

## MECHANISM FOR THE APPEARANCE OF $H^+$ BY ELECTROIONIZATION OF $CH_4$ . A SURPRISAL ANALYSIS

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### Abstract

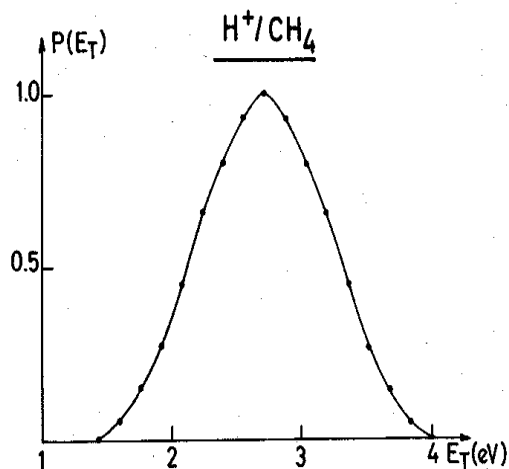
Previous experimental results on the threshold energy and on the energy range of the first wide translational energy distribution of  $H^+$ , resulting from electron impact on  $CH_4$ , are interpreted. The translational energy surprisal of this distribution has been evaluated with respect to a statistically calculated one. The surprisal plot shows a fourth power dependence on  $f_T$  with a negative mean slope associated with a large  $\Delta S_{exc}$  value of  $\approx 4$  eu. An "a priori" calculated  $P^0(E_T|E)$  distribution, including four constraints, fits fairly well the observed translational energy distribution.

### 1. Introduction

Since the last papers dedicated to the appearance of  $H^+$  by electroionization of  $CH_4$  [1,2], it appears firmly established that the lowest threshold energy for the appearance of this ion with a wide kinetic energy distribution lies at  $22.17 \pm 0.1$  eV, this means below the threshold for the appearance of the  $^2A_1$  electronic state of  $CH_4^+$  (22.39 eV) as measured by photoelectron spectroscopy [3,4]. From the onset to at least 25 eV the  $H^+$  ions give rise to a unique kinetic energy distribution starting at 1.44 eV, peaking at 2.72 eV and decreasing down to zero at 4.0 eV, as expressed by the total energy carried by both the  $CH_3$  and  $H^+$  fragments. The distribution of  $H^+$ , as observed at 25 eV and normalized to its maximum is shown in fig. 1. It is noteworthy that the high-lying Rydberg states of the H atoms, induced by electron impact on  $CH_4$  are observed with the same kinetic energy distribution for the same threshold energy [5, 6]. This means that high-lying Rydberg states of  $CH_4$  converging to the  $^2A_1$  state of  $CH_4^+$  are populated at  $22.17 \pm 0.1$  eV and are able to decay either by autoionization to the  $H^+ + CH_3(^2A''_2)$  dissociation limit at 18.1 eV or to the numerous  $H^{**} + CH_3(^2A''_2)$  dissociation limits lying just below 18.1 eV.

Two questions arise from the experimental results: (i) if an excess energy of  $\approx 4.0$  eV with respect to the dissociation limit at 18.1 eV ( $H^+ + CH_3$ ) is needed to produce the whole kinetic energy distribution, why does this distribution start at a minimum kinetic energy of 1.4 eV? (ii) does this distribution show a "surprisal" with respect to a statistical distribution of 2.63 eV total energy between excited rovibrational states of  $CH_3$  and kinetic energy of both fragments? An answer to these questions will be given in the following sections.

**Fig. 1.** Probability distribution of  $CH_3 + H^+$ , normalized to its maximum, as a function of the kinetic energy carried away by both fragments.

