# Electronic supplementary information (ESI) to: Dynamics of third order direct three-body recombination of heavy ions

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In this electronic supplementary information, we provide some details on the choice of the initial conditions for trajectories within the Monte Carlo approach and present the figures not included in the main text of the paper.

Throughout this text, we will use atomic units (unless when stated otherwise). Let $\mu_\mathrm{i}$ be the reduced mass of the ions $\mathrm{M}^+ = \mathrm{Cs}^+$ and $\mathrm{X}^- = \mathrm{F}^-$, $\mathrm{I}^-$, and let $\mu_\mathrm{R}$ be the reduced mass of the ion pair and the atom R = Ar, Xe (the third body).

Let $E_\mathrm{i}$ denote the energy of approach of the ions, $E_\mathrm{R}$ the third body energy, $b_\mathrm{i}$ the impact parameter of the ion encounter, and $b_\mathrm{R}$ the impact parameter of the third body. We set the initial internuclear distance $d_\mathrm{i}$ between the ions to be large and equal to 250 a.u. It was supposed that at the initial time instant $t = 0$, the center of mass of the ion pair coincides with the origin of the fixed Cartesian coordinate frame $Oxyz$ and has zero velocity.

Let $\mathbf{v}_\mathrm{i}$ be the initial velocity of the $\mathrm{M}^+$ ion with respect to the $\mathrm{X}^-$ ion and $\mathbf{d}_\mathrm{i}$ be the vector connecting the ions at $t = 0$ and directed from $\mathrm{X}^-$ to $\mathrm{M}^+$. The direction of the $\mathbf{v}_\mathrm{i}$ vector is characterized by the polar angle $\Theta$ measured from the $Ox$ axis ($0 \le \Theta \le \pi$) and the corresponding azimuthal angle $\Phi$ ($0 \le \Phi < 2\pi$). In other words,

$$\mathbf{v}_\mathrm{i} = v_\mathrm{i}\,\mathbf{e}_{\Theta,\Phi}, \quad v_\mathrm{i} = (2E_\mathrm{i}/\mu_\mathrm{i})^{1/2},$$

where

$$\mathbf{e}_{\Theta,\Phi} = (\cos\Theta,\, \sin\Theta\cos\Phi,\, \sin\Theta\sin\Phi).$$

In the case of a central encounter of the ions ($b_\mathrm{i} = 0$), one has $\mathbf{d}_\mathrm{i} = -d_\mathrm{i}\,\mathbf{e}_{\Theta,\Phi}$. For non-central encounters of the ions ($0 < b_\mathrm{i} \le d_\mathrm{i}$), one needs the third orientation angle $\gamma$ ($0 \le \gamma < 2\pi$) to specify the direction of the $\mathbf{d}_\mathrm{i}$ vector. This angle describes the position of the oriented plane spanned by the vectors $\mathbf{v}_\mathrm{i}$ and $\mathbf{d}_\mathrm{i}$. To be more precise, let $\mathbf{f}_{\Theta,\Phi}$ and $\mathbf{g}_{\Theta,\Phi}$ be two unit vectors (fixed beforehand) orthogonal to each other and to the $\mathbf{e}_{\Theta,\Phi}$ vector. Then

$$\mathbf{d}_\mathrm{i} = -(d_\mathrm{i}^2 - b_\mathrm{i}^2)^{1/2}\,\mathbf{e}_{\Theta,\Phi} + (b_\mathrm{i}\cos\gamma)\,\mathbf{f}_{\Theta,\Phi} + (b_\mathrm{i}\sin\gamma)\,\mathbf{g}_{\Theta,\Phi}.$$

For instance, one can set

$$\mathbf{f}_{\Theta,\Phi} = (-\sin\Theta,\, \cos\Theta\cos\Phi,\, \cos\Theta\sin\Phi),$$
$$\mathbf{g}_{\Theta,\Phi} = (0,\, \sin\Phi,\, -\cos\Phi).$$

Now consider two material points with the reduced mass equal to $\mu_\mathrm{i}$ that move along a straight line towards each other under Coulomb attraction with the potential $-1/r$ ($r$ being the distance between the points). Suppose that $r = d_\mathrm{i}$ at the initial time instant $t = 0$, while the relative kinetic energy of the points is equal to $E_\mathrm{i}$. Assume the total internal energy $E_\mathrm{tot} = E_\mathrm{i} - 1/d_\mathrm{i}$ of the system of the two points to be positive, so that $E_\mathrm{tot}$ is the relative kinetic energy of the points at infinity. Then it is not hard to verify that the points will meet each other in the time equal to

$$\tau = \tau(d_\mathrm{i}, E_\mathrm{i}, \mu_\mathrm{i}) = (\mu_\mathrm{i}/2)^{1/2} \int_0^{d_\mathrm{i}} \frac{r\,dr}{[r(E_\mathrm{tot}r + 1)]^{1/2}} = (\mu_\mathrm{i}/2)^{1/2} E_\mathrm{tot}^{-3/2}[AB - \ln(A + B)], \tag{1}$$

where

$$A = (E_\mathrm{tot}d_\mathrm{i})^{1/2}, \quad B = (A^2 + 1)^{1/2}.$$

For $E_\mathrm{i}$ of the order of several electron volts and for $d_\mathrm{i} = 250$ a.u., the difference between $E_\mathrm{i}$ and $E_\mathrm{tot}$ is not essential for our studies, because $0.004\ E_\mathrm{h} = 0.1088$ eV. Similarly, we do not pay attention to the difference between the impact parameter $b_\mathrm{i}$ at the initial internuclear distance $d_\mathrm{i}$ and the "true" impact parameter $(E_\mathrm{i}/E_\mathrm{tot})^{1/2}b_\mathrm{i}$ at infinity.

