HOW ERGODIC IS THE FRAGMENTATION OF THE PYRIDINE CATION? A MAXIMUM ENTROPY ANALYSIS.

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All statistical theories of mass spectra assume fast randomization of the internal energy before dissociation takes place. A molecule is said to behave ergodically if reactive nuclear trajectories sample the available part of phase space either fully or at least representatively before dissociation. If a dissociation is not totally ergodic, its lack of statisticity is reflected on the kinetic energy release distribution of the fragments. The maximum entropy method compares the experimental kinetic energy distribution and the calculated most statistical distribution and leads to the 'ergodicity index' $F(E)$, that measures the efficiency of phase space sampling as a function of the internal energy of the system E.

The kinetic energy released to the $C_4H_4^+$ and HCN fragments produced by the dissociation of the pyridine ion ($C_5H_5N^+$) has been determined by a retarding field technique up to an internal energy of 4 eV above the reaction threshold. This extends our previous study limited to the metastable domain [1]. Retarding potential curves resulting from dissociative photoionization using the He(I), Ne(I), and Ar(II) resonance lines have been analyzed.

In the maximum entropy formalism, the kinetic energy distribution, i.e., the probability to release a kinetic energy ε on the fragments if the internal energy of the parent is equal to E, is written as

$$P(\varepsilon|E) = P^0(\varepsilon|E) \exp[-\lambda_0(E) - \lambda_1(E)\ A_1(\varepsilon)]$$

where $P^0(\varepsilon|E)$ is the statistical distribution and $A_1(\varepsilon)$ is the dynamical constraint that prevents phase space from being fully explored. $\lambda_0(E)$and $\lambda_1(E)$ are Lagrange parameters. In our experimental setting, pyridine cations are produced in a wide interval of energy. Hence, the experimental distribution is equal to $P(\varepsilon|E)$ averaged over a known internal energy distribution $T(E)$:

$$\int_\varepsilon^\infty P^0(\varepsilon|E) \exp[-\lambda_0(E) - \lambda_1(E) A_1(\varepsilon)]\ T(E)\ dE$$

Knowing $P^0(\varepsilon|E)$ and $T(E)$, this formula is fitted to the experimental curve to determine $\lambda_0(E)$, $\lambda_1(E)$ and $A_1(\varepsilon)$. It can be demonstrated that $F(E) = \exp[\lambda_0(E) + \lambda_1(E)\langle A_1\rangle(E)]$. Subsequently, the ergodicity index can be estimated from the fit.

$F(E)$ is found to decrease steadily as a function of E and to level off at a value of about 50% when $E \geq 2.5$ eV (Figure 1). At these high internal energies where phase space exploration no longer decreases, spontaneous intramolecular vibrational energy redistribution (i.e., resulting from the anharmonicity of the molecular vibrations) is thought to contribute to internal energy randomization to a limited extent only. When the lifetime is short, phase space exploration is believed to result instead from the relaxation of the electronic energy via a cascade of non-radiative transitions, which leads to a great diversity of initial conditions and thus contributes to statisticity.

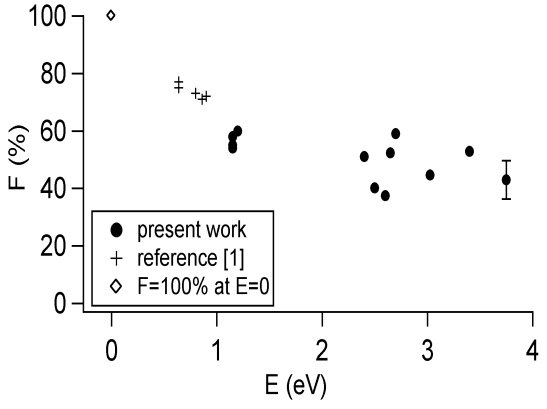

Fig. 1. Ergodicity index F as a function of internal energy E.

References

[1] P. Urbain, B. Leyh, F. Remacle, J.C. Lorquet, Int. J. Mass Spectrom. Ion Proc. **185/186/187**, 155-163 (1999).