Ionization and fragmentation of CCl_2F_2, $CClF_3$, CF_4, and CHF_3 by positron impact

J. Moxom,[1,2] D. M. Schrader,[2] G. Laricchia,[3] J. Xu,[1] and L. D. Hulett[1]
[1]Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
[2]Chemistry Department, Marquette University, P.O. Box 1881, Milwaukee, Wisconsin 53201-1881
[3]Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, United Kingdom
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The fragmentation patterns of the halomethanes CCl_2F_2, $CClF_3$, CF_4, and CHF_3 have been studied by positron impact, in the energy range from threshold to around 50 eV. These data were obtained using a quadratic potential time of flight mass spectrometer, coupled with a Penning trap and a LINAC-based positron source. The present data for positrons are compared with results for electron and photoionization from other works.

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INTRODUCTION

The fragmentation patterns of molecules by collisions with electrons, photons, and other charged particles have been studied for many years, but until recently there has been little work using positron projectiles, largely due to the difficulties associated with producing suitable beams of slow positrons. However, annihilation, positronium (Ps) formation and compound formation by dissociative attachment are possible for positron scattering, and these present interesting reaction channels for investigation.

Ionizing positron-molecule interactions have previously been studied at positron energies both above [1–8] and below the thresholds for Ps formation [9,10]. At energies below the Ps threshold, annihilation of the positron on the molecule, possibly involving the formation of a long-lived positron-molecule resonance [11,12], is possible. If the annihilated electron is not in the highest occupied molecular orbital, the molecule may be left with enough internal energy to cause fragmentation [13]. At energies just below the Ps formation threshold it has been suggested that virtual states of Ps may also cause an enhanced annihilation rate [14], but this idea has been challenged [15]. There has also been some theoretical interest in the formation of Ps compounds [16–18], in which a positronium atom is bound to a neutral fragment. So far the only case to be experimentally confirmed is PsH, formed in dissociative collisions with CH_4 [6].

We have previously reported data for the fragmentation and ionization of CH_3F [19] and CH_3Cl [20] by positron impact and have now extended this work to include four more halomethanes: CCl_2F_2, $CClF_3$, CF_4, and CHF_3. In these experiments, almost monoenergetic beams of slow positrons are scattered from low-density gasses, while the positrons are trapped in a Penning trap and the ionic fragments are analyzed using a quadratic potential time-of-flight mass spectrometer [21]. The yields of the fragment ions are measured as a function of the positron energy.

EXPERIMENT

Positrons are produced in a bremsstrahlung/pair-production process using a 150-MeV electron LINAC at ORNL [22]. The electron beam strikes a water-cooled Ta target, producing an intense shower of γ rays which are intercepted by a W converter to produce positrons by pair production. Some of these positrons are moderated to thermal energies in the W converter, and re-emitted to form the primary positron beam, which is then accelerated to 3 keV. This has previously produced positron beams with intensities in excess of $10^8\ s^{-1}$ [22], although the present measurements were performed with intensities of around $6\times10^6\ s^{-1}$. This is mainly due to degradation of the converter, and to LINAC operating parameters (chosen by the primary user) that are not optimized for positron production.

The Penning trap and mass spectrometer are shown schematically in Fig. 1. The 3-keV positrons from the primary beam are implanted in a 1000-Å W foil, immediately in front of the entrance grid (g_1) of the 10-cm-long Penning trap.

