Modeling Vapor Uptake Induced Mobility Shifts in Peptide Ions Observed with Transversal Modulation Ion Mobility Spectrometry-Mass Spectrometry

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Supplemental Information

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Derivation of probability (P_g) for Model II

In model II we consider that the ions uptake vapor dopants as predicted by the Langmuir adsorption model and upon collision the vapor molecules can bind at specific sites on the ion, with a total of g_{max} available sites. An ion with 'g-1' vapor molecules bound can undergo a collision limited association reaction to bind with a vapor molecule and also an ion with 'g' vapor molecules bound can undergo a dissociation reaction to emit a vapor molecule from its surface. The balance between these two reactions is noted as:

$$n_{g-1} + n_v \rightleftharpoons n_g$$

where n_g is the number concentration (#/m^3) of ions with g vapor molecules bound, n_v is the number concentration of vapor molecules.

The forward reaction rate for this reaction is calculated as:

$$R_f = k_{f,g-1}(1 - \theta_{f,g-1})n_v n_{g-1} \tag{S1a}$$

where $\theta_{f,g-1}$ is the binding coefficient expressed as:

$$\theta_{f,g-1} = \frac{(g-1)}{g_{max}} \tag{S1b}$$

$k_{f,g-1}$ is the forward rate constant expressed as:

$$k_{f,g-1} = \bar{c}_{v,g-1}\pi(r_{g-1} + r_v)^2 \eta[\psi_{D,g-1}] \tag{S1c}$$

where $\eta[\psi_{D,g}]$ is dimensionless enhancement factor for the collision of an ion with g vapor molecules bound and a vapor molecule, as described in the main text, r_g is the effective radius of the ion with g vapor molecules bound, and r_v is the radius of a vapor molecule. $\bar{c}_{v,g}$ is the mean thermal speed of the reduced mass of a vapor dopant molecule and the ion with g vapor molecules bound calculated as:

$$\bar{c}_{v,g} = \sqrt{\frac{8k_B T}{\pi \mu_{g,v}}} \tag{S1d}$$

where $k_B T$ is the thermal energy and $\mu_{g,v}$ is the reduced mass of the vapor dopant and ion with g vapor molecules bound. Similarly, the backward reaction where one vapor molecule dissociates from an ion with g vapor molecules bound can be expressed as:

$$R_b = k_{b,g}\theta_{b,g}n_{v,surf}n_g \tag{S2a}$$

where $\theta_{b,g}$ is the binding coefficient expressed as:

$$\theta_{b,g} = \frac{g}{g_{max}} \tag{S2b}$$

$k_{b,g}$ is the backward rate constant expressed as:

$$k_{b,g} = \bar{c}_{v,g}\pi\left(r_g + r_v\right)^2 \tag{S2c}$$

$n_{v,surf}$ is the vapor molecule concentration at the surface of the ion. This can be expressed in terms of an effective saturation ratio defined as:

$$S_{eff} = \frac{n_v}{n_{v,surf}} \tag{S3}$$

This effective saturation ratio is also described as:

$$S_{eff} = \gamma S \tag{S4}$$

wherein, γ is the ratio of the saturation vapor pressure of the dopant to the vapor pressure of the dopant above binding site on the ion (i.e. γ is an inverse activity coefficient) and S is the dopant saturation ratio. At equilibrium, the forward reaction rate is equal to the backward reaction rate, so we can equate equations (S1a) & (S2a), which leads to the equation:

$$\frac{n_g}{n_{g-1}} = \frac{k_{f,g-1}(\gamma S)(1-\theta_{f,g-1})}{k_{b,g}\theta_{b,g}} \tag{S5}$$

The probability (P_g) that an ion has g vapor molecules bound at any instant of time can be calculated as:

$$P_g = \frac{n_g}{n_{tot}} \tag{S6a}$$

where n_{tot} is the total number concentration of the ions expressed as:

$$n_{tot} = \sum_{j=0}^{g_{max}}(n_j) \tag{S6b}$$

Therefore equation (S6a) can be alternately expressed as:

$$P_g = \frac{\frac{n_g}{n_0}}{1+\sum_{j=1}^{g_{max}}\left(\frac{n_j}{n_0}\right)} \tag{S7a}$$

The numerator of this equation $\left(\frac{n_g}{n_0}\right)$ is further expressed in the form of a multiplicative sum as:

$$\frac{n_g}{n_0} = \prod_{k=1}^{g}\left(\frac{n_k}{n_{k-1}}\right) \qquad\qquad g\geq1 \tag{S7b}$$

$$\frac{n_g}{n_0} = 1 \qquad\qquad g=0 \tag{S7c}$$

Thereafter, equation (S5) can be used to rewrite equation (S7b) in terms of the rate constants as:

$$\frac{n_g}{n_0} = (\gamma S)^g \prod_{k=1}^{g}\left(\frac{k_{f,k-1}(1-\theta_{f,k-1})}{k_{b,k}\theta_{b,k}}\right) \qquad\qquad g\geq1 \tag{S7d}$$

