UNIMOLECULAR DISSOCIATION OF HALOGENOBENZENE CATIONS MODELISED BY PHASE SPACE THEORY.

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Phase space theory in its orbiting transition state version is a very useful tool to calculate the kinetic energy release distribution in an ionic dissociation [1]. This model assumes an ion-induced dipole interaction between receding fragments and an equal probability for all decay states, provided energy E and angular momentum J are conserved. We used it in the cases of three dissociations : $C_6H_5X^+ \rightarrow C_6H_5^+ + X$ with X = I, Br and Cl.

Statistically, the kinetic energy release distribution, i.e., the probability to release a relative translational energy ε on the fragments if the internal energy of the parent is equal to E and its angular momentum is J , is proportional to the convolution product of the vibrational density of states and the rotational-orbital density of states:

$$P(\varepsilon|E,J) \propto \int_0^{E-\varepsilon} \rho_{vib}(E-\varepsilon-E_r)\,\rho_{ro}(E_r,\varepsilon,J)\,dE_r \qquad (1)$$

The crux point of phase space theory is the calculation of $\rho_{ro}(E_r,\varepsilon,J)$. Let j and ℓ be respectively the $C_6H_5X^+$ rotational and the orbital momenta. $\rho_{ro}(E_r,\varepsilon,J)$ results from integration of the $C_6H_5X^+$ rotational density of states $\rho(E_r,j)$ over accessible (j, ℓ) states:

$$\rho_{ro}(E_r,\varepsilon,J) = \iint_{\Omega} \rho(E_r,j)\,d\ell\,dj \qquad (2)$$

where Ω is defined by three conditions:

- The centrifugal barrier induced by the orbital motion must be smaller than the kinetic energy : $\ell \leq \ell_{max}(\varepsilon)$
- The energy conservation prevents j from being too large: $j \leq j_{max}(E_r)$;
- The angular momentum conservation : $$|J-j| \leq \ell \leq |J+j|$$

The molecular fragment is assumed to rotate as a spherical top of rotational constant B, so $\rho(E_r,j)$ is equal to $2j\,\delta(E_r-Bj^2)$. The calculation of Equation (2) shows that the shape of $\rho_{ro}(E_r,\varepsilon,J)$ depends on ε, E_r and J (Figure 1).

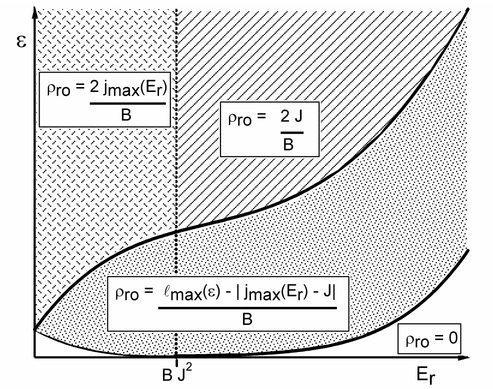

Figure 1: The rotational-orbital states density. The upper black line corresponds to $\ell_{max}(\varepsilon) = j_{max}(E_r)+J$, the lower one to $\ell_{max}(\varepsilon) = |j_{max}(E_r)-J|$.

Figure 2 displays an example of kinetic energy release distribution calculated via Equations (1) and (2). Compared to a prior distribution conserving only E, the conservation of J leads to a reduction of phase space sampling by 5% as shown by a maximum entropy analysis. The experimental distribution [2] is also seen to be more constrained than the PST one, since it involves a reduction of 23% in phase space sampling.

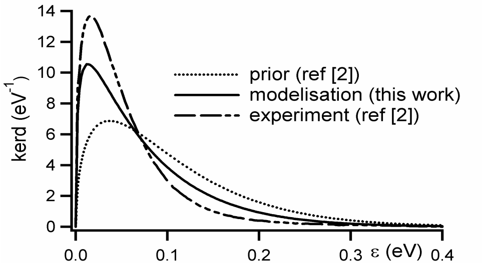

Figure 2 : The calculated and experimental kinetic energy release distributions for the dissociation $C_6H_5Br^+ \rightarrow C_6H_5^+ + Br$.

References

[1] L. M. Bass and M. T. Bowers, J. Chem. Phys. **86**, 2611 (1987).

[2] P. Urbain, F. Remacle, B. Leyh and J.C. Lorquet, J. Phys. Chem. **100**, 8003 (1996)