The appearance of $C_2H_3^+$ ions from C_2H_3F by non-resonant photoionization.
A translational energy surprisal analysis
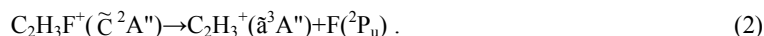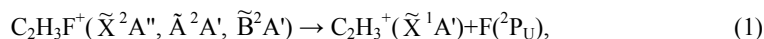
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It is shown that for a photon energy of 16.85 eV, the translational energy surprisal of the $C_2H_3^+$ + F dissociation products from $C_2H_3F^+$ has a bimodal behaviour. The possibility of considering the bimodal surprisal as due to the superposition of two translational energy distributions is consistent with the theoretical assumption of the concurrence of two channels in this dissociation process. The characteristics of these distributions, i.e. the energy width and the relative abundance, are in agreement with the results of an ab initio quantum-mechanical calculation of the dynamics of this dissociation. They are consistent with the simultaneous occurrence of a statistical dissociation of $C_2H_3F^+$ ($\tilde{X}\,^2A'$) into $C_2H_3^+$ ($\tilde{X}\,^1A'$) and an isolated state dissociation of $C_2H_3F^+$ ($\tilde{C}\,^2A''$) into $C_2H_3^+$ ($\tilde{a}^3A''$). The negative λ values obtained for the surprisal of both these distributions indicate an inversion of the translational level population of the dissociation products.

1. INTRODUCTION

When an electronically excited state of a polyatomic molecular ion dissociates in competition with the fastest energy randomizing radiationless transition to the electronic ground state, one claims the existence of an "*isolated state dissociation process*". If the products of this decay are the same as those of the energy randomized molecular cation, their ionic components will appear at the same *m/e* value in a mass spectrometer. The former products will very often differ from the latter, at least by an electronic state. In a recent paper [1], the dissociation of the vinylfluoride cation via an "*isolated state*", has been discussed theoretically. The existence of such a process was suggested by the PIPECO mass spectrum [2].

As schematically shown in fig. 1 from ref. [2], the ion yield of $C_2H_3^+$ shows a second increase when the C state of $C_2H_3F^+$ is excited, probably starting an isolated state decay of the $\tilde{C}$ state. The correlation rules, confirmed by theoretical calculations [1], indicate that the $\tilde{X}\,^2A''$, $\tilde{A}\,^2A'$, $\tilde{B}^2A'$ states of the $C_2H_3F^+$ decay follows the channel (1) and that the $\tilde{C}\,^2A''$ state decays through the channel (2)

$$C_2H_3F^+(\tilde{X}\,^2A'', \tilde{A}\,^2A', \tilde{B}^2A') \rightarrow C_2H_3^+(\tilde{X}\,^1A')+F(^2P_U), \qquad (1)$$

$$C_2H_3F^+(\tilde{C}\,^2A'')\rightarrow C_2H_3^+(\tilde{a}^3A'')+F(^2P_u) . \qquad (2)$$

The present Letter gives an experimental contribution to the investigation of this problem by measuring the translational energy distribution (TED) of the charged dissociation products, for a unique photon energy in excess of both dissociation limits (1) and (2). The total translational energy distribution for both fragments, deduced from the experimental TED, will be discussed by using the surprisal analysis [3].

2. EXPERIMENTAL RESULTS

The TED of $C_2H_3^+$ ions, induced by the Ne (I) resonance lines (16.85 eV photons) was determined by the experimental setup, described in detail elsewhere [4,5]. Briefly, the photoion source is followed by a retarding lens. A quadrupole mass spectrometer (Balzers QMG 311) is used for mass selection. The observed TED for $C_2H_3^+$ ions is shown in fig. 2. The intensity of the fragment ions is recorded with 6 mV retarding potential steps. Using the numerical values of the $C_2H_3^+$ ion intensity, and the energy conservation law, the TED curve of $C_2H_3^+$ is converted into the *total translational energy distribution* (*total* TED) of the products $C_2H_3^+$ +F. The result, as normalized to the maximum ion intensity centered on zero translational energy, is shown as curve *P* in fig. 3. The distribution ranges from 0-1.8 eV.