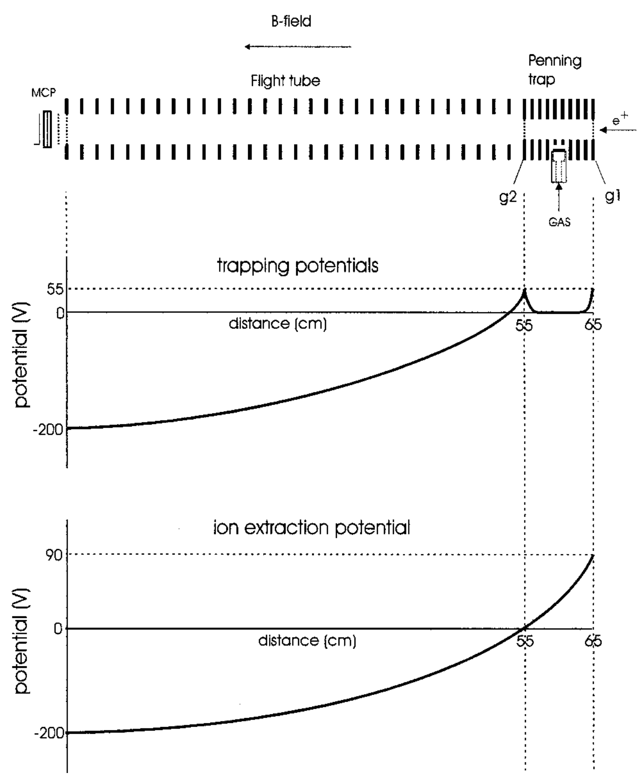

FIG. 1. A schematic diagram of the apparatus and the potentials applied to the spectrometer and the Penning trap (not drawn to scale).

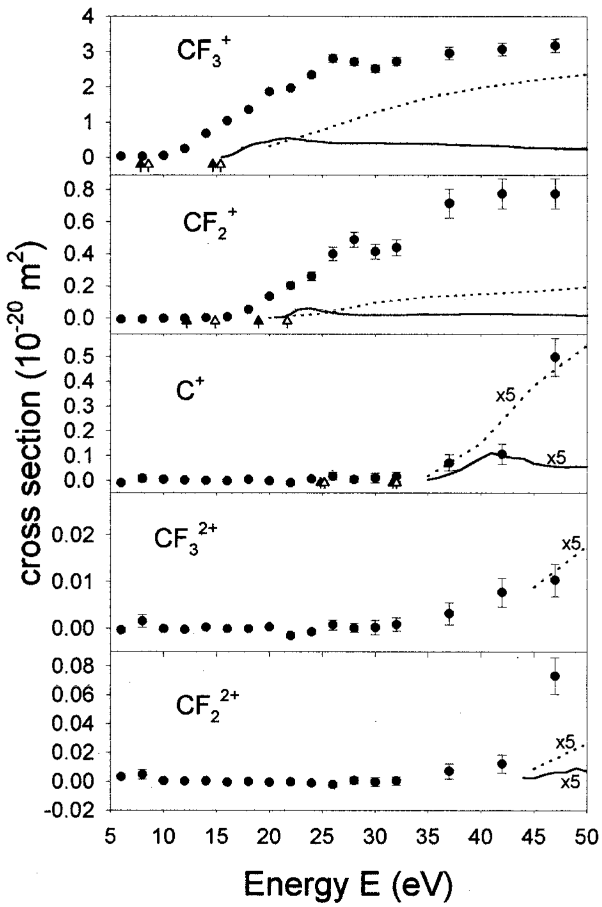

FIG. 2. The fragmentation cross sections for CF_4 by positrons (●), electrons [53] (dotted line), and photons [25] (solid line). The white arrows indicate the AP's, and the black arrows the thermodynamic thresholds.

The positrons are accelerated to the desired energies by applying a positive potential (V_m) to the foil. After remoderation the positrons are injected into the trap and the entrance grid (g_1) is raised from V_m to V_m+3 V, while the exit grid (g_2) is at 55 V, causing the positrons to be trapped. The longitudinal component of the energy distribution of the positrons entering the Penning trap is measured using a retarding field analyzer, and has a full width at half maximum of around 1.3 eV. Ignoring contact potential effects, the mean energy is known to within ± 0.5 eV. A longitudinal magnetic field of around 500 G is used to radially confine the positrons and ions. The sample gas is introduced to the Penning trap through a 10-mm-long multicapillary array perpendicularly to the beam axis. This forms an effusive molecular beam which passes through the center of the Penning trap, where the positron energy is well defined. (The positrons are decelerated near the ends of the trap due to the end grids.) After 65 μs, g_2 is grounded, and the quadratic potential shown in Fig. 1(b) is applied to the Penning trap and spectrometer, accelerating the ions to the microchannel plate detector at the end of the spectrometer flight path. Much longer confinement times are possible, but were found to result in spurious signals from ion-molecule collisions, since the ions are also

