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Cold collisions between linear polar molecules

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Abstract. Cold collisions between electrostatically trapped linear polar molecules are theoretically investigated. It is consequently shown that the inelestic collision cross-section is determined by S-wave scattering alone, while the contribution of D-wave scattering to the elastic collision cross-section becomes significant when the electric field strength is high. It is also shown that as the temperature decreases, it becomes difficult to obtain the evaporative cooling effect without collision loss.

PACS. 31.15.Qg Molecular dynamics and other numerical methods – 33.80.Ps Optical cooling of molecules; trapping – 33.90.+h Other topics in molecular properties and interactions with photons

1 Introduction

Several groups have recently developed effective methods for preparing ultra-cold molecules and confining them in three-dimensional traps. A Harvard group used static magnetic fields to trap paramagnetic CaH molecules pre-cooled using buffer gas collisions [1,2]. Takekoshi *et al.* trapped cesium dimers produced using the photoassociation of laser-cooled Cs atoms in focused CO_2 laser beams [3]. Bethlem *et al.* decelerated ND_3 molecular beams using a time-varying inhomogeneous electric field and loaded them into an electrostatic trap [4].

Bethlem *et al.* took advantage of the ND_3 characteristics of the inversion doublet, which makes the trap loss rate small because of the energy gap between the low- and high-field seeking states. With the aim of expanding the utility of the molecular trapping technology, we investigate the loss rate of electrostatically trapped linear polar molecules ($^1\Sigma$ state). Linear polar molecules can be trapped inside a quadrupole electrode by the second-order Stark effect. We have previously analyzed the loss rate of the linear polar molecules in the $(J = 1, M_J = 0)$ state, caused by the Majorana effect (the transition between quantum states, caused by a change of the electric field direction) [5] and the inelastic collision [6]. Here J denotes the quantum number of the total molecular angular momentum and M_J is the quantum number of the trajectory of the molecular angular momentum parallel to the electric field. The inelastic collision was discussed taking the molecular kinetic energy (T) as 100–500 mK, a value range which has been obtained experimentally [1,4].

The stability of the Bose-Einstein-Condensation (BEC) of polar molecules has recently been discussed [7,8]. BEC can be attained only when the ratio of the collision loss rate to the elastic collision rate is small enough so that the evaporative cooling effect can be obtained without serious collision loss. The characteristics of collisions at $T < 1$ mK are quite different from those at $T > 100$ mK, because the broadening of the molecular wavepacket is larger than the scale size of the intermolecular potential. Bohn analyzed the collision between diatomic polar molecules in $^1\Pi$ states (with Λ-doubling) at ultra-low temperatures [9,10].

This paper discusses the collision of electrostatically trapped linear polar molecules in a $^1\Sigma$ $(J = 1, M_J = 0)$ state at ultra-low temperatures. For linear polar molecules in a $^1\Sigma$ state, the energy gap between the $(J = 1, M_J = 0)$ and $(J = 1, M_J = \pm1)$ states is proportional to the square of the electric field strength, while the energy gap between the low- and high-field seeking states is mainly determined by the Λ-splitting for molecules in the $^1\Pi$ state. The diagonal matrix element of the dipole moment is proportional to the electric field strength, while it is almost independent in the case of polar symmetric top molecules. It is therefore useful to discuss the collision cross-section of linear polar molecules in the $^1\Sigma$ state for different values of electric field strength.

2 Calculation of collision cross-section

We assume here that almost all electrostatically trapped molecules are in the $(J, M) = (1, 0)$ state. This assumption is reasonable as $(J, M) = (1, 0)$ is the lowest low-field seeking state, and the trapping force for molecules in $J > 2$ states are much smaller than for molecules in the $(J, M) = (1, 0)$ state. We also assume that the collisional transition rates to the $(J, M) = (0, 0)$ state or $J > 2$ states are much smaller than to the $(J, M) = (1, \pm1)$ state

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because of large energy gaps [6]. We therefore perform a calculation taking the following collision procedures into account

$$(J_1,M_{J1}) + (J_2,M_{J2}) \to (J_1',M_{J1}') + (J_2',M_{J2}')$$

$$\begin{aligned} J_1 = J_2 = J_1' &= J_2' = 1, \\ M_{J1} &= M_{J2} = 0, \\ M_{J1}' &= 0, 1, -1, \\ M_{J2}' &= 0, 1, -1. \end{aligned}$$

The cross-section of the collisional transition $(1,0) + (1,0) \to (1,M_{J1}') + (1,M_{J2}')$ is described by

$$\sigma_{(M_{J1}',M_{J2}')} = \sum_{L,M_L}\sum_{L'.M_L'} \sigma\left[(M_{J1}', M_{J2}') : (L, M_L) \to (L', M_L')\right]$$

$$\sigma\left[(M_{J1}', M_{J2}') : (L, M_L) \to (L', M_L')\right] = \frac{\pi}{k^2} P\left[(M_{J1}', M_{J2}') : (L, M_L) \to (L', M_L')\right] \quad (1)$$

where k is the incident wave number, $L(L')$ is the quantum number for the total angular momentum of the molecular relative motion before (after) the collision, and $M_L(M_L')$ is the quantum number for the trajectory of the angular momentum of the molecular relative motion parallel to the electric field before (after) the collision. And P is the opacity function [9,11].

