

# EFFECT OF INDUCED DIPOLE-INDUCED DIPOLE POTENTIAL AND THE SIZE OF COLLIDING PARTICLES ON ION-QUADRUPOLEAR MOLECULE COLLISION RATE CONSTANTS

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**ABSTRACT:** *Classical trajectory (Monte Carlo) calculation is used to calculate collision rate constants of ion-quadrupolar molecule interactions for the  $H^- + C_2H_2$  system. The method presented here takes into account the effect of the induced dipole-induced dipole potential on ion-quadrupolar molecule collision rate constants. It is also assumed that the colliding particles have a definite size. The thermal energy collision rate constants are calculated at 300-3000 K temperature range and the kinetic energy dependence of rate constants is examined at a relative kinetic energy of the colliding particles in the range from thermal energy up to  $\sim 1.3$  eV. It is suggested that the induced dipole-induced dipole potential term and the particles size are important factors and should not be ignored when calculating collision rate constants of ion-quadrupolar molecule system.*

**KEY WORDS:** *Classical trajectory (Monte Carlo) calculation, Ion-quadrupolar molecule collision rate constants, Induced dipole-induced dipole potential.*

## INTRODUCTION

There is a growing interest regarding the role of the induced dipole-induced dipole ( $r^{-6}$ ) term in the ion-molecule potential in determining collision rate constants. *Su and Bowers* [1] have tried to calculate theoretically the effect of the  $r^{-6}$  term on ion-

nonpolar molecule collision rate constants. They have shown that the inclusion of the  $r^{-6}$  term arising from the induced dipole-induced dipole interaction slightly increases the theoretical thermal energy capture rate constant, especially when the polariza-

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bility of the ion is large. *Celli, Weddle and Ridge* [2] have shown that the  $r^{-6}$  term is important in determining ion-molecule collision rate constants. A trajectory calculation by *Su and Hu* [3] confirms that the induced dipole-induced dipole term in the ion-polar molecule potential has a significant effect on ion-molecule collision rate constants.

In dealing with ion-quadrupolar molecule interactions, *Su and Bowers* have developed the Average Quadrupole Orientation (AQO) theory [4] which takes into account the ion-quadrupole interaction. This theory is for those molecules that belong to the  $D_{\infty h}$  point group and assumes that the ion behaves as a point charge. However, the AQO theory does not consider the effect of the induced dipole-induced dipole potential on ion-quadrupolar molecule collision rate constants.

*Bohme, Mackay and Tanka* [5] have employed the flowing after glow technique to measure the rate constants for various ion-quadrupolar molecule reactions. They have shown that the AQO theory underestimates collision rate constants by 10-60%. Comparing the measured rate constants with AQO prediction suggests a small contribution of the induced dipole-induced dipole potential to the collision rate constants.

In recent years, little attention has been devoted to the theoretical treatment of the coupling of both the ion-quadrupole potential and the induced dipole-induced dipole potential in calculating ion-quadrupolar molecule collision rate constants.

In this paper, we present the trajectory calculations of collision rate constants at various temperatures and relative kinetic energies for the system  $H^- + C_2H_2$ . The effect of the induced dipole-induced dipole and the size of the colliding particles on the collision rate constants are examined in detail.

## THEORY

In this work, the Monte Carlo classical trajectory method is used to study collision of  $H^-$  with  $C_2H_2$ .

### Temperature dependence of collision rate constants

To determine the thermal energy capture rate constant it is often convenient to consider the micro-

canonical rate constant at a given total energy  $E$  which is given by

$$K_{\text{cap}}(E) = \frac{F_{\text{cap}}(E)}{\rho(E)} \quad (1)$$

where  $F_{\text{cap}}(E)$  is the microcanonical capture flux. The total density of states per unit volume of a point charge and linear rotor at infinite separation,  $\rho(E)$ , is given by

$$\rho(E) = \frac{I(2\mu E)^{3/2}}{3\pi^2 \hbar^5} \quad (2)$$

where  $\hbar = h/2\pi$  and  $h$  is the Planck's constant and  $\mu$  is the reduced mass.  $I$  is the moment of inertia of the polar molecule. The thermal energy capture collision rate constant  $K_{\text{cap}}(T)$  is obtained by averaging  $K_{\text{cap}}(E)$  over a five dimensional Boltzmann energy distribution  $P(T,E)$ ,

$$K_{\text{cap}}(T) = \int_0^{\infty} P(T,E) K_{\text{cap}}(E) dE \quad (3)$$

where

$$P(T,E) = \left(\frac{4}{3\sqrt{\pi}}\right) \left(\frac{1}{K_B T}\right)^{5/2} E^{3/2} \exp(-E/K_B T) \quad (4)$$