Fig. 1. *The production of $C_2H_3^+$ from C_2H_3F: (a) the ion yield of $C_2H_3^+$ from PIPECO measurements of ref. [2], (b) an idealized photoelectron spectrum of C_2H_3F within the energy limits corresponding to the Ne(I) photons, (c) the range of the accessible excitation energy, E, available to $C_2H_3^+ + F$.*
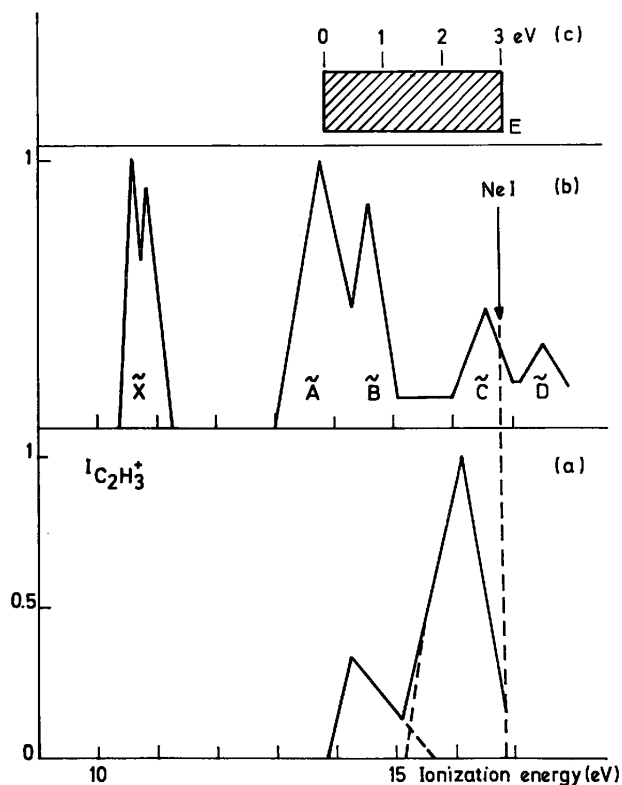
Fig. 2. *The experimentally measured translational energy distribution of $C_2H_3^+$ from C_2H_3F observed with the Ne(I) resonance line.*
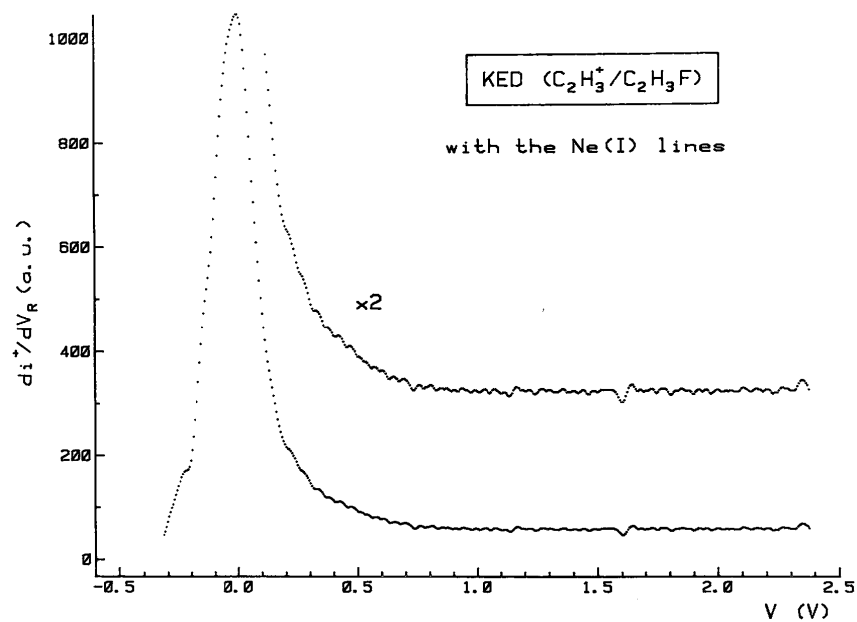
Fig. 3. *Total translational energy distribution of $C_2H_3^+$ +F calculated from fig. 2 ((O) curve P). The partially calculated distribution P_a (□) as well as the P_b distribution (+), resulting from $P—P_a$, are also displayed.*
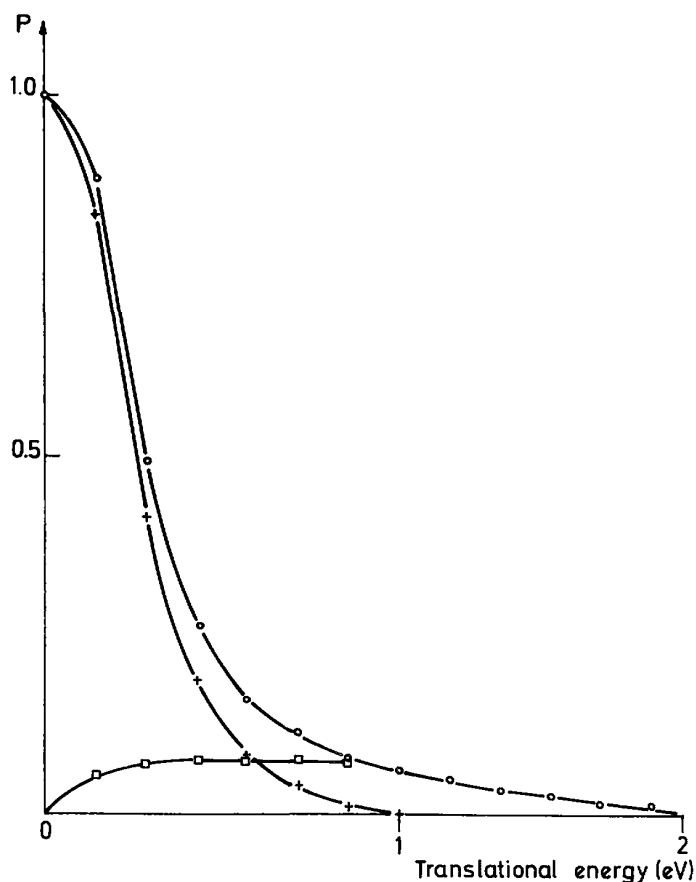
3. THE TRANSLATIONAL ENERGY SURPRISAL