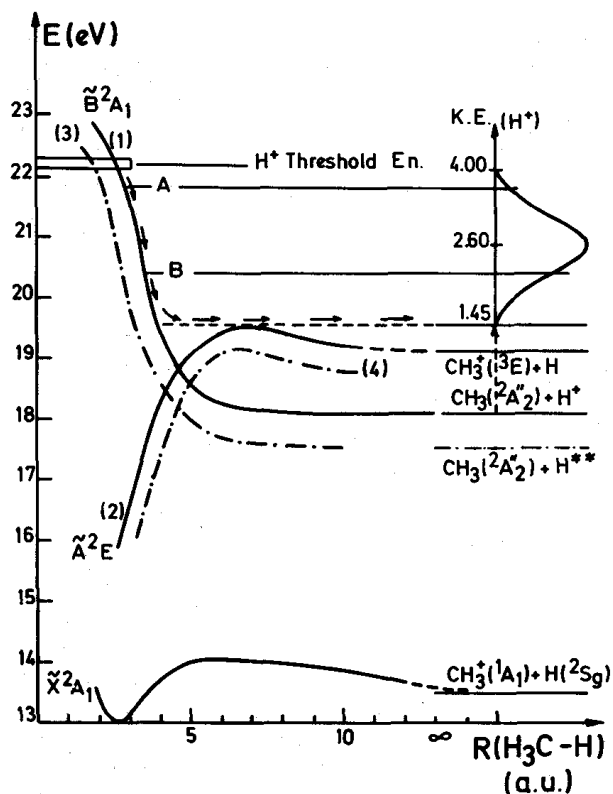


## 2. Theoretical aspects of the appearance of $H^+$

Calculated potential energy curves of the successive electronic states of  $CH_4^+$ , in the  $C_{3v}$  symmetry, correlating with either  $CH_3^+ + H$  or  $CH_3 + H^+$  dissociation channels, are available [7]. These curves, just slightly adapted to the experimental results, are given in fig. 2. In fig. 2, curve 1 is the repulsive  ${}^2A_1$  state correlating with  $CH_3 + H^+$ . Curve 2 is the  ${}^2E$  state of  $CH_4^+$  correlating with  $CH_3^+ + H$ . This curve goes through a maximum around 19.5 eV for a  $R(CH_3-H)$  distance of 7 au. Curve 3 is a tentative drawing of the repulsive part of one high-lying Rydberg state converging to the  ${}^2A_1$  state of  $CH_4^+$  and correlating with  $CH_3 + H^{**}$ . Curve 4 is a tentative drawing of one high-lying Rydberg state converging to the  ${}^2E$  state of  $CH_4^+$ .

The dissociation mechanism leading to  $H^+$  or to  $H^{**}$  is as follows: at 22.1 eV curve 3 is selectively populated and will decay down to  $CH_3 + H^{**}$  or autoionize to curve 1. The decay from 22.1 eV to the dissociation limit lying at 18.1 eV would normally give a kinetic energy distribution ranging from 0 to 4 eV. But from 19.5 eV the figurative points describing this decay are deviated to the top of curve 2. This would explain that the kinetic energy distribution only starts at  $\approx 1.4$  eV excess kinetic energy. The same situation will be encountered for the decay to  $CH_3 + H^{**}$ , leading to the observation of a similar kinetic energy distribution [5,6].

Fig. 2. Potential energy diagram as reproduced from ref. [7].



## 3. Evaluation of the surprisal in the dissociation process

In fig. 2 the  ${}^2A_1$  state of  $CH_4^+$  is represented by a potential energy curve. Actually, this curve has to be represented by a potential energy hypersurface where a rather high number of trajectories are able to be explored by the system, leading to a quasi-continuous sharing of the 2.6 eV excess energy between translational energy of  $CH_3$  and  $H^+$  and rovibrational energy of  $CH_3$ . The only available experimental information on this internal energy sharing is the probability distribution of translational energy. The deviation of the observed distribution  $P(E_T|E)$  from a calculated a priori one,  $P^0(E_T|E)$ , based on pure statistical arguments could be characterized by the generalized surprisal equation proposed by Levine and Bernstein [8]:

