How Hot are your Ions in Differential Mobility Spectrometry?

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Project Overview

Ions can experience significant field-induced heating in a differential mobility cell. To investigate this phenomenon, the fragmentation of several *para*-substituted benzylpyridinium (BP) "thermometer" ions are monitored in a commercial differential mobility spectrometer (DMS). The internal energy of each benzylpyridinium derivative was characterized by monitoring the degree of fragmentation to obtain an effective temperature, T_{eff}, which corresponds to a temperature consistent with treating the observed fragmentation ratio to a unimolecular dissociation rate weighted by a Boltzmann distribution at a temperature T. It was found that ions are sufficiently thermalized after initial activation from the ESI process to the temperature of the bath gas, T_{bath}. Once a critical field strength is surpassed, significant fragmentation of the benzylpyridinium ions was detected. At the maximum bath gas temperature (450 K) and separation voltage (SV; 4400 V) for our instrument, T_{eff} for the BP ions investigated ranged from 667.1 ± 13.6 K (*p*-OMe) to 749.6 ± 2.8 K (*p*-H). The extent of activation at a given SV depends on the ion's mass and degrees of freedom (N_{DoF}). Plots of T_{eff} vs. the product of ion mass and N_{DoF} produce strong linear relationships. This provides an attractive avenue to estimate ion temperatures at a given SV using only intrinsic properties. Moreover, experimentally determined T_{eff} correlate with theoretically predicted T_{eff} using with a self-consistent method based on two-temperature theory.

Determining Ion Temperatures

The area of an ionogram corresponding to MRM transitions of the unimolecular fragmentation of the BP derivatives (R = OMe, Me, F, Cl, H, CN) are monitored to calculate the experimental fragmentation yield (FY) and survival yield (SY).
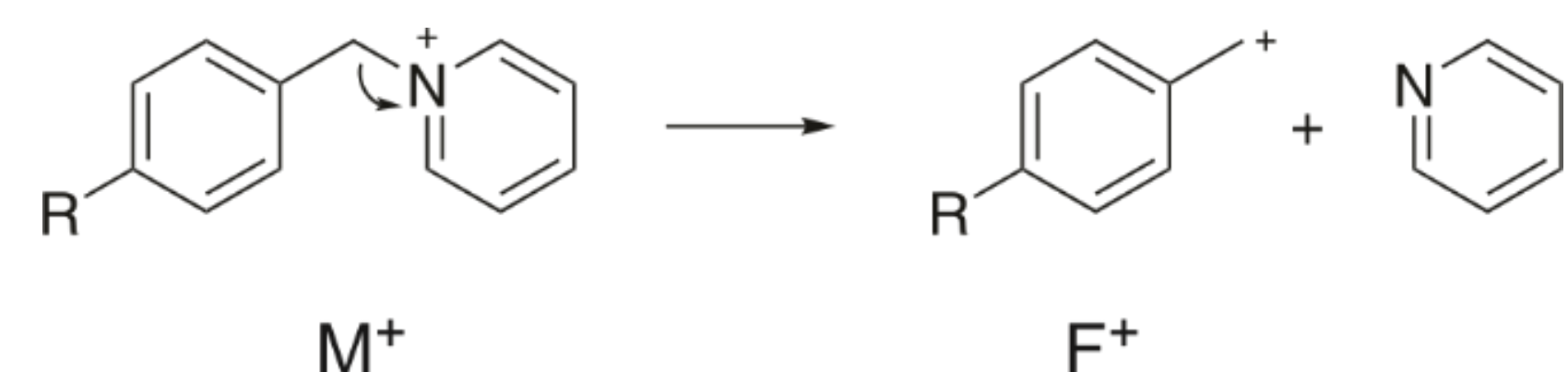
$$FY = \frac{A_{F^+/F^+}}{(A_{M^+/M^+} + A_{M^+/F^+} + A_{F^+/F^+})} = 1 - SY$$

The unimolecular rate constant is defined by Rice–Ramsperger–Kassel–Marcus (RRKM) theory. Unimolecular dissociations are treated in the phase space limit, where transitional modes in the transition state are treated as rotors.[1]