In an ideal experiment, a total TED would be measured simultaneously with the successively increasing values of the excess energy *E* above the first dissociation limit (process 1). In the present experiment the deduced total TED is the sum of such distributions, each being weighted for the ionic abundance observed for each *E* value, under similar conditions.

Any a priori calculated total TED, to be used in the surprisal evaluation, will also be a similarly weighted sum of a priori calculated total TEDs for successively selected values of the excess energy *E*.

Taking 13.85 eV as the appearance energy of $C_2H_3^+$ cations [2], the excess energy *E* to be shared between the dissociation products for 16.85 eV photons, will vary from 0 eV at 13.85 eV to 3.0 eV at 16.85 eV.

In order to evaluate the a priori weighted statistical total TED, i.e. $P°(E_T, E)$, necessary for the sur-prisal evaluation of the distribution *P*, the $P°(E_T, E)$ distributions have been calculated for values of *E* ranging from 0.0-3.0 eV by steps of 0.1 eV using the RRHO approximation [2,3],

$$P°(E_T,E) = CE_T^{1/2}(E-E_T)^{s+r/2-1} . \qquad (3)$$

The weighting factors for each step were obtained from the idealized ion yield curve shown in fig. 1.

In eq. (3), *s* represents the number of vibrational degrees of freedom of $C_2H_3^+$, *r* stands for the number of rotational degrees of freedom of the ion and *C* is a constant which disappears by an appropriate normalization to the maximum of the calculated distribution. In this case *s=9*, *r=3* and $s+r/2-1 = 9.5$ and (3) becomes

$$P^0(E_T,E) = CE_T^{1/2}(E-E_T)^{9.5}. \qquad (4)$$

Remembering that the surprisal is expressed by —In $(P/P°)$, the calculations mentioned above give rise to the surprisal diagram displayed in fig. 4. This diagram shows a rather unusual behaviour, i.e. passing through a maximum value at E_T=0.4 eV, it decreases linearly over the 1.0-1.8 eV range. A bi-modal character of surprisal diagrams has occasionally been reported [6][#1], [7-9] and attributed to the simultaneous existence of two dynamical behaviours in the process under consideration. It may be that the observed diagram, represented in fig. 4, comes from the superposition of the total TEDs generated by two processes, such as (1) and (2). Each process being characterized by its own distribution, it will be assumed that the one giving rise to the linear surprisal could be extrapolated down to E_T—0 eV, through eq. (5),