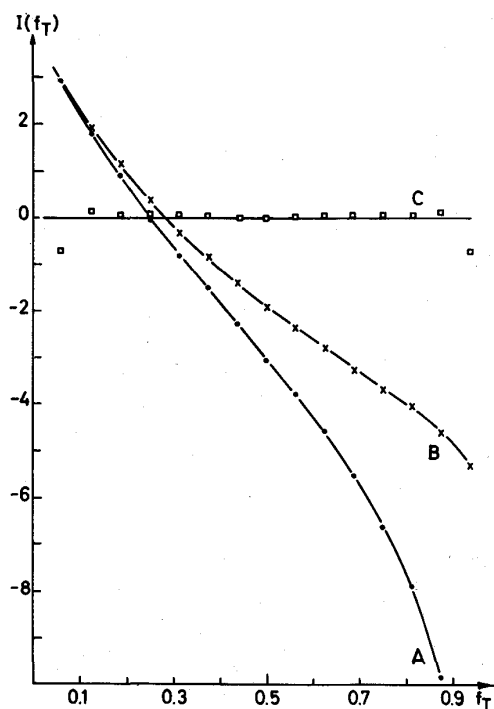
$$P(f_T) = P^0(f_T) \exp\left(-\sum_i \lambda_i f_T^i\right), \quad (1)$$

or

$$I(f_T) = -\ln[P(f_T)/P^0(f_T)] = \sum_{i=0}^n \lambda_i f_T^i. \quad (2)$$

In these equations,  $f_T$  is the reduced energy  $E_T/E$  and to each value of  $\lambda_i$  corresponds a moment of the distribution such as:  $\langle f_T^i \rangle = \sum_T f_T^i P(f_T)$ . The non-vanishing  $\lambda_i$  are those for which the moments are independent pieces of information.  $I(f_T)$  is defined as the surprisal of the experimental distribution with respect to the calculated one. Referring to appendix A for the background needed for one of the best possible evaluations of

**Fig. 3.** Surprisal plot for the dissociation process  $CH_4 \rightarrow CH_3 + H^+$  as a function of  $f_T$ . Curves A and B are calculated with  $P^0(E_T|E)$  evaluated by using the classical and the Whitten-Rabinovitch approximation, respectively. Curve C shows the minimized surprisal when  $P^0(E_T|E)$  is expressed by (6) where  $n = 2.5$ .



$P^0(f_T)$ ,  $I(f_T)$  is shown in fig. 3. This result is obtained using either the classical approximation [formula (A.8)] or the Whitten-Rabinovitch approximation [formula (A.9)] for the calculation of the density of vibrational states of the polyatomic  $CH_3$  radical [9]. As seen in fig. 3, even if the general shape of  $I(f_T)$  is not affected by the approximation used for the calculation of  $P^0(f_T)$ , the mean slope of  $I(f_T)$  is strongly modified. In both cases the surprisal appears to be negative and non-linear. Curve B, corresponding to the use of the Whitten-Rabinovitch approximation, is fitted with a maximum error of  $\approx 1\%$  by the following polynomial:

$$I(f_T) = 3.91 - 16.84f_T + 10.98f_T^2 + 1.92f_T^3 - 5.98f_T^4. \quad (3)$$

The mean value of the negative slope of this surprisal would be  $\lambda_T = -9.9$  from which a mean negative temperature  $T_T$  of the translational distribution is evaluated as

$$\bar{T}_T = (E/k)/\bar{\lambda}_T = -3000 \text{ K}. \quad (4)$$

#### 4. Entropy excess of the experimental distribution

Bernstein and Levine [10] and Ben-Shaul et al. [11] show that the observed distribution is characterized by an entropy excess  $\Delta S_{exc}$  with respect to the calculated one. In the case of continuous and isotropic translational energy distributions, whatever the form of the surprisal is, the entropy excess can be evaluated by:

$$\Delta S(E_T) = R \int P(E_T|E) \times \ln [P(E_T|E)/P^0(E_T|E)] dE_T, \quad (5)$$

the notation  $P(E_T|E)$  implying an average over a small range  $\delta E_T$  of translational energies, such that many internal states fall within that interval, provided the interval is sufficiently narrow that  $P(E_T|E)$  hardly varies over that range

$$P(E_T|E) = \sum_n P(n, E_T|E) / \delta E_T, \quad (6)$$

$$E_T \leq E - E_n \leq E_T + \delta E_T.$$

The evaluation of (5) has been done in the case of the observed distribution and  $\Delta S_{exc}$  was found to be equal to:

$$\Delta S_{exc} = 4.22 \text{eu.}$$

All these results lead to the conclusion that a rather large population inversion appears for the translational energy release in the studied decay process. If the rotational energy distribution of the  $\text{CH}_3$  radical is not too "surprising", it could be inferred that the certainly non-statistical population of the vibrational levels of  $\text{CH}_3$ , will not be inverted at all. The non-linearity of the surprisal expresses also that in the dissociation process, four dynamical constraints have to be considered [12]. In other words, it means that all isoenergetic quantum states prepared by the absorption of the total energy required for the dissociation process, are not equally probable. The large mean negative slope of the surprisal and the consequently large entropy excess are a measure of this deviation.

