^+ . The net effect of allowing for the different isotopes of the daughter ion, not surprisingly, is to reduce the values of $\langle \text{KE} \rangle_t$ from those determined by the programme of Powis et al. Furthermore, the smaller the KE release, the bigger is the percentage reduction in $\langle \text{KE} \rangle_t$.

The procedure assumes that only two products form in the dissociation, corresponding to the breaking of one bond. Strictly, the programme fits the peak shape of the daughter ion, with its isotopic variants, to obtain the kinetic energy released into this ion. The relevant parameter for comparison with statistical and impulsive dynamical models, however, is the mean *total* KE release, given by

$$\langle \text{KE} \rangle_t = \frac{M_{\text{parent ion}}}{M_{\text{neutral fragment}}} \langle \text{KE} \rangle_{\text{daughter ion}} \quad (1)$$

In all fits, the parent ion is assumed to have a single mass, i.e., 117.3 u for BCl_3^+ , 137.5 u for PCl_3^+ and 271 u for PBr_3^+ . The fine detail of the KERD is usually not interpreted, one reason being the relatively high translational temperature, 298 K, of molecules along the axis of the TPEPICO apparatus [7]. Furthermore, the shape of the KERD may show some variation with the fitting parameters ΔE and n . In practice, however, we find that the values of $\langle \text{KE} \rangle_t$ are robust, being relatively insensitive to the form of the KERD.

3. Interpretation of $\langle \text{KE} \rangle_t$ by statistical and impulsive dynamical mechanisms

Statistical dissociations are characterised by a precursor, in this case an excited electronic state of a polyatomic ion, which is long-lived enough that energy randomisation occurs prior to dissociation. Internal conversion occurs to the ground electronic state of the parent ion, and dissociation takes place from that potential energy surface. A relatively small amount of the available energy is partitioned into

translational motion of the two products, the fraction decreasing as the size of the parent ion increases. Assuming that there is no barrier in the exit channel, Klots [1] has demonstrated that E_{avail} and $\langle \text{KE} \rangle_t$ are related by

$$E_{\text{avail}} = \frac{(r-1)}{2} \langle \text{KE} \rangle_t + \langle \text{KE} \rangle_t + \sum_i \frac{h\nu_i}{\exp\left(\frac{h\nu_i}{\langle \text{KE} \rangle_t}\right) - 1}, \quad (2)$$

where E_{avail} is the photon energy minus the 0 K thermochemical threshold energy of the dissociation. r is the number of rotational degrees of freedom and ν_i are the vibrational frequencies of the daughter ion. This equation only gives accurate predictions for statistical processes if the transition state is loose, e.g., a single bond cleavage.

An impulsive dissociation is characterised by a short-lived precursor which dissociates on a timescale comparable to or faster than that of internal molecular motion, IVR, or electronic relaxation. Two models have been proposed which enable the fraction of the available energy channelled into translational

motion of the products, $\langle f \rangle_t$, to be determined. Again, both only apply to a simple two-body dissociation involving the cleavage of a single bond. Momentum and energy are initially localised on the atoms of the breaking bond, with dissociation proceeding along a pseudo-diatomic exit channel of the excited state potential energy surface. First, in the ‘pure’ impulsive model, as the bond breaks the repulsion of the atoms is assumed to be so great that dissociation results in intramolecular collisions between the atoms and the remainder of their recoiling fragments. As a consequence, there is a transfer of energy to vibrational and rotational modes of the fragments. Holdy et al. [2] have shown that $\langle \text{KE} \rangle_t$ and E_{avail} are then related by the simple kinematic equation

$$\langle f \rangle_t = \frac{\langle \text{KE} \rangle_t}{E_{\text{avail}}} = \frac{\mu_b}{\mu_f} \quad (3)$$

where μ_b is the reduced mass of the two atoms whose bond is broken and μ_f is the reduced mass of the two products of the dissociation. Second, in the ‘modified’ impulsive model, the repulsion of the two atoms is not sufficient to cause energy transfer to the vibrational modes of the daughter fragments. They