$K_B$  is the Boltzmann constant and  $T$  is the system temperature. The rate constant at a given total energy is given by

$$K_{\text{cap}}(E) = \frac{3\pi^2}{2I\pi(2\mu E)^{3/2}} \int \chi[p,q] 4LJdLdJ \quad (5)$$

where  $L$  is the orbital angular momentum of the collision partners,  $J$  and  $I$  are the angular momentum and the moment of inertia of the polar molecule respectively.  $\chi[p,q]$  is characteristic function which labels the trajectory with initial condition of momentum and coordinate  $[p,q]$  on  $r$  as reactive or non reactive. To determine the thermal energy capture collision rate constant  $K_{\text{cap}}(T)$ , Eqs. (3), (4) and (5) are combined to obtain

$$K_{\text{cap}}(T) = \frac{2\sqrt{\pi}}{IK_B T(2\mu K_B T)^{3/2}} \int \chi[p,q] 4LJdLdJ \exp(-E/K_B T) dE \quad (6)$$

### Kinetic energy dependence of collision rate constants

The capture rate constant at a given relative kinetic energy  $E_t$  and thermal neutral rotational energy  $E_r$  at temperature  $T$  is given by

$$K_{\text{cap}}(E_t, T) = \frac{G^*(E_t, T)}{\rho(E_t)} \quad (7)$$

where  $G^*(E_t, T)$  is the sum of states (rotational,

vibrational, translational) at  $E_t$  and  $T$  over all phase space (momentum and coordinate) and is given by

$$G^{\ddagger}(E_t, T) = \int \chi[p, q] 2L dL d\gamma_L d\alpha_L P(T, E_t) dE_t \quad (8)$$

where

$$P(T, E_t) = \frac{1}{K_B T} \exp(-E_t/K_B T)$$

is the two-dimensional Boltzmann distribution function.  $\gamma_L$  and  $\alpha_L$  are Euler angles ( $0 \leq \gamma_L, \alpha_L \leq 2\pi$ ) representing the relative orbiting motion of a polar molecule with respect to ion. The translational density of states per unit volume of the colliding partners at infinite separation is defined by

$$\rho(E_t) = \frac{2\pi(2\mu)^{3/2} E_t^{1/2}}{(2\pi\hbar)^3} \quad (9)$$

Thus, the capture rate constant at a given relative kinetic energy  $E_t$  and thermal neutral rotational energy at temperature  $T$  is given by

$$K_{cap}(E_t, T) = \frac{\pi}{\mu^{3/2}(2E_t)^{1/2}K_B T} \int_0^{\infty} \int_0^{L^*} \chi[p, q] 2L dL \exp(-E_t/K_B T) dE_t \quad (10)$$

$$\text{where } L^* = L_{max}(E, E_t) = \zeta_{max}(E) + J \quad (11)$$

and  $\zeta_{max}$  is the maximum total angular momentum that can lead to capture [6]. The total system angular momentum is defined by  $\zeta = L + J$  where  $J = [2I(E - E_t)]^{1/2}$ . Once  $\zeta_{max}(E)$  is determined, Eq. (11) can be used to establish the maximum value of  $L$  as follows.

$$\zeta_{max}^2(E, r) = 2(I + \mu^2 r) [E - V(r, \theta_-)] \quad (12)$$

where  $\theta_-$  is the value of  $\theta$  for which the potential energy for an ion interacting with a quadrupolar molecule  $V(r, \theta)$  has its minimum value.  $r$  is the ion-molecule separation and  $\theta$  is the angle the polar axis makes with  $r$ .  $\zeta_{max}(E)$  can be obtained by setting  $\partial\zeta_{max}(E, r)/\partial r = 0$  which leads to

$$E - V(\theta_-) - (r/2) \left[ 1 + \frac{I}{\mu r^2} \right] \left[ \frac{\partial V(r, \theta_-)}{\partial r} \right] = 0 \quad (13)$$

The solution to Eq. (13), when combined with Eq. (12), defines  $\zeta_{max}(E)$  which is then substituted into Eq. (11) to establish the maximum value of  $L$ . Calculations of kinetic energy dependence of collision rate

constants require integration of trajectories outside-in from  $\approx 60 \text{ \AA}$  to capture radius  $r_c$ . Thus, we have to calculate  $L^*$  such that beyond that no collision occurs. Eqs. (6) and (10) are integrated by the Monte Carlo method. The procedure involves using "pseudo random" numbers which are generated rapidly by the computer in a specific and determined manner. The Monte Carlo technique is known to have a fairly slow rate of convergence; however, it is a method of choice for calculating rate constants by the classical trajectory method.