### 5. Surprisal minimalization: an "a priori" constrained $P^0(E_T|E)$ distribution

The surprisal curve, calculated by using the classical harmonic approximation, being of the same general shape as that calculated by the more exact Whitten-Rabinovitch approximation (fig. 3, curves A and B), the present point will be discussed within the frame of the classical approximation. From appendix A [formula (A.8)],  $P^0(E_T|E)$  is in this case given by:

$$P^0(E_T|E) = CE_T^{1/2} (E - E_T)^{s+r/2-1}, \quad (7)$$

where C is a constant and  $s$  and  $r$  are the number of vibrational and rotational degrees of freedom of the polyatomic radical, respectively.

The experimental distribution  $P(E_T|E)$  being symmetrical with respect to its maximum, an equation similar to (7) has been fitted to the experimental results, but in the general form:

$$P(E_T|E) = CE_T^n (E - E_T)^n. \quad (8)$$

The best fit on the experimental distribution is given by the exponent value of  $n = 2.5$ , except for the two first and two last points. As shown by curve C (fig. 3), for this distribution the surprisal is zero within experimental errors for  $0.15 < f_T < 0.85$ . The exponent  $s + r/2 - 1$  fits the value of 2.5 in two ways: (i)  $s = 3$  with  $r = 1$ , and (ii)  $s = 2$  with  $r = 3$ . In the former way, five constraints are needed on  $P^0(E_T|E)$ , i.e. three vibrational and two rotational degrees of freedom are not excited. In the latter way, only four constraints are needed on  $P^0(E_T|E)$ , i.e. only two vibrational degrees of freedom are active.

As  $I(f_T)$  shows a fourth power dependence on  $f_T$ , illustrating that four constraints are needed, the hypothesis (ii) is apparently the only one to be considered. In this case, the excited vibrations could be the combination of the two non-degenerated vibrations  $\nu_1 + \nu_2$  or one of the two degenerated vibrations only. It could be argued against these conclusions that the 2.5 power calculated for the density of translational states of the fragments, instead of the statistical exponent of 0.5, would be an additional constraint. However, this would not be an independent constraint, but more than probably this behaviour results from the inactivity of four vibrational modes of  $\text{CH}_3$  in the dissociation process.

## 6. Concluding remarks

The present study shows that the appearance of  $H^+$  from  $CH_4$  implies a strong population inversion in the translational energy distribution of both  $H^+$  and  $CH_3$ . The fourth power dependence of the surprisal with respect to  $f_T$  implies that the experimental distribution will go over an a priori calculated distribution which will include four dynamical constraints. In the frame of the classical approximation, it was shown that the inactivity of four vibrational degrees of freedom in  $CH_3$  allows us to calculate a very small surprisal from the statistical distribution. Furthermore, the negative surprisal observed for the translational energy distribution implies that when the rotational energy surprisal is neglected, the vibrational distribution of  $CH_3$  will certainly be non-statistical but without population inversion.

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## Appendix A

If the dissociation process considered is  $AB(\text{polyatomic}) \rightarrow A(\text{polyatomic}) + B(\text{atom})$  and if it gives

rise to a translational energy distribution of both fragments A and B, the evaluation of the surprisal of this distribution needs the calculation of the "a priori" probability to share a total internal energy  $E$  between the vibrational energy  $E_V$ , the rotational energy  $E_R$  of the polyatomic fragment A and the translational energy  $E_T$  of A and B, all isoenergetic quantum states being considered as equally probable. Such an "a priori" probability distribution  $P^0(E_T, E_V, E_R|E)$  is written [13]:

$$\begin{aligned} P^0(E_T, E_V, E_R|E) &= [\rho_T(E_T)\rho_V(E_V)\rho_R(E_R)/\rho(E)] \\ &\times \delta(E - E_T - E_V - E_R). \end{aligned} \quad (\text{A.1})$$

In expression (A.1) the  $\rho_m(E_m)$  are the densities of quantum states for the different types of energy and  $\rho(E)$  is the total density of states. The  $\delta$  function restricts the range of final states to those of a given total energy  $E$ .