We supposed that at the initial time instant, the velocity of the R atom is

$$\mathbf{v}_\mathrm{R} = (-v_\mathrm{R},\, 0,\, 0), \quad v_\mathrm{R} = (2E_\mathrm{R}/\mu_\mathrm{R})^{1/2},$$

and the coordinates of the R atom are

$$(d_\mathrm{R},\, b_\mathrm{R},\, 0), \quad d_\mathrm{R} = (1 + T_\mathrm{del})v_\mathrm{R}\tau(d_\mathrm{i}, E_\mathrm{i}, \mu_\mathrm{i}),$$

where $T_\mathrm{del}$ is the delay parameter.

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For reference purposes, discuss also the problem of *non-central* approach of two material points connected by the Coulomb potential $-1/r$. Let again these points with the reduced mass equal to $\mu_\mathrm{i}$ and with the total internal energy equal to $E_\mathrm{tot} > 0$ move towards each other, but assume the angular momentum of the system of the points to be equal to $L \neq 0$. Suppose again that $r = d_\mathrm{i}$ at the initial time instant $t = 0$. Then it is not hard to verify that the distance $r$ between the points will attain its minimum equal to

$$r_\mathrm{min} = \frac{(4E_\mathrm{tot}\Delta + 1)^{1/2} - 1}{2E_\mathrm{tot}}, \quad \Delta = \frac{L^2}{2\mu_\mathrm{i}},$$

in the time equal to

$$\begin{aligned} &(\mu_\mathrm{i}/2)^{1/2} \int_{r_\mathrm{min}}^{d_\mathrm{i}} \frac{r\,dr}{(E_\mathrm{tot}r^2 + r - \Delta)^{1/2}} \\ &= (\mu_\mathrm{i}/2)^{1/2} E_\mathrm{tot}^{-3/2} (\mathcal{A} - \mathcal{B} + \mathcal{C}), \end{aligned} \tag{2}$$

where

$$\begin{aligned} \mathcal{A} &= [E_\mathrm{tot}(E_\mathrm{tot}d_\mathrm{i}^2 + d_\mathrm{i} - \Delta)]^{1/2}, \\ \mathcal{B} &= \tfrac{1}{2}\ln(2\mathcal{A} + 2E_\mathrm{tot}d_\mathrm{i} + 1), \\ \mathcal{C} &= \tfrac{1}{4}\ln(4E_\mathrm{tot}\Delta + 1). \end{aligned}$$

If $L = 0$, then $r_\mathrm{min} = 0$ and eqn (2) turns to eqn (1).

## References


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2 E. K. Parks, M. Inoue and S. Wexler, Collision induced dissociation of CsI and $Cs_2I_2$ to ion pairs by Kr, Xe, and $SF_6$, *J. Chem. Phys.*, 1982, **76**, 1357–1379.


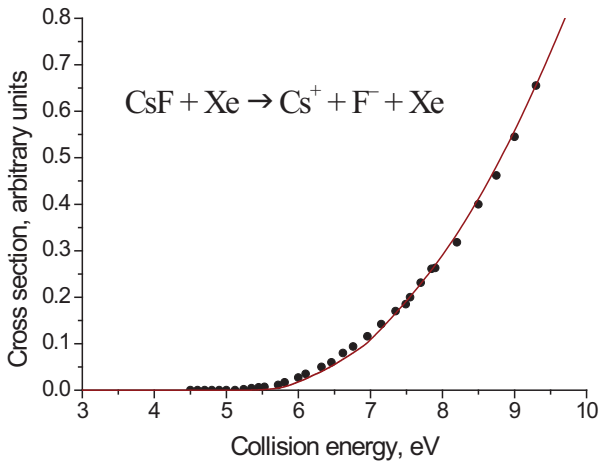


Fig. S1 The excitation functions of the reaction CsF + Xe → $Cs^+ + F^- + Xe$: the experiment[1] (the dots) and the trajectory simulation (the solid line).

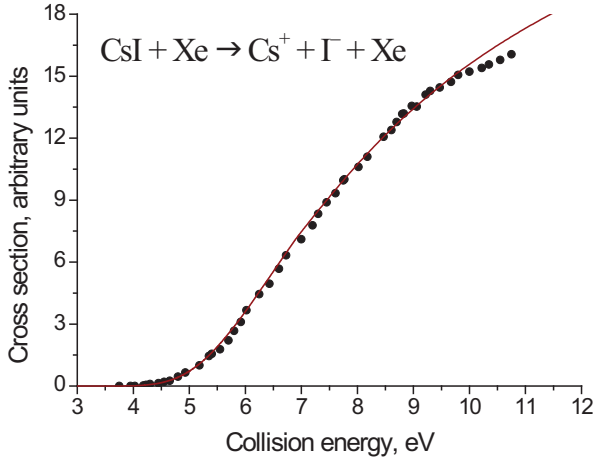


Fig. S2 The excitation functions of the reaction CsI + Xe → $Cs^+ + I^- + Xe$: the experiment[1,2] (the dots) and the trajectory simulation (the solid line).

