Direct Observation of an Isolated State in the Ion $C_2F_6^+$: a Violation of the Quasi-equilibrium Theory of Mass Spectra

By IAN G. SIMM,* C. JOHN DANBY, and JOHN H. D. ELAND
(*Physical Chemistry Laboratory, South Parks Road, Oxford* OX1 3QZ)

Summary It is shown on the basis of photoelectron–photoion coincidence measurements, that ions in the first excited state of $C_2F_6^+$ decompose without prior internal conversion into the ground state, thus violating a basic assumption of the quasi-equilibrium theory of mass spectra.

MEASUREMENTS on C_2F_6 using the technique of photoelectron–photoion coincidence spectrometry[1,2] have shown that at least one of the excited states of $C_2F_6^+$ is isolated; *i.e.*, ions in that state decompose without prior internal conversion into the ground state. This is the first direct observation of an isolated electronic state in a polyatomic ion.

The coincidence technique, by selecting electrons emitted in photoionization with a single kinetic energy, allows observation of the breakdown products from molecular ions produced with a single internal energy. We measure the time-of-flight mass spectrum of ions in coincidence with electrons of the selected kinetic energy. Photoionization is caused by radiation from a helium resonance lamp [giving mainly the He-$(I)_\alpha$ line of energy 21·22 eV] where it intersects a jet of sample vapour admitted through a hypodermic needle. The electrons emitted are energy selected in a parallel plate deflection analyser of the type described by Eland and Danby.[3] The ions are accelerated out of the source region, and separated by mass in a drift tube, as in a time-of-flight mass spectrometer. The time-of-flight mass spectrum of ions in coincidence with electrons of the selected kinetic energy is accumulated in a 256 channel store, each channel of which normally corresponds to a time interval of 100 ns.

The Figure shows a photoelectron spectrum of C_2F_6 taken point by point under the low resolution conditions required for the coincidence experiment,[1] with a field of 3·75 V cm^{-1} in the ionization region. The energy scale is calibrated by comparison with a high resolution spectrum having argon as an internal calibrant. The appearance potentials for CF_3^+ and $C_2F_5^+$ obtained by Noutary[4] under photoionization

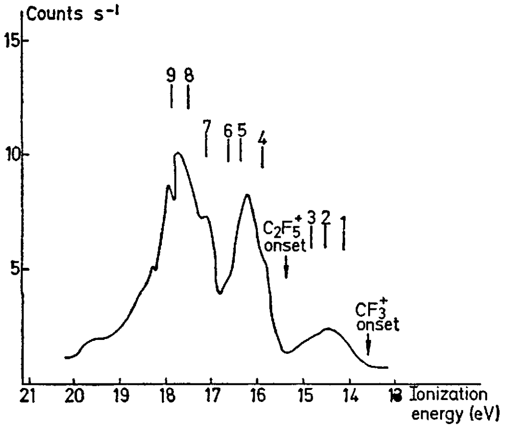

FIGURE. Photoelectron spectrum of C_2F_6

are marked on the Figure together with the positions at which coincidence measurements were made. The products observed at the various ionization energies are listed in the Table. The Table shows that $C_2F_6^+$ ions in their ground state ($\tilde{X}$) decompose only to CF_3^+, while those in the first excited state ($\tilde{A}$) give nearly all $C_2F_5^+$. At point 6 (ionization energy 16·64 eV) no CF_3^+ is observed within experimental error, and estimates of the collection efficiencies for $C_2F_5^+$ and CF_3^+ show that CF_3^+ does not contribute more than 3·5% of the total ionization observed at any point within the $\tilde{A}$ band.

The formation of $C_2F_5^+$ from $C_2F_6^+$ in the $\tilde{A}$ state is accompanied by kinetic energy releases of up to 1 eV, whereas the CF_3^+ ions from ground state $C_2F_6^+$ are formed mainly with low kinetic energy releases of less than 0·1 eV. As a result, the collection efficiency for CF_3^+ is greater than that for $C_2F_5^+$,[5] and the relative intensities observed have to be corrected for this effect.