The expressions of  $\rho_m$  are given by:

$$\rho_T(E_T) = C_T E_T^{1/2}, \quad (\text{A.2})$$

from refs. [14,15]. Using the classical approximation [16]:

$$\rho_R(E_R) = C_R E_R^{r/2-1}, \quad (\text{A.3})$$

where  $r$  is the number of rotational degrees of freedom, and

$$\rho_V(E_V) = C_V E_V^{s-1}, \quad (\text{A.4})$$

where  $s$  is the number of vibrational degrees of freedom to be considered in the polyatomic radical A. The  $C_m$  are combinations of constants. Introducing (A.2), (A.3) and (A.4), (A.1) becomes:

$$\begin{aligned} P^0(E_T, E_V, E_R|E) &= K E_T^{1/2} E_R^{r/2-1} E_V^{s-1} \\ &\times \delta(E - E_T - E_V - E_R). \end{aligned} \quad (\text{A.5})$$

$K$  being a constant given by  $C_T C_R C_V / \rho(E)$ . Integration of (A.5) over  $E_R$  yields:

$$\begin{aligned} P^0(E_T, E_V|E) &= K E_T^{1/2} E_V^{s-1} \int_0^{E-E_T-E_V} E_R^{r/2-1} \\ &\times \delta(E - E_T - E_V - E_R) dE_R. \end{aligned} \quad (\text{A.6})$$

Owing to the property of the  $\delta$  function  $\int f(x)\delta(x - x_0) dx = f(x_0)$

$$P^0(E_T, E_V|E) = K E_T^{1/2} E_V^{s-1} (E - E_T - E_V)^{r/2-1}. \quad (\text{A.7})$$

Integration of (A.6) over  $E_V$  leads to:

$$\begin{aligned} P^0(E_T|E) &= K E_T^{1/2} \int_0^{E-E_T} E_V^{s-1} \\ &\times (E - E_T - E_V)^{r/2-1} dE_V. \end{aligned}$$

As

$$\begin{aligned} & \int_a^b (x-a)^m (b-x)^n dx \\ &= (b-a)^{m+n+1} \frac{\Gamma(m+1)\Gamma(n+1)}{\Gamma(m+n+2)} \\ &= K'(b-a)^{m+n+1}. \end{aligned}$$

When  $m, n > -1$  and  $b > a$

$$\begin{aligned} P^0(E_T|E) &= KK'E_T^{1/2} (E-E_T)^{s+r/2-1} \\ &= CE_T^{1/2} (E-E_T)^{s+r/2-1}. \end{aligned} \quad (\text{A.8})$$

When a better approximation is needed for the evaluation of the density of vibrational states of the polyatomic radical A, the Whitten-Rabinovitch approximation will be used [9]:

$$\begin{aligned} P^0(E_T|E) &= CE_T^{1/2} \int_0^{E-E_T} (E_V + aE_V)^{s-1} \\ &\quad \times (E-E_T-E_V)^{r/2-1} dE_V. \end{aligned} \quad (\text{A.9})$$

As  $a$  in expression (A.9) is a rather complex function of  $E_V$ , (A.9) is evaluated numerically. In each case  $P^0(E_T|E)$  is normalized to its maximum as  $P(E_T|E)$ , in order to avoid the calculation of constants.

## Appendix B

The vibrational frequencies of  $\text{CH}_3$  used in the calculations are from ref. [17]:  $\nu_1(\text{I})=3044 \text{ cm}^{-1}$ ;  $\nu_2(\text{I})=617 \text{ cm}^{-1}$ ;  $\nu_3(\text{II})=3162 \text{ cm}^{-1}$ ;  $\nu_4(\text{II})=1396 \text{ cm}^{-1}$ .