To model T_{eff} in the DMS, we use a combination of RRKM theory and Boltzmann statistics. With collisions occurring in the nanosecond regime over a millisecond residence time, ions are sufficiently thermalized and thus can be characterized by a Boltzmann distribution at temperature $\rho(E,T)$.

$$k(E) = \frac{G^{\ddagger}(E - E_0)}{h \cdot \rho(E)} \qquad \rho(E,T) = \frac{\rho(E) \cdot exp(-E/kT)}{\int_0^{\infty} \rho(E) \cdot exp(-E/kT)\, dE}$$

This is a case where there is rapid energy exchange compared to dissociation; the dissociation rate, $k(T)$, becomes a function of the microcanonical rate $k(E)$ from RRKM weighted by a Boltzmann energy distribution $\rho(E,T)$ at a temperature T.

$$k(T) = \int_{E_0}^{\infty} k(E) \cdot \rho(E,T) = \int_{E_0}^{\infty} \frac{G^{\ddagger}(E - E_0)}{h} \cdot \frac{exp(-E/kT)}{\int_0^{\infty} \rho(E) \cdot exp(-E/kT)\, dE}\, dE$$

Given that SY = 1 – FY, the point at which the experimental SY matches that of $k(T)$ for a BP derivative is taken as T_{eff} where τ is the timescale for dissociation within the DMS cell.

$$P_d(T) = FY(T) = 1 - exp(-k(T) \cdot \tau) \qquad \qquad \tau = \frac{V_{cell}}{Q}$$

Calculated survival yields are fit with a 5-parameter logistic function (Equation 10), which is rearranged to correlate experimental SYs to T_{eff}.

$$SY_{theor} = A_{min} + \frac{(A_{max} - A_{min})}{\left[1 + \left(\frac{x_o}{T_{eff}}\right)^h\right]^s} \qquad T_{eff} = x_0 \left(\sqrt[s]{\frac{(A_{min} - A_{max})}{(A_{min} - SY_{expt})}} - 1\right)^{-\frac{1}{h}}$$