For the purpose of calculating ion-molecule collision rate constants, it is generally assumed that the ion can be treated as a point charge. This assumption may break down if the ion is sufficiently large. The model considered here consists of an ion with definite size interacting classically with a rigid quadrupole. We examine the effect of the induced dipole-induced dipole potential as well as the size of the colliding particles on the ion-quadrupolar molecule collision rate constants. The system Hamiltonian (with the motion of the center of mass removed) is given by [7,8] the following equation

$$H = \frac{p_r^2}{2\mu} + \frac{L^2}{2\mu r^2} + \frac{J^2}{2I} + V(r, \theta) \quad (14)$$

where  $p_r$  is the radial momentum of the collision partners. It is often convenient to rewrite Eq. (14) as

$$H = \frac{p_r^2}{2\mu} + \frac{J^2}{2I} + V_{eff}(L, r, \theta) \quad (15)$$

where the effective potential,  $V_{eff}(L, r, \theta)$ , is given by

$$V_{eff}(L, r, \theta) = \frac{L^2}{2\mu r^2} + V(r, \theta) \quad (16)$$

The potential energy for an ion interacting with a quadrupole molecule of  $D_{\infty h}$  symmetry is assumed to have the form [7,8]

$$V(r, \theta) = \frac{-q^2\alpha}{2r^4} + \frac{Qq(3\cos^2\theta - 1)}{2r^3} - \frac{C}{r^6} \quad (17)$$

where  $Q$  is the static quadrupole moment of the  $C_2H_2$  molecule,  $r$  is the ion-molecule separation,  $\alpha$  is the angle-average molecular polarizability,  $q$  is the charge of the ion and  $\theta$  is the angle of the quadrupolar axis with  $r$ .

Here  $C$  is a constant for an ion-molecule pair which is given by [9]

$$C = \frac{3}{2} a_0^{1/2} q^2 \left[ \frac{\alpha_1 \alpha_2}{\frac{\alpha_1^{1/2}}{N_1} + \frac{\alpha_2^{1/2}}{N_2}} \right] \quad (18)$$

where  $\alpha_1$  and  $\alpha_2$  are the polarizabilities of the neutral molecule and the ion respectively,  $a_0$  is the Bohr radius (0.529 Å), and  $N_1$  and  $N_2$  are the number of outer shell electrons of the neutral and the ion respectively. In Eq. (17), the first term is the charge induced-dipole potential ( $r^{-4}$ ), the second term is the charge quadrupole potential ( $r^{-3}$ ) and the last term is the induced dipole-induced dipole potential ( $r^{-6}$ ).

The angle ( $\theta$ ) can be calculated from [6,10]

$$\cos\theta = - \left[ \frac{\xi^2 - L^2 - J^2}{2LJ} \right] \sin\gamma_L \sin\gamma_J - \cos\gamma_L \cos\gamma_J \quad (19)$$

where  $\xi$  is the total system angular momentum,  $\gamma_L$  and  $\gamma_J$  are Euler angles ( $0 \leq \gamma_L, \gamma_J \leq 2\pi$ ) corresponding to the relative orbiting and rotating motion of molecule respectively.