In conclusion the probability (P_g) can be expressed in terms of the effective saturation ratio, the rate constants and the binding and dissociation coefficients by utilizing equations (S7a), (S7c) and (S7d):

$$P_0 = \frac{1}{1+\sum_{j=1}^{gmax}\left((\gamma S)^j \prod_{k=1}^{j}\left(\frac{k_{f,k-1}(1-\theta_{f,k-1})}{k_{b,k}\theta_{b,k}}\right)\right)} \tag{S7e}$$

$$P_g = \frac{(\gamma S)^g \prod_{j=1}^{g}\left(\frac{k_{f,j-1}(1-\theta_{f,j-1})}{k_{b,j}\theta_{b,j}}\right)}{1+\sum_{j=1}^{gmax}\left((\gamma S)^j \prod_{k=1}^{j}\left(\frac{k_{f,k-1}(1-\theta_{f,k-1})}{k_{b,k}\theta_{b,k}}\right)\right)} \qquad g\geq 1 \tag{S7f}$$

Now substituting in equations (S7e) & (S7f) for the forward and backward rate constants using equations (S1c) & (S2c) and for binding and dissociation coefficients using equations (S1b) and (S2b), P_g can be described by the equations:

$$P_0 = \frac{1}{1+\sum_{j=1}^{gmax}\left((\gamma S)^j \prod_{k=1}^{j}\left(\frac{1-\frac{k-1}{gmax}}{\frac{k}{gmax}}\right)\left(\frac{\mu_{k,v}}{\mu_{k-1,v}}\right)^{1/2}\left(\frac{r_{k-1}+r_v}{r_k+r_v}\right)^2 \eta[\psi_{D,k-1}]\right)} \tag{S8a}$$

$$P_g = \frac{(\gamma S)^g \prod_{j=1}^{g}\left(\left(\frac{1-\frac{j-1}{gmax}}{\frac{j}{gmax}}\right)\left(\frac{\mu_{v,j}}{\mu_{v,j-1}}\right)^{1/2}\left(\frac{r_{j-1}+r_v}{r_j+r_v}\right)^2 \eta[\psi_{D,j-1}]\right)}{1+\sum_{j=1}^{gmax}\left((\gamma S)^j \prod_{k=1}^{j}\left(\frac{1-\frac{k-1}{gmax}}{\frac{k}{gmax}}\right)\left(\frac{\mu_{k,v}}{\mu_{k-1,v}}\right)^{1/2}\left(\frac{r_{k-1}+r_v}{r_k+r_v}\right)^2 \eta[\psi_{D,k-1}]\right)} \qquad g\geq 1 \tag{S8b}$$

Derivation of probability (P_g) for Model III

In model III the classical nucleation theory approach is used to predict the uptake of dopant molecules on the surface of ions and vapor molecules can bind continuously regardless of the site on surface of the ion. The association and dissociation reaction can be expressed in this case as:
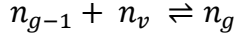
$$n_{g-1} + n_v \rightleftharpoons n_g$$

The forward reaction rate for this reaction is calculated as:

$$R_f = k_{f,g-1} n_v n_{g-1} \qquad\qquad (S9a)$$

$k_{f,g-1}$ is the forward rate constant expressed as:

$$k_{f,g-1} = \bar{c}_{v,g-1} \pi (r_{g-1} + r_v)^2 \eta [\psi_{D,g-1}] \qquad\qquad (S9b)$$

Similarly, the backward reaction can be expressed as:

$$R_b = k_{b,g} n_{v,surf} n_g \qquad\qquad (S10a)$$

$k_{b,g}$ is the backward rate constant expressed as:

$$k_{b,g} = \bar{c}_{v,g} \pi (r_g + r_v)^2 \qquad\qquad (S10b)$$

$n_{v,surf}$ is the vapor molecule concentration at the surface of the ion which can be expressed as:

$$n_{v,surf} = n_{sat} exp\left(-\frac{\Delta E_g}{k_B T}\right) \qquad\qquad (S10c)$$

where n_{sat} is the number concentration of vapor molecules at saturation and ΔE_g is the change in enthalpy of an ion upon uptake of a vapor molecule (*g-1* to *g* molecules bound):

$$\Delta E_k = -\sigma \delta A_k - \frac{(ze)^2}{8\pi\varepsilon_0}\left(1 - \frac{1}{\varepsilon_r}\right)\delta\left(\frac{1}{r_k}\right) \qquad\qquad (S10d)$$