Ion T_{eff} due to the Separation Field

The observation of diminishing SV_{crit} values as T_{bath} is increased while the initial SY remains unchanged supports our hypothesis that ions are thermalized to the temperature of the bath gas after the ESI process. T_{eff} is found to depend linearly on the mass weighted degrees of freedom of the BP derivative.
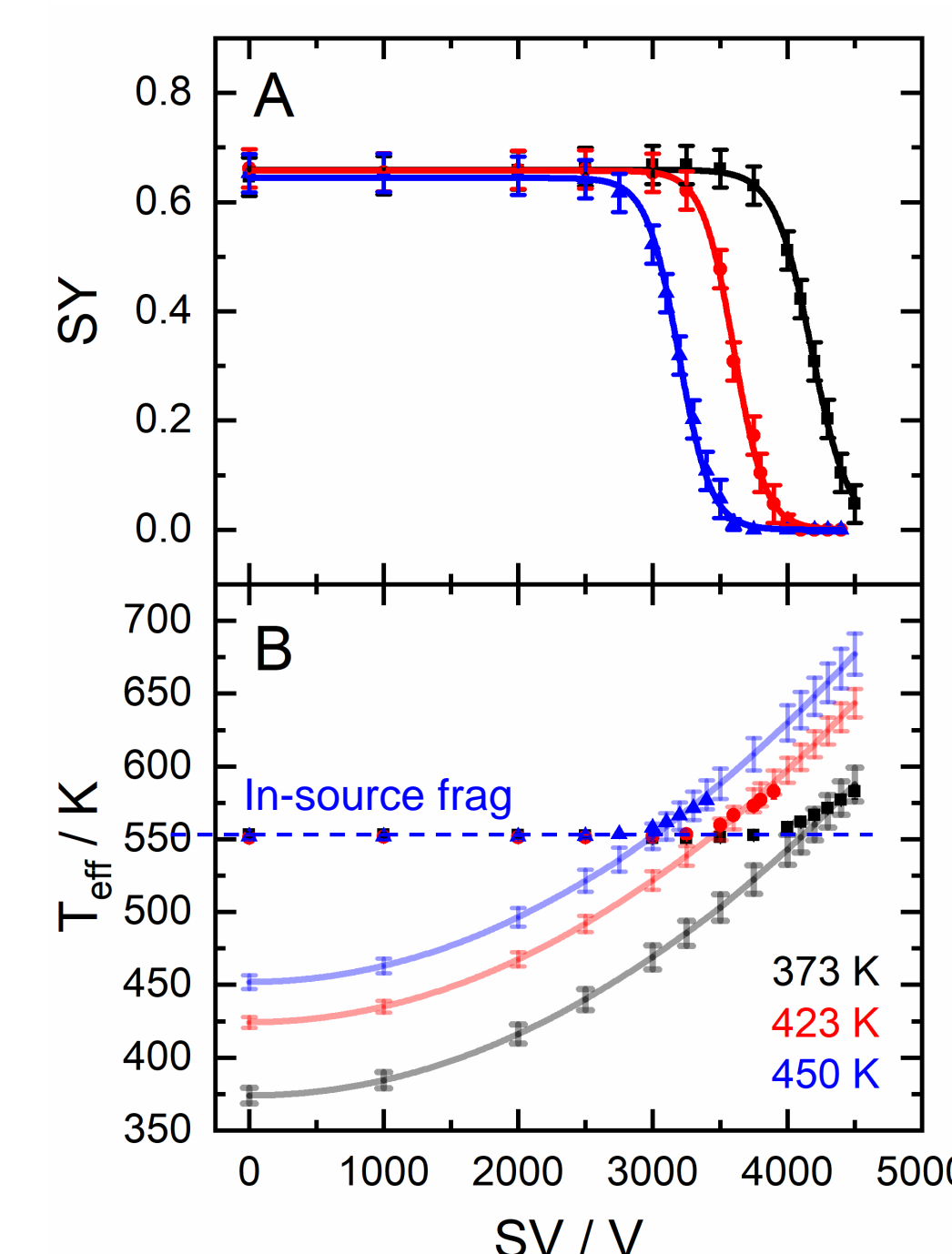