The reactive trajectories are obtained by solving the equations of motion to determine which trajectories lead to capture. In Hamiltonian form the equations of motion for the canonical pair [ $p_i, q_i$ ] are [11,12]

$$\frac{\partial H}{\partial p_i} = \dot{q}_i, \quad \frac{\partial H}{\partial q_i} = -\dot{p}_i \quad (i = 1, 2, \dots) \quad (20)$$

where  $p_i$  and  $q_i$  are momentum and coordinate of the  $i$ th component and  $\dot{p}_i$  and  $\dot{q}_i$  are their respective time derivatives. The computations are based on classical mechanics and the system under investigation possesses three coordinates ( $r, \gamma_L, \gamma_J$ ) and three corresponding momenta ( $p_r, L, J$ ), thus appearing to require the integration of six equations of motion in Hamiltonian form. These equations are as follows

$$\frac{\partial H}{\partial L} = \frac{d\gamma_L}{dt} = \frac{L}{\mu r^2} + \frac{3Qq \cos\theta (L^2 + \xi^2 - J^2) \sin\gamma_L \sin\gamma_J}{2L^2 r^3 J} \quad (21)$$

$$\frac{\partial H}{\partial J} = \frac{d\gamma_J}{dt} = \frac{J}{I} - \frac{3Qq \cos\theta \sin\theta (\sin\gamma_L \sin\gamma_J) (J^2 + \xi^2 - L^2)}{2L r^3 J^2} \quad (22)$$

$$\frac{\partial H}{\partial p_r} = \frac{dr}{dt} = \frac{p_r}{\mu} \quad (23)$$

$$\frac{\partial H}{\partial \gamma_L} = \frac{-dL}{dt} = \frac{-3Qq \cos\theta \sin\theta \left[ \left( \frac{\xi^2 - L^2 - J^2}{2LJ} \right) \cos\gamma_L \sin\gamma_J + \sin\gamma_L \cos\gamma_J \right]}{r^3} \quad (24)$$

$$\frac{\partial H}{\partial \gamma_J} = \frac{-dJ}{dt} = \frac{-3Qq \cos\theta \sin\theta \left[ \left( \frac{\xi^2 - L^2 - J^2}{2LJ} \right) \cos\gamma_J \sin\gamma_L + \sin\gamma_J \cos\gamma_L \right]}{r^3} \quad (25)$$

$$\frac{\partial H}{\partial r} = \frac{-dp_r}{dt} = \frac{L^2}{\mu r^3} + \frac{3Qq(3 \cos^2 \theta - 1)}{2r^4} + \frac{6C}{r^7} \quad (26)$$

The above equations were integrated numerically. A fourth-order Runge-Kutta-Gill [13] procedure was used to initiate the trajectory and it was then completed by a faster fourth-order Adams-Moulton method [14].

Using computer, the initial conditions for each trajectory are chosen by a random process with an appropriate ion-molecule separation. The time interval  $\Delta t$  associated with the increments for numerical integration is taken to be  $1.0 \times 10^{-6}$  sec which is short enough to assure accurate computations. It is clear that given an initial set of coordinates and momenta, integration of Hamilton's equations will yield values of the coordinates and momenta at later times after which the iterative cycle is repeated.

The capture radius  $r_c$  is the ion-molecule separation which has the property that any trajectory reaching  $r_c$  with  $p_r \leq 0$  must ultimately reach  $r=0$ . *Su* and *Bhowmik* [15] have calculated the capture radius  $r_c$  by a method called the "solution by radical" [16]. Depending upon the charge of ion, there are two cases to be considered:

$$(i) \text{ Even case} \\ r_c = \pm \frac{U^{1/2}}{2} \pm \frac{U^{1/2} (\pm 2CU^{-3/2} - 1)^{1/2}}{2} \quad (27)$$

where :

$$U = X + \frac{4D}{3X} \\ X = \left[ \frac{C^2}{2} \pm \frac{(C^4 - \frac{256D^3}{27})^{1/2}}{2} \right]^{1/3}$$

$$C = \frac{Qq}{2E}$$

$$D = \frac{-\alpha q^2}{2E}$$

(ii) Odd case

In this case the expression for the capture radius is the same as the even case except that  $C = -Qq/2E$ .

For calculations of thermal energy collision rate constants, the trajectory calculations were done using the method suggested by Keck [17] and implemented by Anderson et al. [18] of beginning the trajectories in the interaction region and integrating them outward toward infinite separation. Thus, the trajectories are begun at the size of colliding partners ( $r = 4.19 \text{ \AA}$ ) and are integrated to  $r = 65 \text{ \AA}$ . The thermal energy capture rate constant  $k_{\text{cap}}(T)$  is determined as described previously and is given by

$$K_{\text{cap}}(T) =$$

$$\frac{2\sqrt{\pi}}{IK_{\text{B}}T(2\mu K_{\text{B}}T)^{3/2}} \int \chi[p,q]4LJdLdJ \exp(-E/K_{\text{B}}T)dE \quad (28)$$

Note that when the size of colliding partners is not taken into consideration, the trajectories are begun at the capture radius  $r_c$  and integrated to  $r = r_c + 60 \text{ \AA}$ .