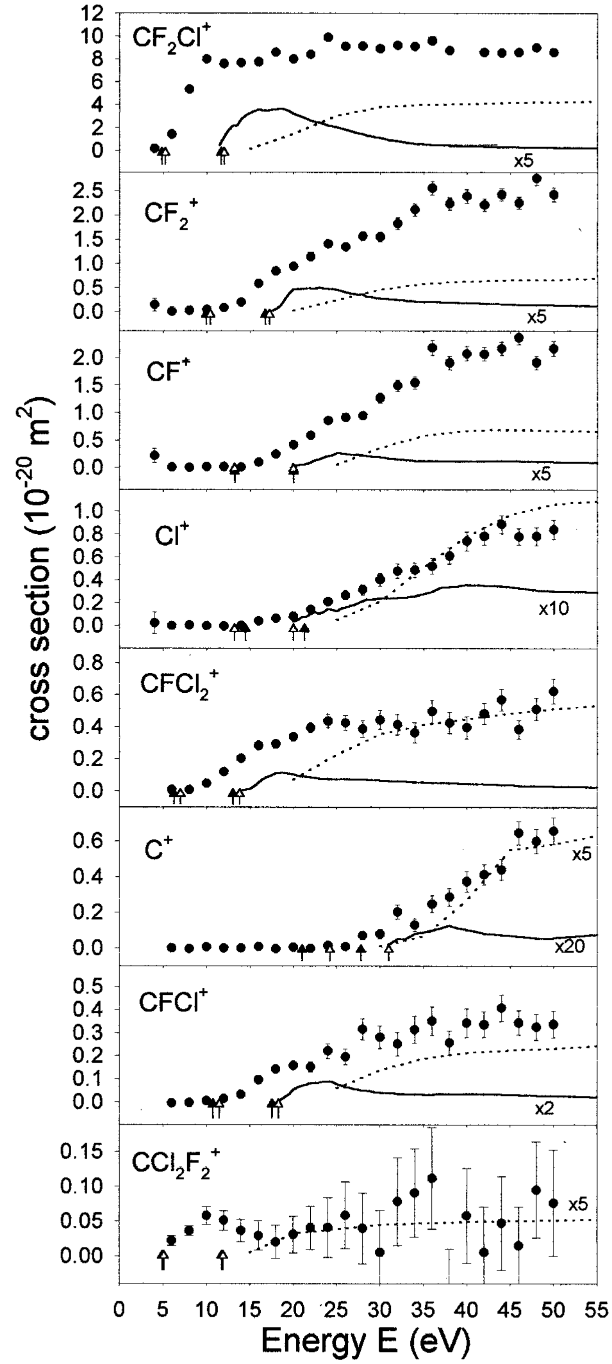

FIG. 3. The fragmentation cross sections for CCl_2F_2 by positrons (●), electrons [56] (dotted line), and photons [43] (solid line). The white arrows indicate the AP's, and the black arrows the thermodynamic thresholds.

confined in the trap with the positrons and can react with the neutral molecules there. A pressure study was performed to ensure that under the conditions of gas density and confinement times used, these effects are negligible in the present data.

Data are accumulated in the form of ion time-of-flight spectra, which, after background subtraction, are integrated to calculate the ion yields. The data are converted into cross-section values by normalizing the ion yields of the four test

TABLE I. The thermodynamic thresholds (E_{th}'s) and the mean appearance potentials (AP's) for the observed fragments.