Figure 1. **(A)** *p*-OMe BP survival yields and **(B)** T_{eff} at T_{bath} of 373 (black), 423 (red) and 450 K (blue). Curves are fits to $y = ax^2 + b$
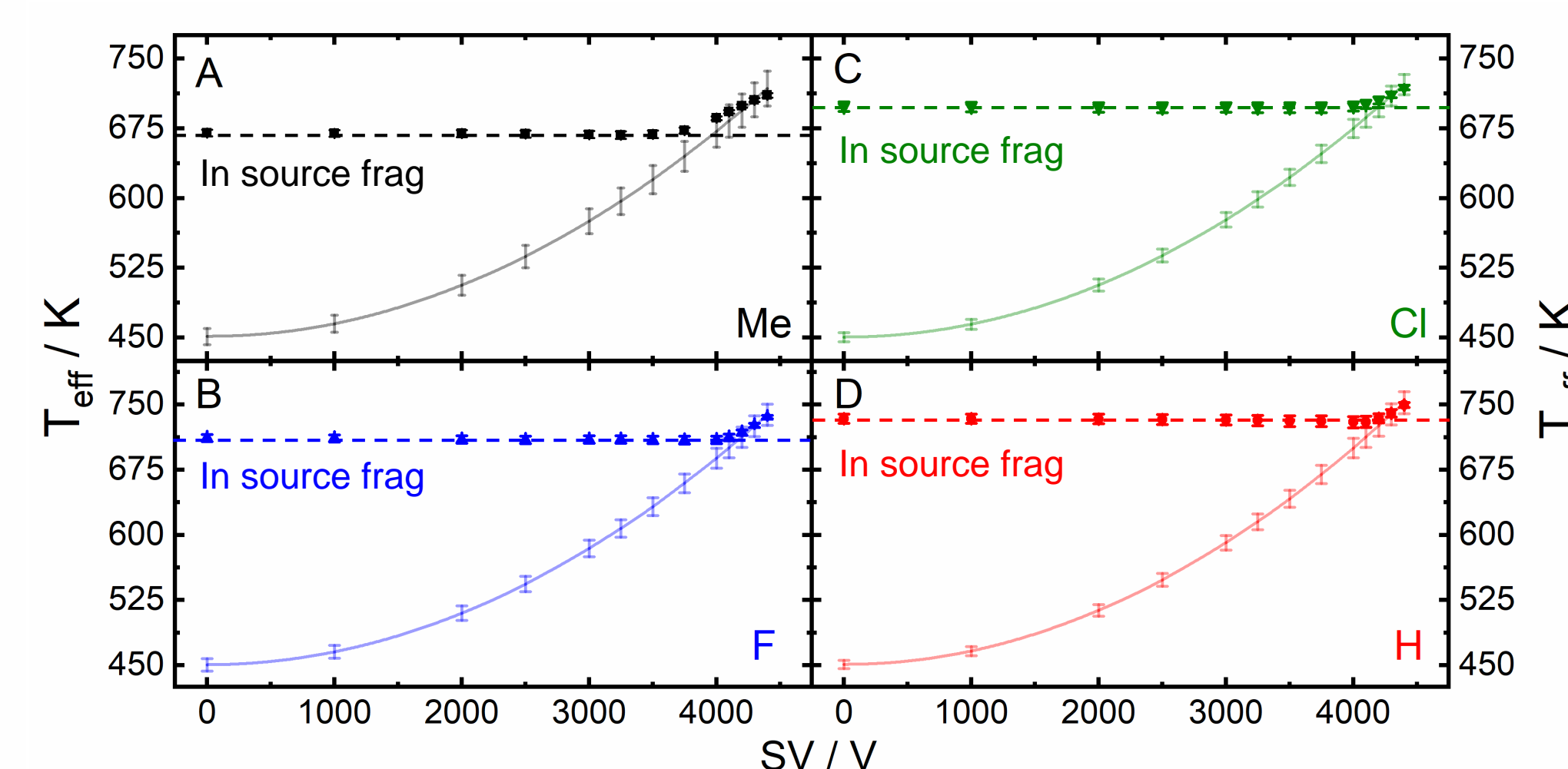
Figure 2. Effective temperatures for the *para*-substituted