Table 1

Mean total translational kinetic energy releases, $\langle \text{KE} \rangle_t$, from photofragmentation of excited valence states of BCl_3^+ , PCl_3^+ and PBr_3^+

Daughter ion	Parent ion and electronic state	$h\nu/\text{eV}$	$E_{\text{avail}}/\text{eV}$	$\langle \text{KE} \rangle_t/\text{eV}$ (no isotopes)	$\langle \text{KE} \rangle_t/\text{eV}$ (with isotopes)	$\langle f \rangle_t^a$ (no iso.)	$\langle f \rangle_t^a$ (with iso.)	$\langle f \rangle_t$ (statistical)	$\langle f \rangle_t$ (pure impulsive)	$\langle f \rangle_t$ (modified impulsive)
BCl_2^+	$\text{BCl}_3^+ \tilde{\text{C}}^2\text{A}_2'$	14.40	2.10	0.57 (8)	0.37 (2)	0.27	0.18	0.20 ^b	0.33	1.00
	$\text{BCl}_3^+ \tilde{\text{D}}^2\text{E}'$	15.51	3.21	0.72 (10)	0.45 (4)	0.22	0.14	0.19 ^b	0.33	1.00
	$\text{BCl}_3^+ \tilde{\text{E}}^2\text{A}_1$	17.70	5.40	0.86 (10)	0.56 (5)	0.16	0.10	0.19 ^b	0.33	1.00
PCl_2^+	$\text{PCl}_3^+ \tilde{\text{B}}^2\text{E}$	12.08	0.48	0.34 (3)	0.17 (2)	0.71	0.35	0.23 ^c	0.63	0.66
	$\text{PCl}_3^+ \tilde{\text{C}}^2\text{E}$	13.05	1.45	0.48 (4)	0.25 (4)	0.33	0.17	0.21 ^c	0.63	0.66
	$\text{PCl}_3^+ \tilde{\text{D}}^2\text{A}_1$	14.25	2.65	0.79 (9)	0.57 (4)	0.30	0.22	0.21 ^c	0.63	0.66
	$\text{PCl}_3^+ \tilde{\text{E}}^2\text{E}$	15.12	3.52	0.86 (13)	0.74 (10)	0.24	0.21	0.20 ^c	0.63	0.66
PBr_2^+	$\text{PBr}_3^+ \tilde{\text{B}}^2\text{E}$	11.15	0.35	0.15 (4)	0.07 (1)	0.43	0.20	0.23 ^d	0.40	0.43
	$\text{PBr}_3^+ \tilde{\text{C}}^2\text{E}$	11.81	1.01	0.26 (5)	0.17 (2)	0.26	0.17	0.21 ^d	0.40	0.43
	$\text{PBr}_3^+ \tilde{\text{E}}^2\text{E}$	14.14	3.34	0.42 (4)	0.26 (2)	0.13	0.08	0.20 ^d	0.40	0.43

^aDefined as $\langle \text{KE} \rangle_t/E_{\text{avail}}$.

^bAssuming vibrational frequencies for BCl_2^+ of 658, 396, 396 and 1535 cm^{-1} (values for ground state of CS_2 [13]).

^cAssuming vibrational frequencies for PCl_2^+ of 522, 201 and 502 cm^{-1} (values for ground state of SiCl_2 [14]).