Parent	fragments	E_{th} (eV)[52]	E_{th}-6.8 eV	AF (eV)	AP-6.8 eV
CF_4	CF_3^++F	14.63	7.83	15.38 [25–36]	8.58
	CF_2^++F_2	18.97	12.17	21.66 [25–29]	14.86
	C^++4F	31.65	24.85	32.0 [25,27,28]	25.2
CCl_2F_2	CF_2Cl^++Cl	11.76	4.96	12.02 [37–40,43]	5.22
	$CF_2Cl_2^+$	11.75	4.95	11.92 [37,38,41,42]	5.12
	$CFCl_2^+$+F	13.05	6.25	13.81 [37,38,40,43]	7.01
	CF_2^++2Cl	16.75	9.95	17.23 [37,38,43]	10.43
	$Cl_2^+Cl_2$	14.24	7.44	14.9 [40]	8.1
	$CFCl^+$+F+Cl	17.56	10.76	18.28 [38,40,43]	11.48
	Cl^++CF+FCl	21.28	14.48	20.0 [43]	13.2
	Cl^++CF_2+Cl	18.29	11.49	18.76 [40]	11.96
	Cl^++?			16 [44]	9
	CF^++F+2Cl	20.03	13.23	20.01 [37,40,43]	13.21
	CF^++F+Cl_2	17.52	10.72	17,5 [37,40]	10.7
	C^++2F+2Cl	27.79	20.99	31 [43]	24
	C^++?			22 [44]	15
CF_3Cl	CF_3Cl^+	12.39	5.59	12.63 [28,38,41,42,45–47]	5.83
	$CClF_2^+$+F	13.65	6.85	15.08 [28,39,45–47]	8.28
	CF_3^++Cl	12.75	5.95	12.71 [28,32,38,45–48]	5.91
	CF_2^++F+Cl	18.73	11.93	19.42 [28,38,40,45–47]	12.62
	Cl^++CF_3	16.81	10.01	19.66 [40]	12.86
	Cl^++CF_2+F	20.27	13.47	20.5 [28,45,46]	13.7
	CF^++2F+Cl	22.01	15.21	23.7 [28,45,46]	16.9
	CF^++F_2+Cl	20.38	13.58	20.28 [40]	13.48
	C^++3F+Cl	29.77	22.97	32 [28,45]	25
CH_2F	CF_3^++H	13.59	6.79	14.45 [32,49,50]	7.65
	CHF_2^++F	14.35	7.55	16.32 [29,49,51]	9.52
	CF^++HF+F	16.96	10.16	20.55 [49,51]	13.75
	C^++H^++3F	30.61	23.36		

gases to that of Ar, for which the total single ionization cross section is known [23,24]. First the energy dependencies of the yields are determined by normalizing the number of ion counts to the beam intensity, run times, and collision path lengths for the positrons in the Penning trap. Once the energy dependencies and branching ratios are determined, the yields are normalized at 40 eV to absolute cross-section values. By collecting calibration spectra for the four test gases and Ar, under the same conditions of retention time and beam intensity, while accurately measuring the drive pressure with a capacitance manometer, we can assign absolute cross-section values to the measured ion yields. This is only expected to provide an approximate calibration, due to the combined uncertainties in pressure measurement, the cross section for Ar, and possible variations in the detection efficiencies for different ion species. The total uncertainties in the absolute cross sections are estimated to be around 25%, and the error bars in the figures only indicate the statistical uncertainties.

RESULTS AND DISCUSSION

The appearance potentials (AP's) for the fragments by electron or photoionization are listed in Table I. To obtain the expected AP's for positron impact with Ps formation, these values have to be shifted down by 6.8 eV, the binding energy of Ps. Since there is some scatter between AP's reported by different workers [25–51] the mean values have been assumed. Also given are the thermodynamic thresholds (E_{th}) for the various processes [52], and these are the thresholds that would be observed if the fragments had zero kinetic energies. If Ps compounds such as PsF and PsCl were formed, the thresholds would be reduced by their binding energies (around 2–3 eV [16–18]). However, within the noise limitations of our spectrometer, there is no evidence of this. Where available, the fragmentation cross sections by photon and electron impact obtained by others are shown in the figures for comparison.

The results for CF_4 are shown in Fig. 2, with corresponding data for electron [53] and photoionization [25]. Since there is no vertical transition from the ground state of CF_4 to a bound state of CF_4^+, no parent ions are formed and the most abundant species is CF_3^+. At 47 eV, the highest energy studied, the branching ratios for CF_3^+, CF_2^+, C^+, CF_2^{2+}, and CF_3^{2+} are 70%, 17%, 11%, 1.6%, and 0.22%, respectively.