When $1/k$ is much smaller than the scale size of the intermolecular potential, (1) is rewritten as

$$\sigma_{(M_{J1}',M_{J2})} = \int_0^\infty 2\pi b P_{(M_{J1}',M_{J2}')}(b)\,\mathrm{d}b$$

$$b = \frac{1}{k}\left(L + \frac{1}{2}\right). \quad (2)$$

Here, b is called the impact parameter [11]. Equation (2) is actually valid for $T > 100$ mK [6]. For $T \ll 1$ mK, we can calculate the collision cross-section using (1) taking just a few partial incident waves into account.

When we consider the collision between the same kind of molecules with Bose statistics, the wave function must be transformed to the symmetric form

$$|M_{J1}', M_{J2}'\rangle \to \frac{1}{\sqrt{2\left(1 + \delta\left(M_{J1}, M_{J2}\right)\right)}} \times \left(|M_{J1}', M_{J2}'\rangle + |M_{J2}', M_{J1}'\rangle\right). \quad (3)$$

As a result of this treatment, the molecular wave function becomes zero for odd numbers of L and L'. The elastic and inelastic collision cross-sections are given by

$$\sigma_{\text{elastic}} = \sigma_{(0,0)} \quad (4)$$

$$\sigma_{\text{inelastic}} = 2\left(\sigma_{(0,1)} + \sigma_{(0,-1)} + \sigma_{(1,-1)}\right) + \sigma_{(1,1)} + \sigma_{(-1,-1)}. \quad (5)$$

The coefficients in (5) are obtained by the treatment shown by (3). For $(M_{J1}', M_{J2}') = (1,1), (-1,-1)$ or $(1,-1)$, two molecules are lost in one collision. The collision loss rate can therefore be obtained from the collision loss cross-section, given by

$$\sigma_{\text{loss}} = 2\sigma_{(0,1)} + 2\sigma_{(0,-1)} + 4\sigma_{(1,-1)} + 2\sigma_{(1,1)} + 2\sigma_{(-1,-1)}. \quad (6)$$

Here we assume that the intermolecular potential is mainly determined by the dipole-dipole interaction. For linear polar molecules in the field free space, the matrix elements of dipole moment $\langle J, M\,|\mu|\,J, M\rangle$ and $\langle J, M\,|\mu|\,J, M \pm 1\rangle$ are zero. However these matrix elements become non-zero under electric field because of the mixture of the wave functions. According to the first order perturbation theory, the wave function $|J, M\rangle$ under electric field is given by

$$|J, M\rangle = |J, M\rangle_0 + \frac{\langle J, M\,|\mu_z|\,J-1, M\rangle E}{2hBJ}\,|J-1, M\rangle_0 - \frac{\langle J, M\,|\mu_z|\,J+1, M\rangle E}{2hB\,(J+1)}\,|J+1, M\rangle_0 \quad (7)$$

where $|J, M\rangle_0$ denote the wave functions at the field free space. B is the rotational constant, μ is the molecular permanent dipole moment, and E is the electric field strength. The matrix elements of the dipole moment are given by

$$\left|\langle J = 1, M = 0\,|\mu|\,J = 1, M = 0\rangle\right|^2 = \frac{\mu^4 E^2}{25h^2B^2} \quad (8)$$

$$\left|\langle J = 1, M = 0\,|\mu|\,J = 1, M = \pm 1\rangle\right|^2 = \frac{9\mu^4 E^2}{400h^2B^2} \quad (9)$$

$\sigma\left[(M_{J1}', M_{J2}') : (L, M_L) \to (L', M_L')\right]$ is obtained using the Distorted Wave Born Approximation (DWBA) [12]. DWBA is the Born Approximation taking the intermolecular exchange force (repulsive force) into account. Actually $j_L'(kr)$ (shown below)

$$\begin{aligned} j_L'(kr) &= j_L(kr) \qquad r > r_0 \\ j_L'(kr) &= 0 \qquad\qquad r < r_0 \end{aligned}$$

is used instead of $j_L(kr)$, where r_0 the scale size of the intermolecular exchange force. In this paper, we take $r_0 = 5$ A. The collision cross-section is not sensitive to the value of r_0 [10]. If just the dipole-dipole interaction is taken into account, $\sigma\left[(M_{J1}', M_{J2}') : (L, M_L) \to (L', M_L')\right]$ is obtained as