benzylpyridinium ions (R = H, Cl, F, Me) at T_{bath} = 450 K.
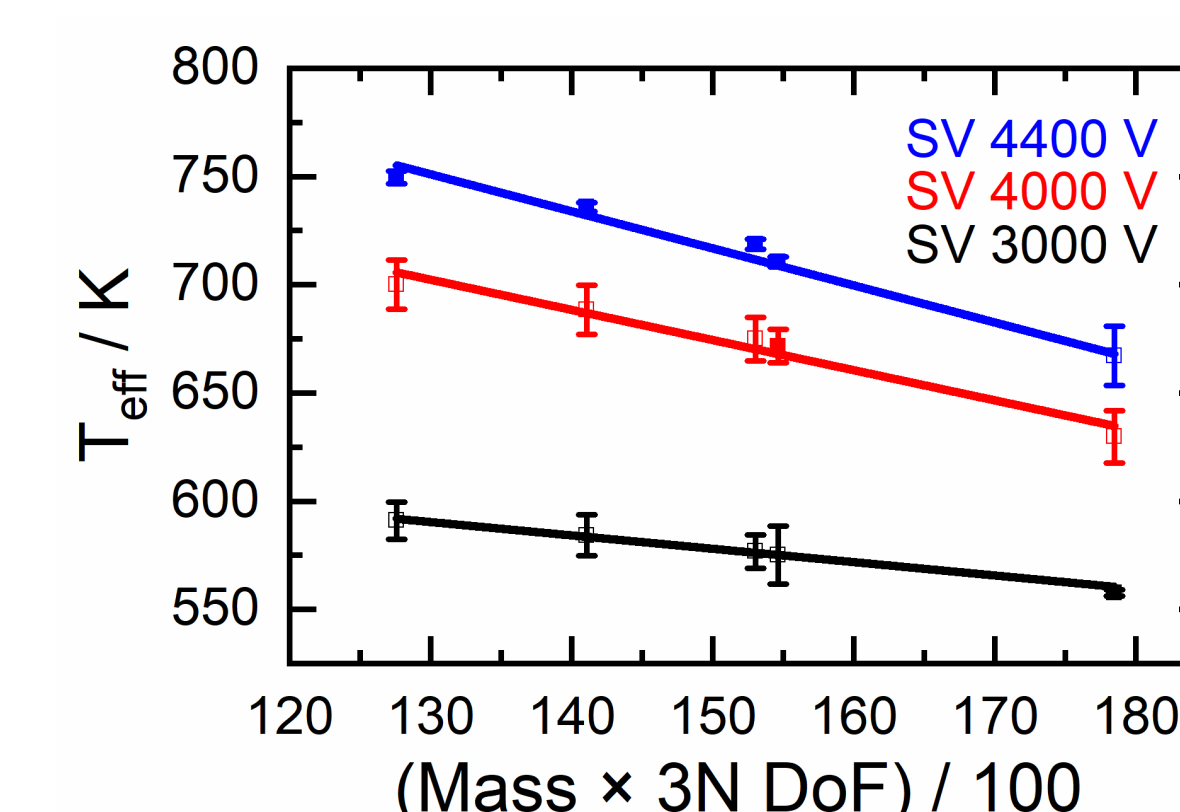
Figure 3. Correlation of T_{eff} determined at SV = 4400 V (blue), 4000 V (red), and 3000 V (black) with ion mass and 3N degrees of freedom (T_{bath} = 450 K).