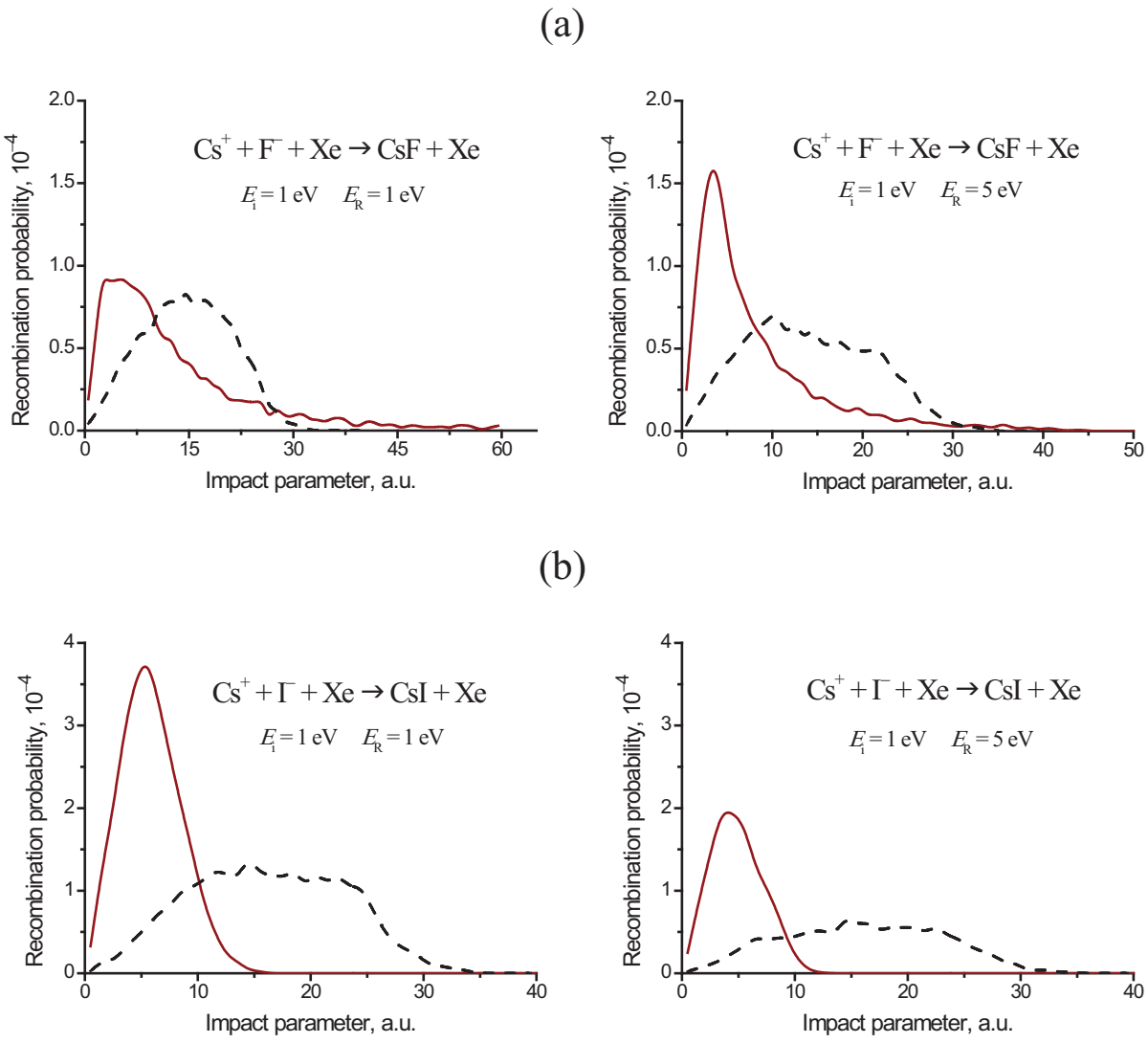


Fig. S3 The $b_{\rm i}$ (the dashed lines) and $b_{\rm R}$ (the solid lines) opacity functions of recombination $Cs^+ + F^-$ (a) and $Cs^+ + I^-$ (b) in the presence of Xe as the third body for $E_{\rm i} = 1$ eV and $E_{\rm R} = 1$ or 5 eV ($T_{\rm del} = 0$).