TABLE

Products observed from the decomposition of $C_2F_6^+$ at various ionization energies

Measurement no. (as on Figure)	Internal energy of $C_2F_6^+$ (eV)	State of $C_2F_6^+$	Products[a]
1	14·14	$\tilde{X}$	CF_3^+
2	14·54	$\tilde{X}$	CF_3^+
3	14·84	$\tilde{X}$	CF_3^+
4	15·89	$\tilde{A}$	$\underline{\underline{C_2F_5^+}}$, CF_3^+ (≤3·5%)]
5	16·37	$\tilde{A}$	$\underline{\underline{C_2F_5^+}}$, CF_3^+ (≤2·7%)]
6	16·64	$\tilde{A}$	$\underline{\underline{C_2F_5^+}}$
7	17·14	?	$\underline{\underline{C_2F_5^+}}$, CF_3^+ (≤5·5%)
8	17·52	?	$\underline{\underline{CF_3^+}}$, $C_2F_5^+$, CF^+
9	17·89	?	$\underline{\underline{CF_3^+}}$, CF^+

[a] Where more than one product is observed, the predominant product is underlined.

In the higher energy part of the C_2F_6 photoelectron spectrum individual electronic states are difficult to distinguish. As higher ionization energies are reached, CF_3^+ once more becomes the dominant product, and no $C_2F_5^+$ ions are observed at or above 17·89 eV (measurement 9).

The abrupt change in products between the ground state and the first excited state of $C_2F_6^+$ makes it clear that the decomposition of ions in the excited state does not involve prior internal conversion to the ground state. This observation violates one of the basic assumptions of the quasi-equilibrium theory of mass spectra, and confirms a suggestion made by Lifshitz and Long.[6] They found that, under electron impact, the yield of $C_2F_5^+$ from C_2F_6 relative to that of CF_3^+ was much greater than could be accounted for by quasi-equilibrium theory calculations with any reasonable parameters, and therefore suggested that an isolated state of $C_2F_6^+$ is involved in the production of $C_2F_5^+$. We find that the ratio of $C_2F_5^+$ to CF_3^+ in the photoionization mass spectrum at 21·22 eV is 0·6, which is even higher than the ratio found by Lifshitz and Long using 70 eV electron impact.

Simple molecular orbital considerations suggest that the ground states of $C_2F_6^+$, CF_3^+, and CF_3 all belong to the totally symmetric representation (A_1) in C_{3v}, the symmetry we assume to be conserved in the decomposition. Since this representation is non-degenerate, the ground state of $C_2F_6^+$ will correlate directly and uniquely with the ground states of the products CF_3^+ and CF_3, according to the correlation rules. An ion in an excited state of $C_2F_6^+$ will only be able to decompose to give CF_3^+ and CF_3 in their ground states *via* internal conversion into the ground state of $C_2F_6^+$. Without such internal conversion, decomposition of an excited $C_2F_6^+$ ion must take place through another channel; either, as is observed in the $\tilde{A}$ state, by decomposition to $C_2F_5^+$ and a fluorine atom, or to ground state CF_3^+ and an excited state of CF_3. The reappearance of CF_3^+ as dominant product at higher ionization energies may be due to a process of this latter sort, or may involve consecutive reactions.

We thank Mr. J. R. Crellin for supplying a high resolution photoelectron spectrum, and the S.R.C. for financial support.

(*Received*, 24*th August* 1973; *Com.* 1214.)

---

[1] J. H. D. Eland, *J. Mass Spectrometry Ion Phys.*, 1972, **8**, 143.

[2] C. J. Danby and J. H. D. Eland, *J. Mass Spectrometry Ion Phys.*, 1972, **8**, 153.

[3] J. H. D. Eland and C. J. Danby, *J. Sci. Instr.*, *Ser.* 2, 1968, **1**, 408.

[4] C. J. Noutary, *J. Res. Nat. Bur. Stand.*, *Sect. A*, 1968, **72**, 479.

[5] J. H. D. Eland, *J. Mass Spectrometry Ion Phys.*, 1972, **9**, 397; 1973, in the press.

[6] C. Lifshitz and F. A. Long, *J. Phys. Chem.*, 1965, **69**, 3746.