For kinetic energy dependence collision rate constants, the trajectories are begun at  $\approx 60 \text{ \AA}$  ion-molecule separation and are integrated inward toward the capture radius  $r_c$  or the size of the colliding partners, whichever is larger. In this case the rotational temperature of the reactant neutral remains at 300 K, while the ion-molecule relative kinetic energy is varied from near thermal energies to a few eV. The trajectory calculated capture rate constant at a given relative kinetic energy  $E_r$  and thermal neutral rotational energy  $E_r$  at temperature  $T$  is determined as described previously and is given by

$$K_{\text{cap}}(E_r, T) =$$

$$\frac{\pi}{\mu^{3/2}(2E_r)^{1/2}K_{\text{B}}T} \int_0^\infty \int_0^{L^*} \chi[p,q]2LdL \exp(-E_r/K_{\text{B}}T)dE_r \quad (29)$$

## RESULTS AND DISCUSSION

The results presented here are the outcome of over 100,000 trajectories. This large number of tra-

jectories was necessary to make the statistical error sufficiently small to provide confidence in the trends observed.

Table 1 summarizes the polarizabilities, the quadrupole moment, the moment of inertia, and the hard sphere radii of the neutral molecule and the ion.

Table 1: Polarizabilities, quadrupole moment, moment of inertia, and radii of the neutral molecule and the ion.

Molecule/ ion	$(\alpha \text{ \AA}^3)$ [19]	$Q \times 10^{26} (\text{esu.cm}^2)$ [20]	$I (\text{amu \AA}^2)$ [21]	$r (\text{\AA})$ [22]
$\text{C}_2\text{H}_2$	3.33	+ 7.2	14.15	2.11
$\text{H}^-$	26.8	—	—	2.08

Table 2 shows the thermal energy capture rate constants at different temperatures for a model ion-molecule system ( $\text{H}^- + \text{C}_2\text{H}_2$ ). Table 3 gives the theoretical collision rate constants for the  $\text{H}^- + \text{C}_2\text{H}_2$  system at relative kinetic energies of the colliding partners in the range from thermal energy up to  $\sim 1.3 \text{ eV}$ . Fig. 1 is a plot of the theoretical rate constant versus the relative kinetic energy. The theoretical results were obtained with and without consideration of the induced dipole-induced dipole potential and the size of the colliding particles, and finally without the induced dipole-induced dipole potential but with the consideration of the colliding particles.

Table 2: Thermal energy rate constants for a model ion-molecule system ( $\text{H}^- + \text{C}_2\text{H}_2$ ) (All rate constants  $\times 10^8 \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ).

Temperature (K)	(I)	(II)	(III)
	Without $C/r^6$ and the size of particles	Without $C/r^6$ and with the size of particles	With $C/r^6$ and the size of particles
300	0.577	0.583	0.693
1000	0.483	0.520	0.756
3000	0.478	0.608	0.860

Table 2 shows the theoretical thermal capture rate constants at different temperatures for the ion-molecule system  $\text{H}^- + \text{C}_2\text{H}_2$ . Several conclusions

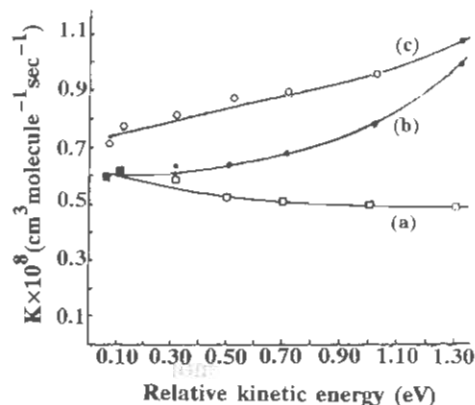
may be drawn from the results in Table 2: (1) The calculated collision rate constants without considering the induced dipole-induced dipole potential ( $r^{-6}$  term) and the size of the colliding pair (column I) decrease as the temperature increases. This indicates that ion-quadrupole interactions are substantial at low energies and further, their importance increases with decreasing temperature. This is not surprising since the neutral molecule has a moderately large quadrupole moment ( $+7.2 \times 10^{-26}$  esu.  $\text{cm}^2$ ). (2) When only the size of the colliding pair is taken into account (column II), the calculated collision rate constant decreases with increasing temperature at first but then increases at higher temperatures. This means that the effect of the colliding pair size is large at higher temperatures. (3) The results show a significant increase in the rate constants over the temperature range (300-3000 K) when both the  $r^{-6}$  term and the size of the colliding pair are included (column III). This suggests that at high temperatures the effect of the  $r^{-6}$  term becomes more important.