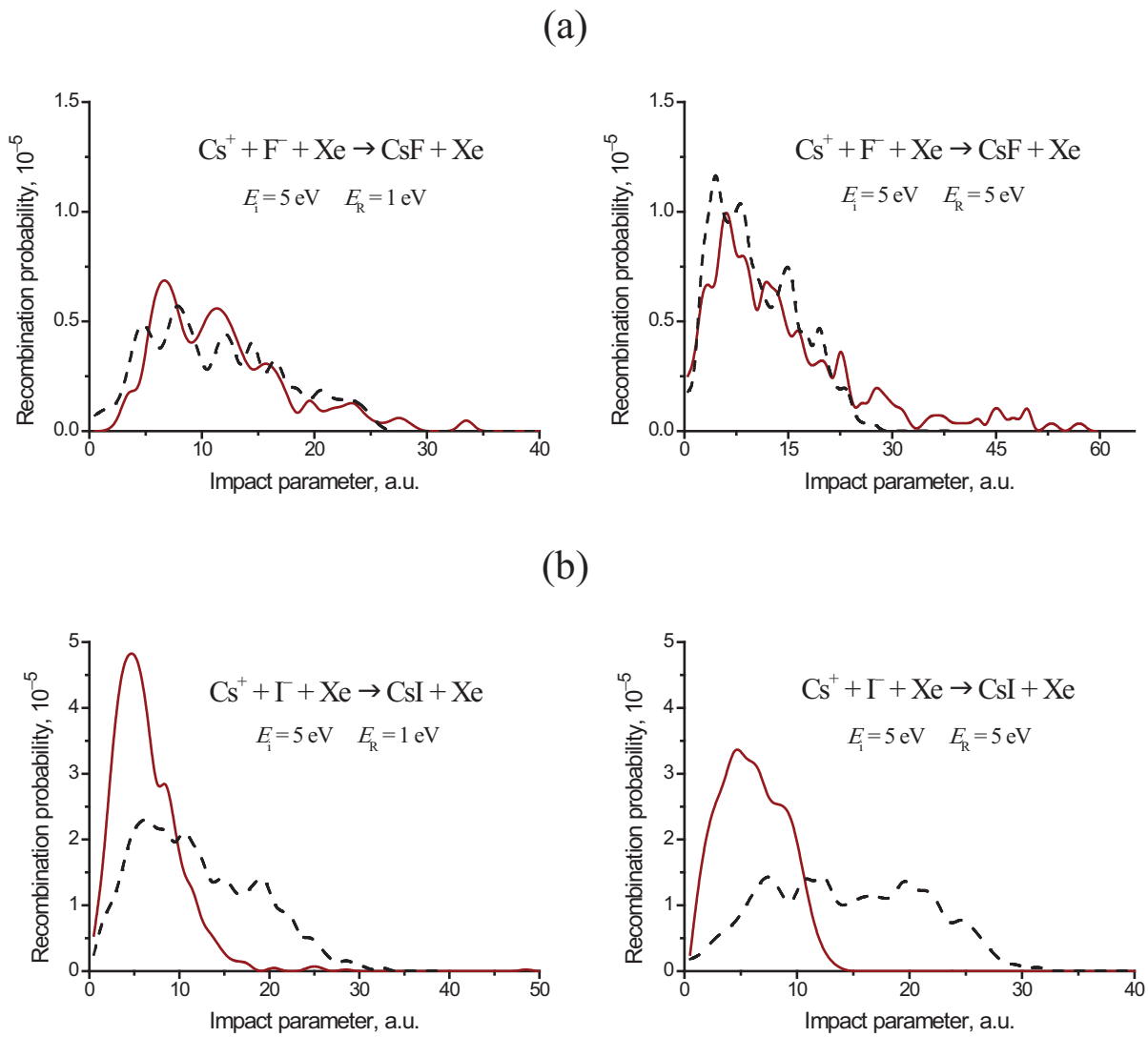


Fig. S4 The $b_{\rm i}$ (the dashed lines) and $b_{\rm R}$ (the solid lines) opacity functions of recombination $Cs^+ + F^-$ (a) and $Cs^+ + I^-$ (b) in the presence of Xe as the third body for $E_{\rm i} = 5$ eV and $E_{\rm R} = 1$ or 5 eV ($T_{\rm del} = 0$).

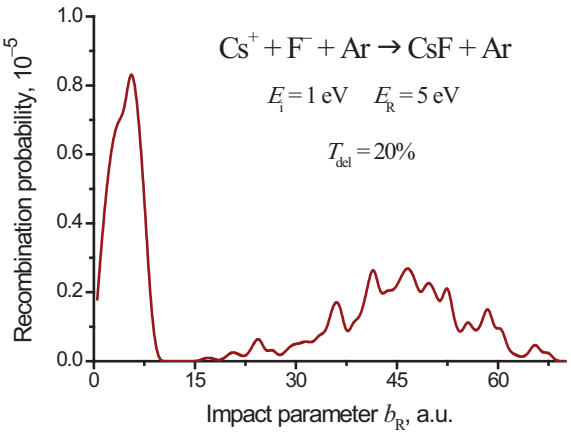


Fig. S5 The $b_{\rm R}$ opacity function of recombination $Cs^+ + F^-$ in the presence of Ar as the third body for $E_{\rm i} = 1$ eV, $E_{\rm R} = 5$ eV ($T_{\rm del} = 20\%$).