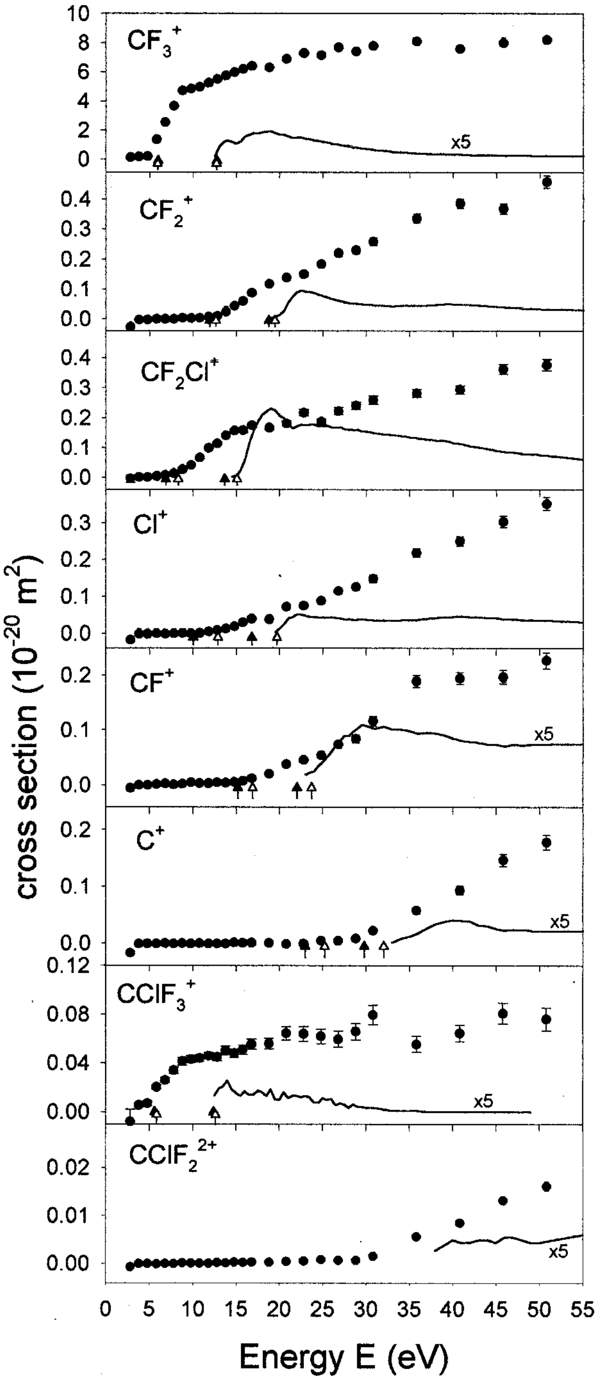

FIG. 4. The fragmentation cross sections for $CClF_3$ by positrons (●) and photons [45] (solid line). The white arrows indicate the AP's, and the black arrows the thermodynamic thresholds.

The cross sections for producing $CF_3{}^+$ and $CF_2{}^+$ rise from background approximately 6.8 eV below the AP's for electron or photoionization, due to the formation of Ps. In comparison, the C^+ yield rises from background much more gradually and, within the statistical uncertainties, there is no significant signal in the energy range 6.8 eV below the AP for electron or photons, indicating a lack of Ps with the formation of the C^+ ion at these energies. This is similar to

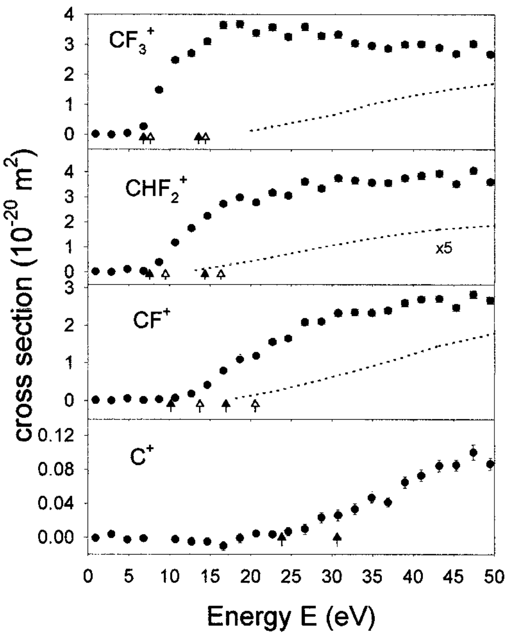

FIG. 5. The fragmentation cross sections for CHF_3 by positrons (●) and electrons [49] (dotted line). The white arrows indicate the AP's, and the black arrows the thermodynamic thresholds.

what was observed in CO_2 by Bluhme *et al.* [2], who suggested that the reason may be the increased ''violence'' of the process since, in order to extract the C atom from its center, the molecule must be atomized. A similar suppression of Ps formation was also observed in the double ionization of the noble gases [54,55]. At higher energies, the relative yields for C^+ and the doubly charged species are significantly larger for positrons compared to the other projectiles.