The equation (S10d) integrates the combined influences of Kelvin and Thomson effects in model III as described in the main text. At equilibrium, the forward reaction rate is equal to the backward reaction rate, so we can equate equations S9a and S10a which leads to the equation:

$$\frac{n_g}{n_{g-1}} = \frac{k_{f,g-1} S}{k_{b,g}} exp\left(\frac{\Delta E_g}{k_B T}\right) \qquad\qquad (S11)$$

Following a similar approach as model II and using equations (S7a), (S7b) and (S7c) with equation (S11), P_g can be expressed in this case by the equations:

$$P_0 = \frac{1}{1 + \sum_{j=1}^{\infty}\left((S)^j \prod_{k=1}^{j}\left(\frac{k_{f,k-1}}{k_{b,k}} exp\left(\frac{\Delta E_k}{k_B T}\right)\right)\right)} \qquad\qquad (S12a)$$

$$P_g = \frac{(S)^g \prod_{j=1}^{g}\left(\frac{k_{f,j-1}}{k_{b,j}}exp\left(\frac{\Delta E_j}{k_B T}\right)\right)}{1+\sum_{j=1}^{\infty}\left((S)^j \prod_{k=1}^{j}\left(\frac{k_{f,k-1}}{k_{b,k}}exp\left(\frac{\Delta E_k}{k_B T}\right)\right)\right)} \qquad g\geq1 \qquad (S12b)$$

It should be noted that unlike model II, there is no limiting value for g in model III and the vapor sorption continues as g→∞. Further substituting for the forward and backward rate constants using equations (S9b) and (S10b) in equations (S12a) and (S12b), P_g can be described by the equations:

$$P_0 = \frac{1}{1+\sum_{j=1}^{\infty}(S)^j \prod_{k=1}^{j}\left(exp\left(\frac{\Delta E_k}{k_B T}\right)\left(\frac{\mu_{k,v}}{\mu_{k-1,v}}\right)^{1/2}\left(\frac{r_{k-1}+r_v}{r_k+r_v}\right)^2 \eta[\psi_{D,k-1}]\right)} \qquad (S13a)$$

$$P_g = \frac{(S)^g \prod_{j=1}^{g}\left(exp\left(\frac{\Delta E_j}{k_B T}\right)\left(\frac{\mu_{j,v}}{\mu_{j-1,v}}\right)^{1/2}\left(\frac{r_{j-1}+r_v}{r_j+r_v}\right)^2 \eta[\psi_{D,j-1}]\right)}{1+\sum_{j=1}^{\infty}(S)^j \prod_{k=1}^{j}\left(exp\left(\frac{\Delta E_k}{k_B T}\right)\left(\frac{\mu_{k,v}}{\mu_{k-1,v}}\right)^{1/2}\left(\frac{r_{k-1}+r_v}{r_k+r_v}\right)^2 \eta[\psi_{D,k-1}]\right)} \qquad g\geq1 \qquad (S13b)$$