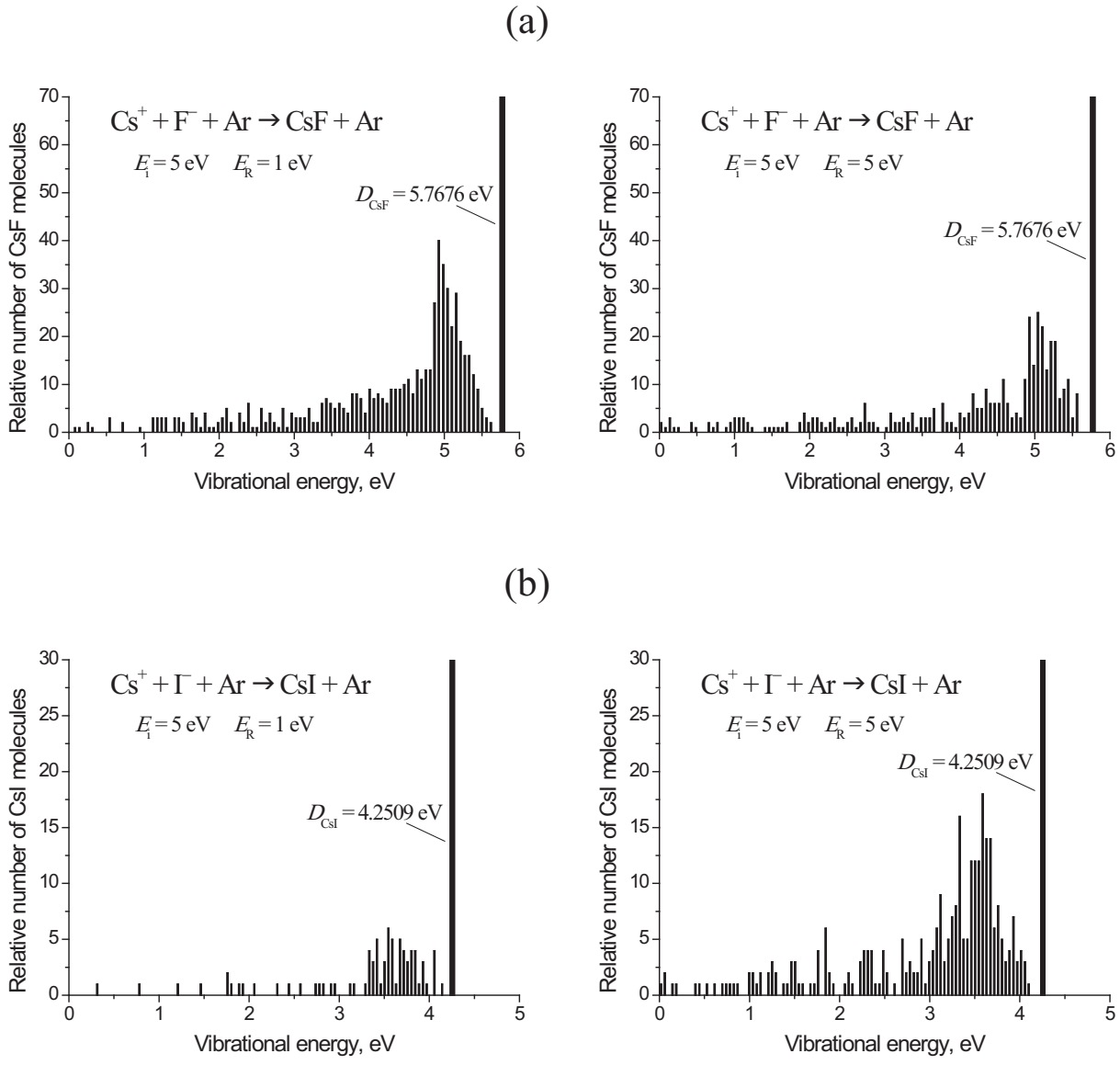


Fig. S6 The vibrational energy distributions of the salt molecules formed in recombination $Cs^+ + F^-$ (a) and $Cs^+ + I^-$ (b) in the presence of Ar as the third body for $E_i = 5$ eV and $E_R = 1$ or 5 eV ($T_{del} = 0$).

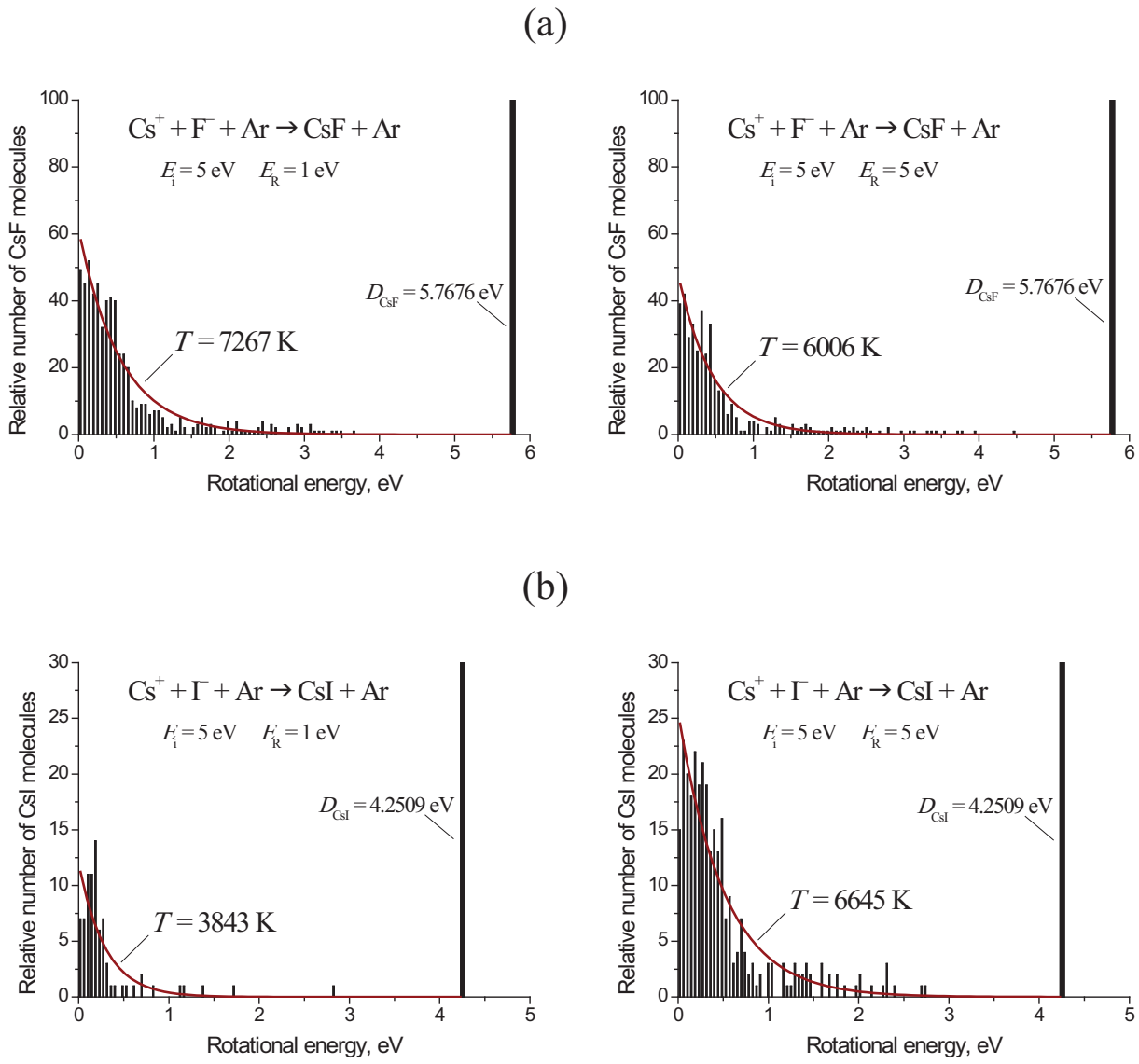


Fig. S7 The rotational energy distributions of the salt molecules formed in recombination $Cs^+ + F^-$ (a) and $Cs^+ + I^-$ (b) in the presence of Ar as the third body for $E_i = 5$ eV and $E_R = 1$ or 5 eV ($T_{del} = 0$). The solid lines show the Boltzmann rotational distributions at the temperatures indicated.