$$-\ln a \left(\frac{P_a}{P^o} \right) = 3.603 - 4.65 \, E_T$$

The calculated distribution, P_a, drawn in fig. 1, increases from E_T=0 eV to a flat maximum; at 1 eV it merges in the P distribution. By subtraction of P_a from P, one gets the P_b distribution which is maximum at E_T=0 eV and drops to zero at E_T= 1 eV. From the surfaces limited by the P_a and the P_b distributions respectively, the relative abundances, I_a and I_b, of the $C_2H_3^+$ ions corresponding to these distributions are expressed by the ratio I_a/I_b. This ratio is found to be equal to three. In other words, the $C_2H_3^+$ ions distributed over the kinetic energy range of 0.0-1.0 eV are three times more abundant than those characterized by the total TED spreading over the 0-1.8 eV range.

4. DISCUSSION

4.1. Comparison with the ab initio calculations

As expected from the correlation rules, the ab initio calculations of the potential energy surfaces of the $\tilde{X}$, $\hat{A}$, $\tilde{B}$, and $\tilde{C}$ states of $C_2H_3F^+$ [1] confirm that the former $\tilde{X}$, $\hat{A}$ and $\tilde{B}$ states are asymptotically connected with the first dissociation limit (1) and the last $\tilde{C}$ state with the second dissociation (2). A single avoided crossing between $\tilde{X}\,^2A''$ and $\tilde{C}\,^2A''$ has been shown to occur. It is centered at an internuclear distance $R(C-F)$ of about 2 Å with a minimum energy gap of 0.96 eV. The occurrence of this crossing divides the reaction flux into two parts.

The first part flows through the "diabatic path" by jumping from the $\tilde{C}\,^2A''$ state to the $\tilde{X}\,^2A''$ state, while retaining its momentum. This fraction dissociates via a direct, short lifetime mechanism and leads to $C_2H_3^+$ ($\tilde{X}\,^1A'$) +F fragments, with broad total TED, representing about 35% of the total flux.

The other part remains on the adiabatic potential energy hypersurface of the $\tilde{C}$ state and dissociates with a smaller translational energy release into $C_2H_3^+$ ($\tilde{a}^3A''$)+F. This fraction represents about 65% of the total flux.

Both these mechanisms are fast ($\approx 10^{-13}$ s) and branching ratio between the second and first being calculated to be of the order of 2, compares favourably with the I_b/I_a ratio deduced from the result of this work, i.e. I_b/I_a=3. This qualitative agreement allows us to ascribe the P_a distribution to the reaction flux (1) and the P_b distribution to the reaction flux (2). These results also show that the use of TEDs surprisal calculation allows us to disentangle the simultaneous occurrence of concurrent dissociation processes in the decay of electronically excited molecular ions.
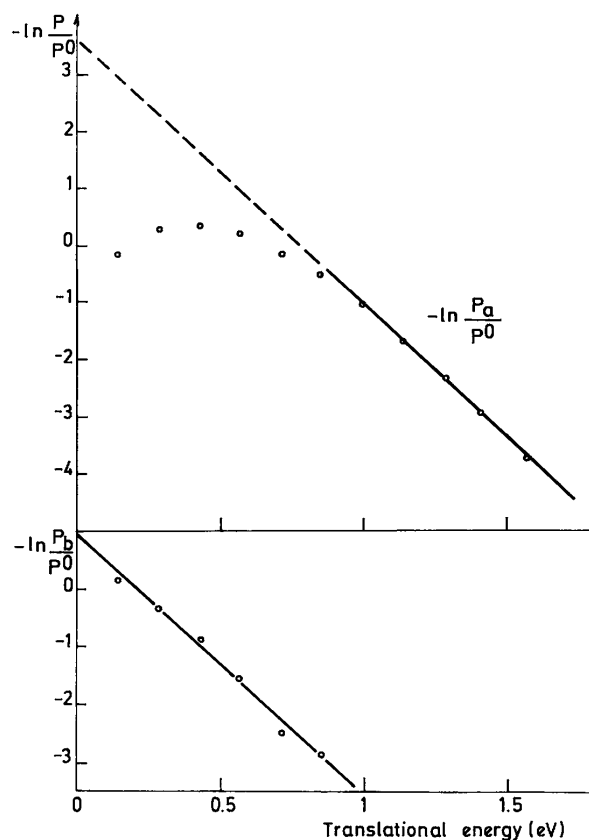
4.2. The surprisal of the P_b distribution