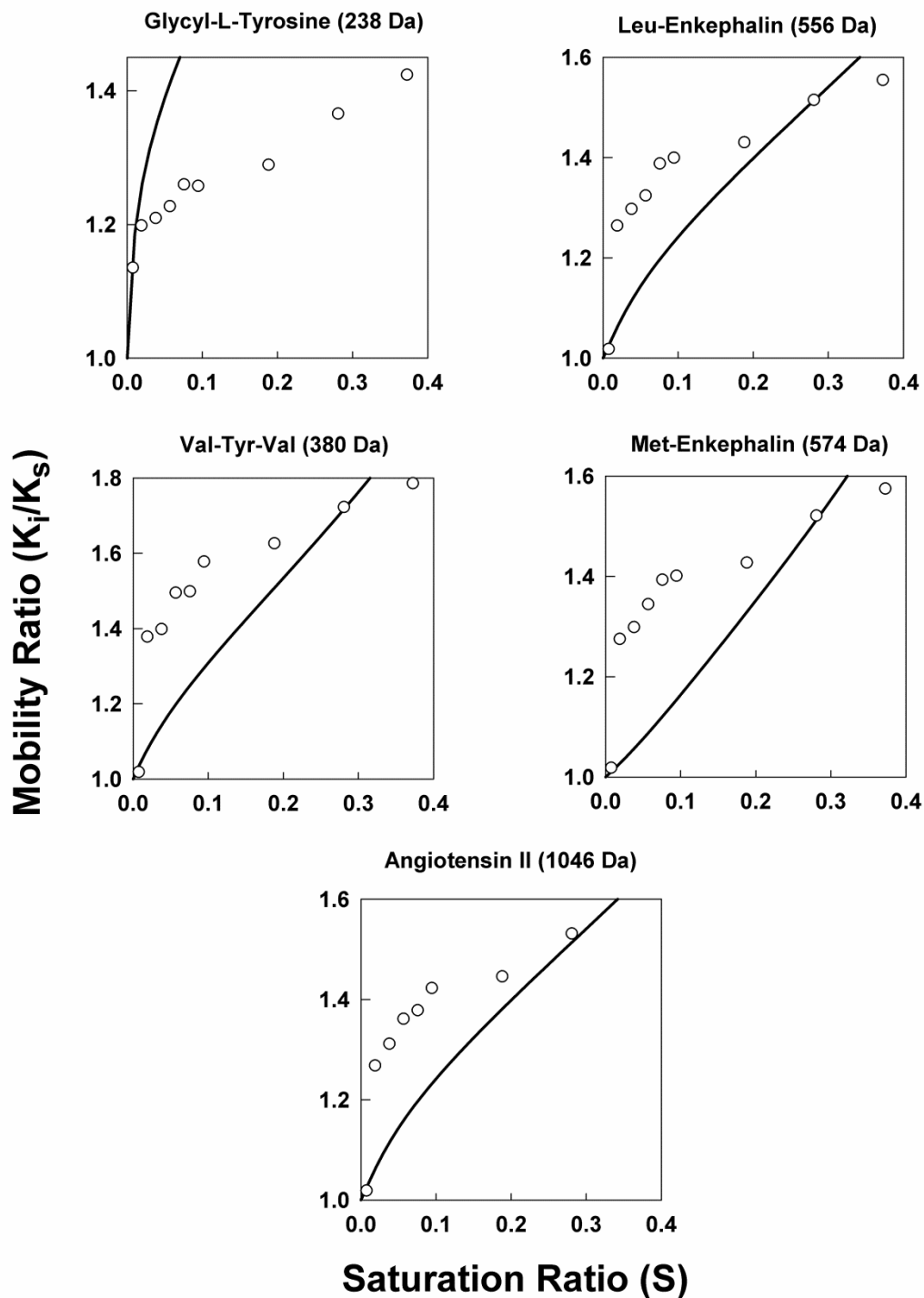# Model III Comparison to Peptide Measurements

Figure S1. A comparison of experimental measurements of the ratio (K_i/K_S) for five peptide ions to model III predictions.

Variable dictionary

Variables:

A	surface area of an ion
$\bar{c}$	mean thermal speed
E	enthalpy of an ion
e	unit electron charge
f	friction factor
g	number of vapor molecules bound
g_{max}	number of available sites in an ion for vapor uptake
K	electrical mobility
k_B	Boltzmann constant
k_f	forward rate constant
k_b	backward rate constant
L	collision cross section enhancement factor for the ion induced dipole potential
n	number concentration
P_g	probability that an ion has g vapor molecules bound
R_f	forward reaction rate
R_b	backward reaction rate
r_b	radius of bath gas molecule
r_g	radius of ion with g vapor molecules bound
r_v	radius of vapor molecule
S	saturation ratio
S_{eff}	effective saturation ratio
T	temperature
z	ion charge state
α	polarizability of bath gas molecules
ε_o	permittivity of free space
ε_r	dielectric constant of vapor dopant
γ	ratio of the saturation vapor pressure to the vapor pressure of the dopant
η	dimensionless enhancement factor for the ion-dipole interaction
μ	reduced mass
μ_D	dipole potential
θ_f	binding coefficient
θ_b	dissociation coefficient
ρ	density
σ	surface tension of vapor dopant
Ω	collision cross section of a ion
ξ	momentum scattering factor
Ψ_D	ion dipole potential energy to thermal energy ratio
Ψ_{pol}	polarization to thermal energy ratio

Subscripts:

0	bath gas molecule and bare ion
0,0	bare ion immersed in pure bath gas
0,g	bath gas molecule and ion with g vapor molecules bound
0,v	bare ion immersed in vapor dopant as a bath gas
b,0	pure bath gas
b,s	bath gas with vapor dopant saturation ratio S
g	ion with g vapor molecules bound
g,0	ion with g vapor molecules bound in pure bath gas
g,v	ion with g vapor molecules bound immersed in vapor dopant as a bath gas
i	initial
j	summation index for vapor molecules
k	summation index for vapor molecules
s	at saturation ratio S
sat	at saturated conditions of vapor dopant
surf	at surface of the ion
tot	total
v	vapor molecule and bare ion
v,g	vapor molecule and ion with g vapor molecules bound