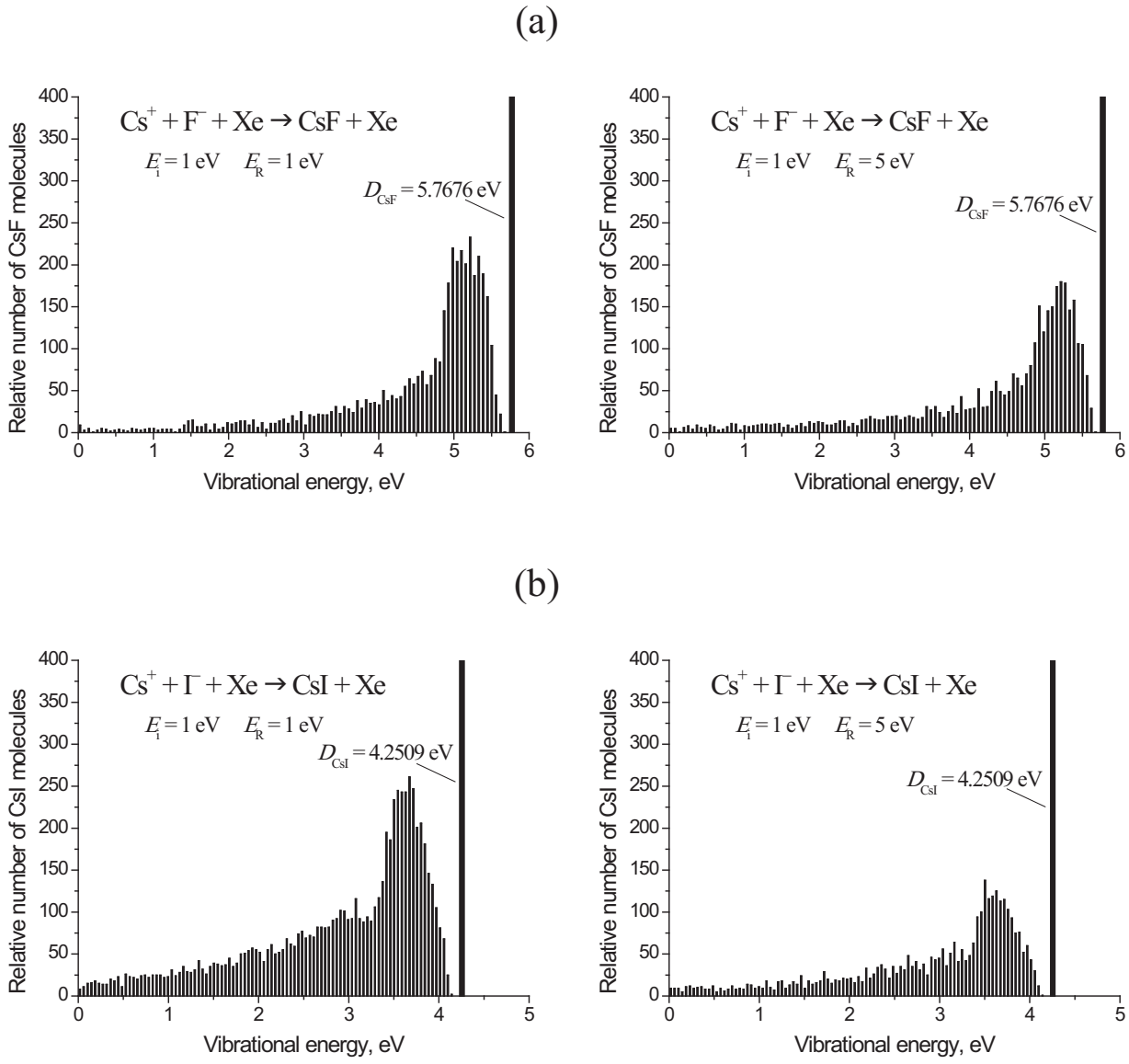


Fig. S8 The vibrational energy distributions of the salt molecules formed in recombination $Cs^+ + F^-$ (a) and $Cs^+ + I^-$ (b) in the presence of Xe as the third body for $E_i = 1$ eV and $E_R = 1$ or 5 eV ($T_{del} = 0$).

