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: 

\[ \text{C}_6\text{H}_5\text{X}^+ \rightarrow \text{C}_6\text{H}_5^+ + \text{X} \text{ with } \text{X} = \text{I, Br and Cl}. \]

Statistically, the kinetic energy release distribution, i.e., the probability to release a relative translational energy \( \varepsilon \) 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:

\[
P(\varepsilon | E, J) \propto \int_0^{E-E_r} \rho_{\text{vib}}(E-\varepsilon-E_r) \rho_{\text{ro}}(E_r, \varepsilon, J) \, dE_r \tag{1}
\]

The crux point of phase space theory is the calculation of \( \rho_{\text{ro}}(E_r, \varepsilon, J) \). Let \( j \) and \( \ell \) be respectively the \( \text{C}_6\text{H}_5\text{X}^+ \) rotational and the orbital momenta. \( \rho_{\text{ro}}(E_r, \varepsilon, J) \) results from integration of the \( \text{C}_6\text{H}_5\text{X}^+ \) rotational density of states \( \rho(E_r, j) \) over accessible \((j, \ell)\) states:

\[
\rho_{\text{ro}}(E_r, \varepsilon, J) = \int_{\Omega} \rho(E_r, j) \, dj \, d\ell \tag{2}
\]

where \( \Omega \) is defined by three conditions:

- The centrifugal barrier induced by the orbital motion must be smaller than the kinetic energy: \( \ell \leq \ell_{\text{max}}(\varepsilon) \)
- The energy conservation prevents \( j \) from being too large: \( j \leq j_{\text{max}}(E_r) \);
- 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 \( \rho_{\text{ro}}(E_r, \varepsilon, J) \) depends on \( \varepsilon \), \( E_r \) and \( J \) (Figure 1).

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

Figure 2: The calculated and experimental kinetic energy release distributions for the dissociation \( \text{C}_6\text{H}_5\text{Br}^+ \rightarrow \text{C}_6\text{H}_5^+ + \text{Br} \).

References