^dAssuming vibrational frequencies for PBr_2^+ of 403, 160 (estimated) and 400 cm^{-1} (values for ground state of SiBr_2 [14]).

recoil as rigid bodies, and no energy is partitioned into vibrational modes of the fragments. Energy transfer may still take place to the rotational degrees of freedom of the fragments if the geometry of the dissociation can induce a torque. Busch and Wilson [3] have shown that in this case the rotational energy transferred to each fragment, E_r , is given by

$$E_r = E_{\text{total}} \left[\frac{\sin^2 \theta}{\left(1 - \frac{\mu_b}{\mu_f}\right)^{-1} - \cos^2 \theta} \right], \quad (4)$$

where E_{total} is the total energy transferred to the fragment, and θ is the angle between the breaking bond and the line which links the centre of mass of the fragment to the atom in the fragment closest to the breaking bond. Note that $E_r = 0$ for $\theta = 0$, which is the situation when a B–Cl bond breaks from the planar BCl_3^+ parent ion. For pyramidal PCl_3^+ and PBr_3^+ we estimate that $\theta \approx 109^\circ$ when a P–Cl or P–Br bond dissociates. Thus $\langle f \rangle_t$ can be calculated for halogen atom loss from BCl_3^+ , PCl_3^+ and PBr_3^+ by the modified impulsive mechanism.

The $\langle f \rangle_t$ values calculated for statistical, pure impulsive and modified impulsive mechanisms in BCl_3^+ , PCl_3^+ and PBr_3^+ are given in Table 1. In both impulsive models, we should note that the fraction of energy channelled into translation is substantially greater than that for a statistical dissociation.

4. Results and discussion

The TOF distributions for BCl_2^+ from state-selected BCl_3^+ and for PX_2^+ ($X = \text{Cl}, \text{Br}$) from state-selected PX_3^+ were analysed both with and without the effects of B, Cl and Br isotopes. Values of $\langle \text{KE} \rangle_t$ and the corresponding values of $\langle f \rangle_t$, with and without the effects of isotopic broadening, are shown in Table 1. As expected, the effect of correct allowance for isotopes is to decrease the value of $\langle \text{KE} \rangle_t$, and the fractional decrease in $\langle \text{KE} \rangle_t$ is greater the smaller its value. As an example, the value of $\langle \text{KE} \rangle_t$ for the dissociation of the $\tilde{\text{B}}^2\text{E}$ state of PCl_3^+ to $\text{PCl}_2^+ + \text{Cl}$ drops from 0.34 to 0.17 eV, a decrease of 50%. The energy available for partitioning is 0.48 eV, so $\langle f \rangle_t$

reduces from 0.71 to 0.35, and we note that statistical and impulsive theories predict $\langle f \rangle_t$ to be 0.23 and 0.63–0.66, respectively. Thus, we concluded [5] that dissociation from the $\tilde{\text{B}}^2\text{E}$ state does not completely follow an impulsive mechanism, although there is probably an element of isolated-state behaviour in the Franck–Condon region. For dissociation from the $\tilde{\text{E}}^2\text{E}$ state of PCl_3^+ to $\text{PCl}_2^+ + \text{Cl}$, however, $\langle \text{KE} \rangle_t$ only reduces by 14% from its larger value of 0.86 to 0.74 eV. Similar effects in the magnitude of the reduction in $\langle \text{KE} \rangle_t$ are observed for BCl_3^+ and PBr_3^+ (Table 1).

To show such results diagrammatically, results for the dissociation of the $\tilde{\text{D}}^2\text{E}'$ state of BCl_3^+ to $\text{BCl}_2^+ + \text{Cl}$ at an excitation energy of 15.51 eV are shown in Figs. 1 and 2. In Fig. 1, isotope effects are