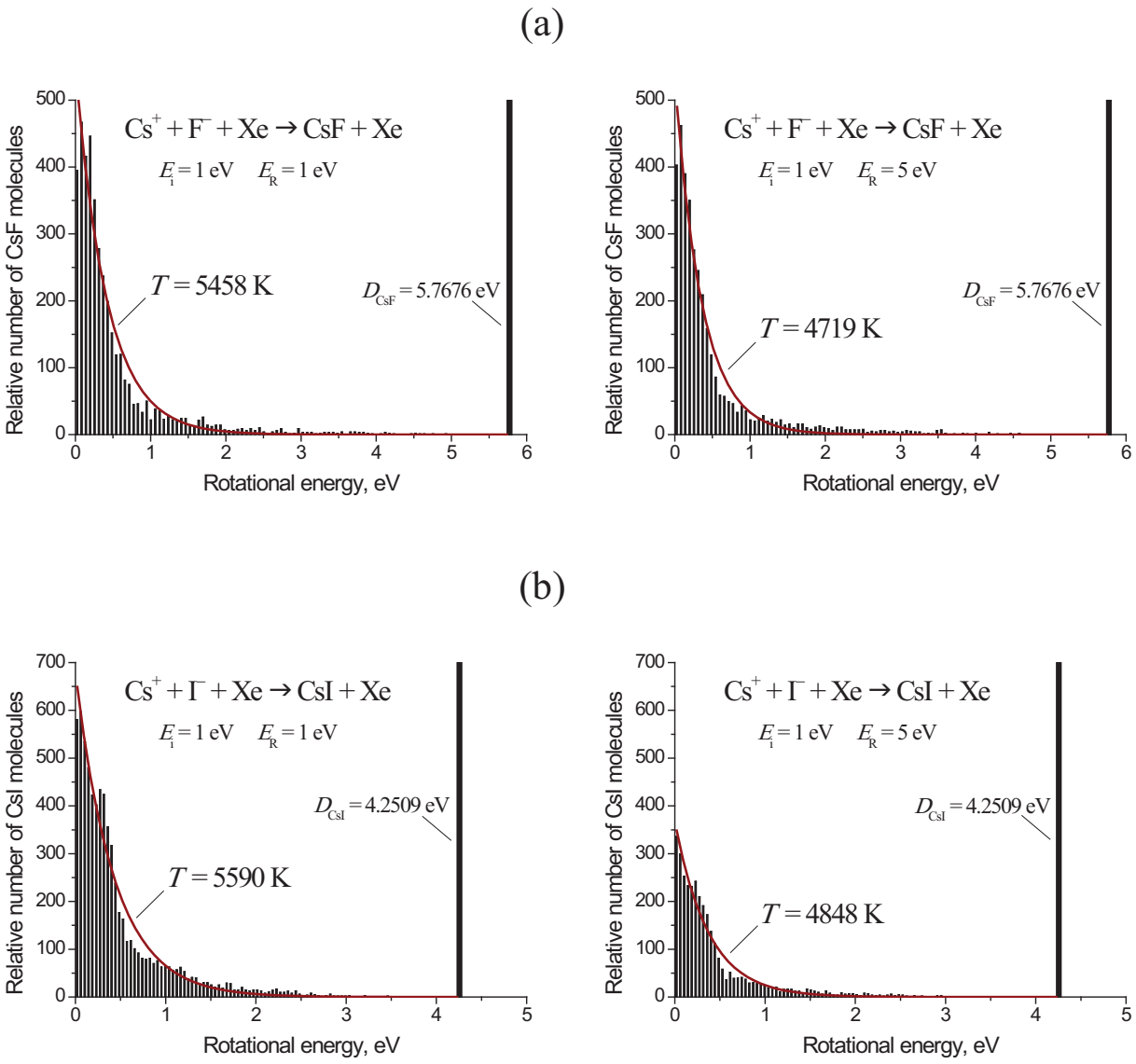


Fig. S9 The rotational energy distributions of the salt molecules formed in recombination $Cs^+ + F^-$ (a) and $Cs^+ + I^-$ (b) in the presence of Xe as the third body for $E_i = 1$ eV and $E_R = 1$ or 5 eV ($T_{del} = 0$). The solid lines show the Boltzmann rotational distributions at the temperatures indicated.