**Table 3: The kinetic energy dependence of the collision rate constants for a model ion-molecule system ( $\text{H}^- + \text{C}_2\text{H}_2$ ) (All rate constants  $\times 10^8 \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ).**

Relative kinetic energy (eV)	Without $C/r^6$ and the size of particles	Without $C/r^6$ and with the size of particles	With $C/r^6$ and the size of particles
0.05	0.60	0.60	0.727
0.10	0.621	0.621	0.776
0.30	0.595	0.635	0.810
0.50	0.530	0.637	0.871
0.70	0.519	0.685	0.890
1.00	0.503	0.784	0.960
1.30	0.494	0.995	1.074

Although these trends are apparent from Table 2, there is need to explain these results by some other means. The kinetic energy dependence study of the system can provide us with more information to rationalize the above observations.

Table 3 and Fig. 1 are the results of trajectory calculations of the capture collision rate constants as



**Fig. 1: Trajectory calculations of the kinetic energy dependence of the collision rate constant for the ion-molecule system ( $\text{H}^- + \text{C}_2\text{H}_2$ ). Curve (a) without the  $r^{-6}$  term and without the size of the colliding particles. Curve (b) without the  $r^{-6}$  term and with the size of the particles. Curve (c) with the  $r^{-6}$  term and the size of the colliding particles.**

a function of relative kinetic energy  $E$  with the reactant neutral at 300 K. the calculations were performed for three different cases. Curve (a) is the theoretical calculated results of the kinetic energy dependent rate constant in which neither the induced dipole-induced dipole potential ( $r^{-6}$  term) nor the size of the colliding pair was taken into account. Curve (b) is the calculated results without considering the  $r^{-6}$  potential but with the consideration of the size of the particles. Curve (c) is the calculated results with the consideration of both the  $r^{-6}$  potential and the size of the particles. The effect of the size is apparent from curves (a) and (b) in Fig. 1. The results reveal that at relatively low kinetic energies (e.g., 0.1, 0.05 eV), curves (a) and (b) coincide. This indicates that at very low kinetic energies, there is no contribution from the size of the colliding pair simply because the capture radius becomes larger than the size. It is clear that the gap between curves (a) and (b) increases with increasing relative kinetic energies. This shows that the effect of size become more significant at higher kinetic energies due to a decrease in the capture radius. Comparison of curves (b) and (c) indicates the effect of the induced-dipole induced dipole potential. The results of this study reveals that the calculated collision rate constants including the induced-dipole induced dipole potential are larger than those without considering the induced dipole

induced dipole potential. This is because the induced dipole-induced dipole term in the interaction potential (the third term in Eq. 17) varies as  $r^{-6}$ ; therefore, one expects that the  $r^{-6}$  term would dominate over other potential terms at smaller values of  $r$ . It is predicted that this effect will be most important at higher relative kinetic energies or higher temperatures where the capture radius becomes smaller. Keep in mind that the effect of the  $r^{-6}$  term on collision rate constants become more vigorous for ion-polar molecule system involving ions with large polarizabilities [3]. One final note is needed before concluding this discussion. It can be seen from Fig. 1 that curves (b) and (c) approach each other with increasing relative kinetic energy. This exhibits that at extremely high relative kinetic energies there is little contribution from the  $r^{-6}$  term compared to the effect of size. Thus, the size of the colliding pair becomes the dominant factor in determining the collision rate constant and the collision cross section approaches the size of the ion-molecule pair.

## CONCLUSIONS

Overall, based on the trajectory calculations, our study reveals that the inclusion of the induced-dipole induced dipole potential ( $r^{-6}$ ) and the size of the colliding pair substantially increases the collision rate constant. We thus suggest that the  $r^{-6}$  term and the size of the colliding pair should not be ignored when calculating collision rate constants of ion-molecule system.

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