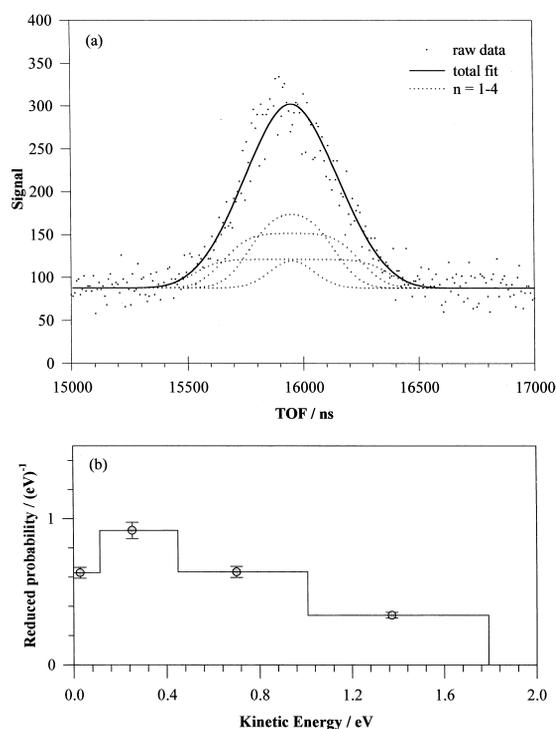


Fig. 1. (a) Coincidence TOF spectrum (dots) of BCl_2^+ photoionised at 15.51 eV into the $\tilde{\text{D}}^2\text{E}'$ state of the parent ion. The BCl_2^+ daughter ion is assumed to be a single isotopomer of mass 81.8 u. The solid line gives the best fit to the data, comprised of four contributions ($n = 1, 2, 3, 4$) with $\varepsilon_t(n) = 0.028, 0.252, 0.7$ and 1.372 eV. The reduced probability of each contribution, defined in Section 2, is shown in (b). The fit yields a total mean translational kinetic energy, $\langle \text{KE} \rangle_t$, into $\text{BCl}_2^+ + \text{Cl}$ of 0.72 ± 0.10 eV which constitutes 22% of the available energy.

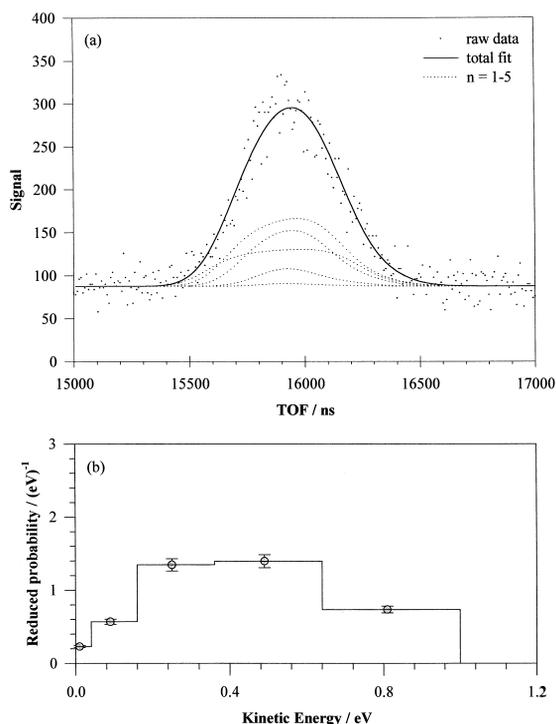


Fig. 2. (a) Coincidence TOF spectrum (dots) of BCl_2^+ photoionised at 15.51 eV into the $\tilde{\text{D}}^2\text{E}'$ state of the parent ion. The BCl_2^+ daughter ion is now assumed to have six different isotopomers, all of different mass (see text), which contribute to the experimental peak shape. The solid line gives the best fit to the data, comprised now of five contributions ($n=1,2,3,4,5$) with $\epsilon_i(n) = 0.01, 0.09, 0.25, 0.49$ and 0.81 eV. The reduced probability of each contribution, defined in Section 2 of the text, is shown in (b). The fit yields a total mean translational kinetic energy, $\langle \text{KE} \rangle_t$, into $\text{BCl}_2^+ + \text{Cl}$ of 0.45 ± 0.04 eV which constitutes 14% of the available energy.

ignored and BCl_2^+ is assumed to have a single mass of 81.8 u. In Fig. 2, the six isotopomers of BCl_2^+ are explicitly allowed for. The net effect is to reduce $\langle \text{KE} \rangle_t$ from 0.72 ± 0.10 to 0.45 ± 0.04 eV, and the reduction in the value of the 2σ error should be noted. Possibly of equal significance is the fact that when isotope effects are considered, the experimental spectrum fits best to a larger number of discrete energies ($n=5$, cf. $n=4$), and ΔE is significantly lower (0.010, cf. 0.028 eV). Both effects are observed in many of the TOF analyses when allowance for isotopes is made, and are indicative of a better-quality fit.