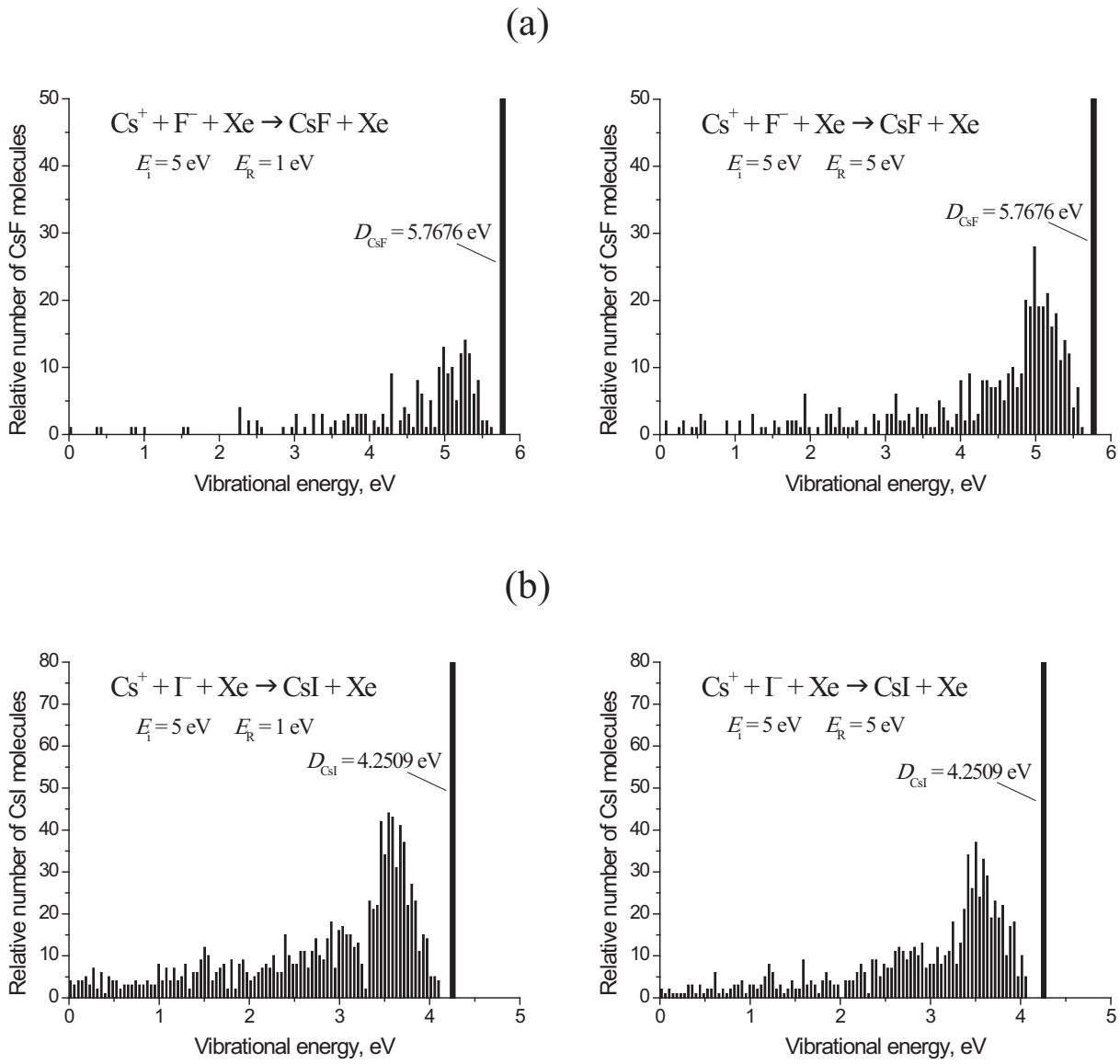


Fig. S10 The vibrational energy distributions of the salt molecules formed in recombination $Cs^+ + F^-$ (a) and $Cs^+ + I^-$ (b) in the presence of Xe as the third body for $E_i = 5$ eV and $E_R = 1$ or 5 eV ($T_{del} = 0$).

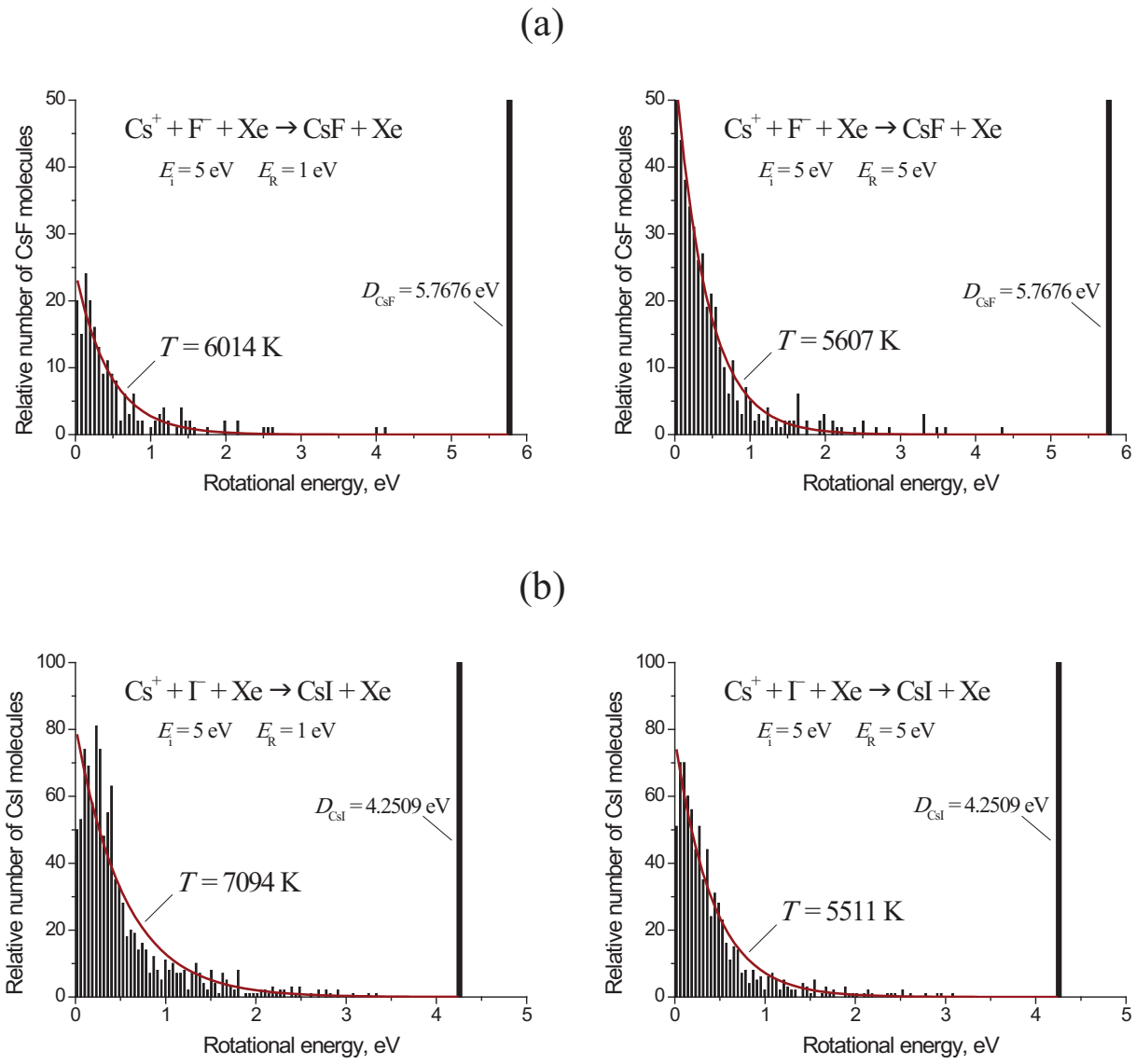


Fig. S11 The rotational energy distributions of the salt molecules formed in recombination $Cs^+ + F^-$ (a) and $Cs^+ + I^-$ (b) in the presence of Xe as the third body for $E_i = 5$ eV and $E_R = 1$ or 5 eV ($T_{del} = 0$). The solid lines show the Boltzmann rotational distributions at the temperatures indicated.