For the distribution being ascribed to the sudden dissociation of the $\tilde{C}$ state through process (2), its surprisal has to be evaluated with respect to this dissociation limit. The excitation energy of $C_2H_3^+$ ($\tilde{a}\,^3A''$) with respect to $C_2H_3^+$ ($\tilde{X}\,^1A'$) is not known experimentally. Referring to fig. 1, one can extrapolate the $C_2H_3^+$ ionic abundances to zero, coinciding with the evolution of the $\tilde{B}$ state. The ionic abundance of $C_2H_3^+$, ascribed to the fate of the $\tilde{C}$ state excitation, could then be estimated. A probable value of 15.15 eV for the appearance energy

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[#1] See fig. 2 of ref. [6].

of $C_2H_3^+$ ($\tilde{a}^3A''$) is obtained. At the ionizing photon energy of 16.85 eV an excess energy value of 1.70 eV is calculated for process (2) with respect to its probable dissociation limit. The distributions $P^0(E_T/E)$ have been evaluated by using eq. (4) for E values ranging from zero to 1.7 eV, weighted by the ionic abundances of $C_2H_3^+$ observed simultaneously, from 15.15 eV up to 16.85 eV, and finally summed in order to obtain the a priori distribution $P°(E)$. The surprisal $-\ln[P_b/P^0(E)]$ is shown in fig. 4.

Fig. 4. *Surprisal analysis of the P distribution. The upper part shows the total E_T surprisal with its linear part (and extrapolation) defining the P_a distribution. The lower part shows the surprisal calculated for the P_b distribution. The slope of the P_a surprisal is $\lambda_a=4.65$ and the slope of the P_b surprisal is $\lambda_b= -4.5$. Within probable errors $\lambda_a=\lambda_b$.*

4.3. Comments about P_a and P_b surprisals

From the surprisal analysis of the translational energy distributions P_a and P_b, it has to be inferred that both surprisals are negative and therefore that a population inversion of the translational energy levels is expected. This allows us to conclude that the $C_2H_3^+$ ions, either in the $\tilde{X}\ ^1A'$ or in the $\tilde{a}^3A''$, are vibrationally not statistically populated, but that their population is not inverted. The negative value of λ for both distributions suggests that the dissociation in both channels (1) and (2) should be a fast process.

5. Conclusion

Evidence has been given in this Letter about a concurrence between an "isolated state" decay of the $\tilde{C}$ state of $C_2H_3F^+$ and a randomized ground state decay of the same ion. The former gives rise to a rather narrow width of the total TED, with the highest ionic abundance. The latter gives rise to a rather broad total TED with the lowest ionic abundance. Both these processes are characterized by a translational energy distribution inversion. It is therefore clear that both electronically different $C_2H_3^+$ ions appear with non-statistical but not inverted vibrational populations.

Acknowledgement

References

[1] A.J. Lorquet, M. Roorda and J.C. Lorquet, J. Phys. Chem. 95(1991) 9188.

[2] J. Dannacher, A. Schmelzer, J.P. Stadelmann and J. Vogt, Intern. J. Mass Spectrom. Ion Processes 31 (1979) 175.

[3] A. Ben Shaul, Y. Haas, K.L. Kompa and R.D. Levine, Springer series in chemical physics, Vol. 10. Lasers and chemical change (Springer, Berlin, 1981).

[4] R. Locht and J. Schopman, Intern. J. Mass Spectrom. Ion Phys. 15 (1974) 361.

[5] J. Momigny, R. Locht and G. Caprace, Chem. Phys. 102 (1986) 275.

[6] A. Ben Shaul, R.D. Levine and R.B. Bernstein, J. Chem. Phys. 57 (1972)5427.

[7] W.H. Breckenridge, Reactions of small transient species, eds. A. Fontyn and M.A.A. Clyne (Academic Press, New York,1983) p. 208.

[8] R. Locht and J. Momigny, Intern. J. Mass Spectrom. Ion Processes 71 (1986) 141.

[9] C. Lifshitz, Intern. J. Mass Spectrom. Ion Processes 43 (1982) 179.