The present results for CCl_2F_2 are shown in Fig. 3, along with data for photoionization [43] and for electron scattering [56]. In the present data the most abundant ion detected is CF_2Cl^+, with only a relatively small yield of the parent molecular ion, $CCl_2F_2{}^+$. At 50 eV the measured branching ratios are 55%, 16%, 14%, 5.4%, 4.0%, 4.2%, 2.1%, and 0.4% for $CClF_2{}^+$, $CF_2{}^+$, CF^+, Cl^+, CCl_2F^+, C^+, $CClF^+$, and $CCl_2F_2{}^+$, respectively.

Most of the fragments show evidence of their production accompanied by Ps formation, with their AE's approximately 6.8 eV below those for electron or photoionization. The yield of CF_2Cl^+ rises more abruptly from threshold than the other fragments and, with the possible exception of Cl^+, the C^+ yield rises the most slowly. In this respect C^+ has an energy dependence more similar to that for electron impact and, while the C^+ signal below the threshold for direct ionization is not zero, it is relatively small compared with most of the other fragments. This is also true of Cl^+, and indicates that for this molecule Ps formation may also play a less significant role in liberating these ions.

The fragmentation patterns of $CClF_3$ by positrons and photons [45] are shown in Fig. 4. The most abundant species observed is $CF_3{}^+$, with only a relatively small contribution from the parent molecular ion. The branching ratios for $CF_3{}^+$, $CF_2{}^+$, $CClF_2{}^{2+}$, Cl^+, CF^+, C^+, $CClF_3{}^+$, and $CClF_2{}^{2+}$ are 83%, 4.6%, 3.8%, 3.6%, 2.3%, 1.8%, 0.77%, and 0.16%, respectively. In each case the yields rise from background around the Ps threshold, although for C^+, Cl^+, and CF^+ the onset is more gradual, and the yield is relatively small below the threshold for electron and photoionization.

Results for CHF_3 are presented in Fig. 5. Since the mass resolution of the spectrometer is not sufficient to resolve the differences between CHF_3 and CF_3, the peak with its maximum at 69 mass units is assumed to be entirely $CF_3{}^+$. The yield of the parent ion is probably relatively small since for electron impact at 70 eV the relative yield of $CHF_3{}^+$ is only 1.3% that of $CF_3{}^+$ [57]. The mass difference between $CHF_2{}^+$ and $CF_2{}^+$ is also unresolvable, and these ions are counted together. The yield is probably mostly due to CHF_2^+, since the relative cross sections by electron impact are, for example, in the ratio 5.2:1 at 40 eV [49]. At 50 eV the branching ratios for $CF_3{}^+$, $CHF_2{}^+$, CF^+, and C^+ are 30%, 39%, 29%, and 0.98%, respectively. For all of the fragments, the yield rises from background around the expected thresholds for Ps formation. No C^+ from electron impact was reported [49], but for positrons its onset is more gradual than the other fragments, as with the other molecules studied, indicating the relative contribution from Ps is the least for C^+ at energies below the threshold for direct ionization.

CONCLUSIONS

The fragmentation of the halomethane molecules CCl_2F_2, $CClF_3$, CF_4, and CHF_3 have been measured following positron impact. The fragmentation patterns have certain features in common for the four gases. At low energies the cross sections for positron scattering exceed those for electrons, as expected, due to the Ps formation channel, and the yields for most of the fragments rise from the background approximately 6.8 eV below the AP's measured by electron or photoionization. However, the C^+ ion cross sections are consistently among the slowest rising above threshold, and for CF_4 the signal is indistinguishable from zero below the threshold for direct ionization. This suggests that the Ps channel is less important for production of the C^+ fragments, close to threshold, particularly in the case of CF_4. This is similar to the suppression of the Ps channel that was previously reported in positron scattering from CO_2 [2]. It was suggested that this may be due to the more destructive nature of the processes, which probably results in the complete atomization of the parent molecule, and may also be the case for the molecules studied here.

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