The $\text{PX}_2^+/\text{PX}_3^+$ data were analysed correctly with allowance for isotopes [5], and the conclusions are therefore still valid. The earlier $\text{BCl}_2^+/\text{BCl}_3^+$ data [4] were analysed with no allowance for isotopomers, although we wrote at the time that we were ignoring them. The new values for $\langle \text{KE} \rangle_t$ and $\langle f \rangle_t$ in Table 1 mean that some re-interpretation of this data is necessary. Dissociation from the $\tilde{\text{C}}^2\text{A}''_2$ state of the parent ion results in 18% of the available energy being channelled into translational energy of $\text{BCl}_2^+ + \text{Cl}$. This figure is just below the statistical prediction of 20%, whereas impulsive models predict anything between 33 and 100% dependent on whether a pure- or modified- mechanism is dominant. We now believe that fragmentation of this state occurs by a statistical mechanism following internal conversion and dissociation from the ground-state potential energy surface. The relatively long lifetime of the $\tilde{\text{C}}$ state that this mechanism entails is then consistent with resolved vibrational structure (in the ν_1 mode) being observed in the photoelectron spectrum of this state. Our earlier analysis gave $\langle f \rangle_t = 0.27$, and we interpreted this figure as showing a degree of isolated-state, impulsive dynamical behaviour in the $\tilde{\text{C}}^2\text{A}''_2$ state. This mechanism could only be consistent with the presence of resolved vibrational structure in the photoelectron spectrum if the non-radiative decay rate of this state was very slow, which seemed at the time to be surprising. Dissociation from the $\tilde{\text{D}}^2\text{E}'$ and $\tilde{\text{E}}^2\text{A}'_1$ states of BCl_3^+ now yield $\langle f \rangle_t$ values of 0.14 and 0.10, to be compared with values of 0.22 and 0.16 when no allowance is made for isotopes. Both new values lie below the statistical limit of 0.19 and, as before [4], we assume that dissociation from these states follows essentially a statistical mechanism off the ground-state potential energy surface. A possible interpretation of why these $\langle f \rangle_t$ values are significantly lower than the statistical prediction, that dissociation is to a low-lying excited electronic state of BCl_2^+ thereby reducing E_{avail} , seems unlikely. An excited singlet state of BCl_2^+ lying ≈ 4 eV above the ground state has been observed in fluorescence experiments [8], but ab initio calculations place the lowest excited linear state of BCl_2^+ as high as 6 eV above the ground state [9].

In conclusion, we have shown that allowance must be made for the full range of daughter ion isotopomers when analysing high-resolution TOF

distributions in (T)PEPICO experiments. Otherwise, values for $\langle KE \rangle_t$ and $\langle f \rangle_t$ are obtained which are too large, which may lead to the wrong conclusions being drawn about the mechanism of the unimolecular photofragmentation. Fortunately, the conclusions we now draw from the correct $\langle KE \rangle_t$ results for BCl_2^+/BCl_3^+ only differ slightly from those already published [4], the only significant difference being in our interpretation of the dissociation mechanism of the $\tilde{C}^2A''_2$ state of the parent ion. In our previous TPEPICO work on state-selected fragmentation of fluorine-containing cations (e.g., CF_4^+ [7], SF_6^+ [7], saturated and unsaturated perfluorocarbon cations $C_xF_y^+$ [10,11]), isotope effects can be ignored because the contribution of the minor isotopes of F, C and S is insignificant. These effects become especially important for chlorine- and bromine-containing ions, and have been accommodated in our most-recent analyses of fragmentation of state-selected $CXCl_3^+$ cations ($X = F, H, Br$) [12].

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