How does T_{eff} compare with two-temperature theory?

Briefly, the drift velocity v of each BP derivative is evaluated in the typical way, where ion mobility K is defined by the Mason-Schamp relation modified by the alpha (a) function.

$$v = KE = K_0N_0\left(\frac{E}{N}\right) \qquad K(0) = \frac{\sqrt{18\pi}}{16}\sqrt{\frac{1}{m_{ion}} + \frac{1}{m_{gas}}}\frac{ze}{\sqrt{k_bT}}\frac{1}{\Omega}\frac{1}{N} \qquad K\left(\frac{E}{N}\right) = K(0) \cdot \left[1 + \alpha\left(\frac{E}{N}\right)\right]$$

K was evaluated using temperature-dependent CCS calculations performed in MobCal-MPI.[2] The CCSs were fit to a function of the form $a + bT_{eff}^c$. This velocity is then used to evaluate T_{eff} using two-temperature theory, which is then used to re-evaluate ion velocity. The process is completed iteratively until T_{eff} converges to a pre-defined threshold ($\Delta T_{eff} < 10^{-4}$ K).

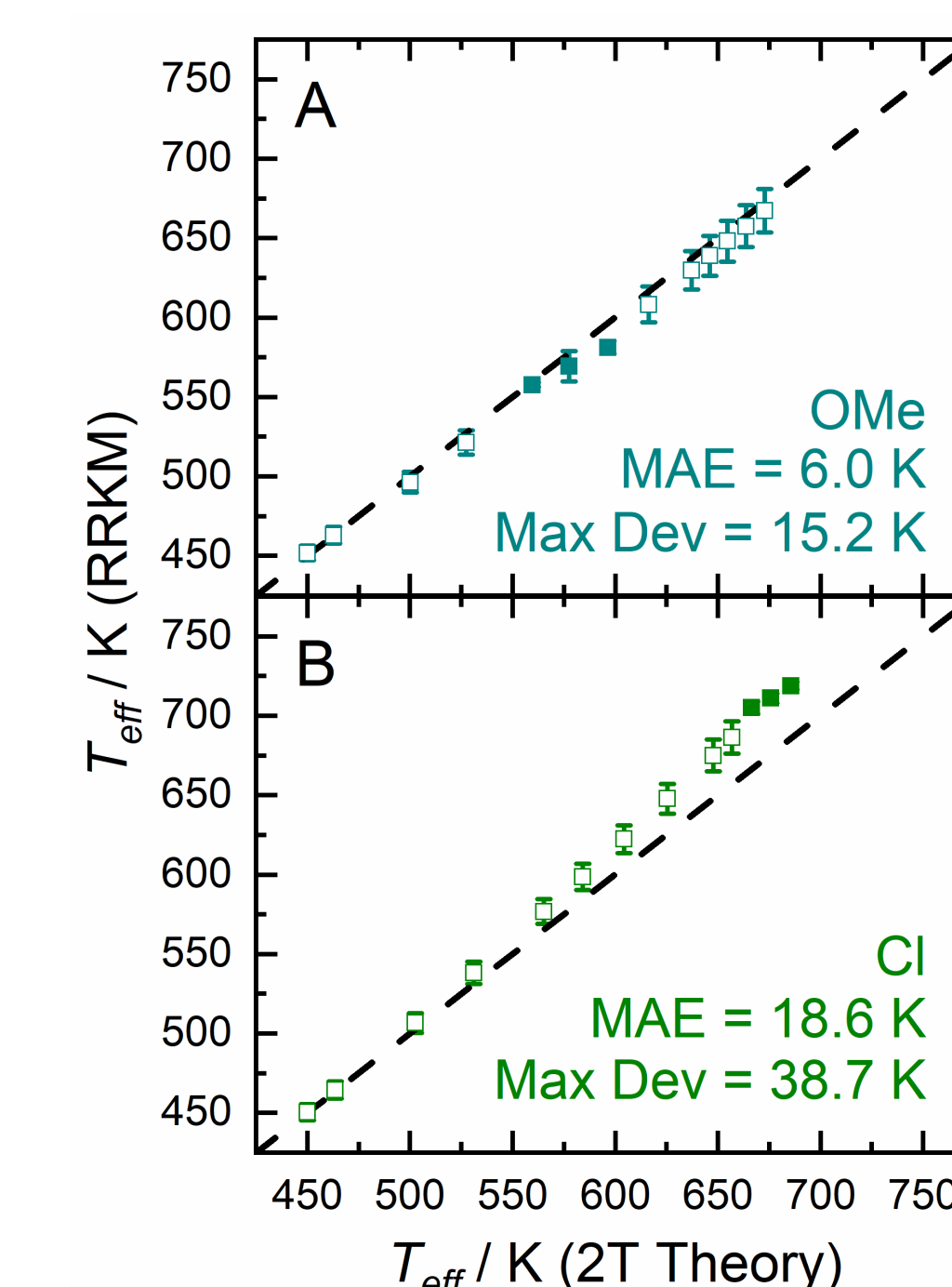$$T_{eff} = T_{bath} + T_{field} \approx T_{bath} + \frac{M}{3k_b}v^2 = T_{bath} + \frac{M}{3k_b}(KE)^2$$

Figure 4. A comparison of experimental and theoretical T_{eff} determined using a self-consistent two temperature theory approach for the **(A)** p-OMe and **(B)** p-Cl BP derivatives. The dashed line corresponds to y = x. Open squares indicate extrapolated T_{eff} determined from the quadratic fit.

Concluding Remarks

The extent of ion heating during DMS experiments is evaluated experimentally by using the survival yields of BP thermometer ions. By characterizing ion temperatures and establishing a correlation between T_{eff} and ion properties, this work provides a step towards elucidating the principles that underpin the phenomenon of differential ion mobility.

References and Acknowledgements

1 M. T. Rodgers, K.M. Ervin, and P.B. Armentrout, *J. Chem. Phys.*, 1997, **106**, 4499–4508.

2 C. Ieritano, J. Crouse, J.L Campbell, and W.S Hopkins, *Analyst*, 2019, **144**, 1660–1670.