$$\sigma\left[(M_{J1}', M_{J2}') : (L, M_L) \to (L', M_L')\right] = \frac{\pi}{k^2}\left|\frac{m\sqrt{kk'}}{\hbar^2}\int H(r,\theta,\varphi)\,Y_{L,M_L}^*(\theta,\varphi)\,Y_{L',M_L'}(\theta,\varphi) \times j'^*(kr)\,j'(k'r)\,r^2\sin\theta\,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi\right|^2$$

$$H(r,\theta,\varphi)=\frac{1}{4\pi\varepsilon_0 r^3}\left[\langle 0\,|\boldsymbol{\mu}|\,M'_{J1}\rangle\cdot\langle 0\,|\boldsymbol{\mu}|\,M'_{J2}\rangle\right.$$
$$\left.-\frac{3}{r^2}\left(\langle 0\,|\boldsymbol{\mu}|\,M'_{J1}\rangle\cdot\mathbf{r}\right)\left(\langle 0\,|\boldsymbol{\mu}|\,M'_{J2}\rangle\cdot\mathbf{r}\right)\right]. \quad (10)$$

Here m is the molecular reduced mass and k' is the wave number of the scattering wave. H is the intermolecular potential caused by the dipole-dipole interaction. Using equations (8, 9), equation (10) is rewritten as

$$\sigma\left[(M'_{J1},M'_{J2}):(L,M_L)\to(L',M'_L)\right]=$$
$$A\left[(M'_{J1},M'_{J2})(L,M_L)(L',M'_L)\right]D^2U^2G_{L,L'}(\beta_n) \quad (11)$$

$$D=\frac{2\pi m\mu^2}{\varepsilon_0 h^3 B} \quad (12)$$

$$U=\frac{\mu^2E^2}{10hB} \quad (13)$$

$$G_{L,L'}(\beta_n)=\beta_n\left[\int j'^{*}_{L}(kr)\,\frac{1}{R}\,j'_{L'}(\beta_n kr)\,\mathrm{d}r\right]^2 \quad (14)$$

$$\beta_n=\frac{k'}{k}=\sqrt{1+\frac{3mU}{\hbar^2k^2}n} \quad (15)$$

$$n=|M'_{J1}|+|M'_{J2}|. \quad (16)$$

Values of $A\left[(M'_{J1},M'_{J2})(L,M_L)(L',M'_L)\right]$ are listed in Table 1 and U is the trapping potential energy of the molecule in the $(J,M)=(1,0)$ state, obtained by the second-order perturbation theory. The energy discrepancy between $(1,0)$ and $(1,\pm1)$ states is $3U/2$, and (15) is derived by

$$\frac{\hbar^2k'^2}{2m}=\frac{\hbar^2k^2}{2m}+\frac{3}{2}U$$
$$(M'_{J1},M'_{J2})=(0,1),\ (0,-1)$$

$$\frac{\hbar^2k'^2}{2m}=\frac{\hbar^2k^2}{2m}+3U$$
$$(M'_{J1},M'_{J2})=(1,1),\ (1,-1),\ (-1,-1).$$

Equations (7–16) are valid for $\mu E\ll hB$. This calculation should be performed with $0\le L\le L_{\max}$, where $DUk\ll L_{\max}^3$ is satisfied. In this paper, we take just $(L,L')=(0,2)$, $(2,0)$, and $(2,2)$ into account.

The term representing the dipole-dipole interaction becomes zero for $(L,L')=(0,0)$ and the short range intermolecular interaction ($\propto r^{-6}$) is significant. Only the following 2 terms, which are obtained by solving the Schrödinger equation with the assumption of $k\to0$ (DWBA is not used) [13], are considered

$$\sigma\left[(0,0):(0,0)\to(0,0)\right]=\frac{\mu^2}{8\varepsilon_0}\sqrt{\frac{2m}{5h^3B}}\frac{\Gamma^2\left(\frac{3}{4}\right)}{\Gamma^2\left(\frac{5}{4}\right)} \quad (17)$$

$$\sigma\left[(1,-1):(0,0)\to(0,0)\right]=\frac{\mu^2}{8\varepsilon_0}\sqrt{\frac{3m}{10h^3B}}\frac{\Gamma^2\left(\frac{3}{4}\right)}{\Gamma^2\left(\frac{5}{4}\right)}\cdot \quad (18)$$

Table 1. Values of $A\left[(M'_{J1},M'_{J2})(L,M_L)(L',M'_L)\right]$, used in (11).

$A[(0,0)(0,0)(2,0)]$	$16\pi/125$
$A[(0,0)(2,0)(0,0)]$	$16\pi/125$
$A[(0,0)(2,0)(2,0)]$	$64\pi/1225$
$A[(0,0)(2,\pm1)(2,\pm1)]$	$144\pi/1225$
$A[(0,0)(2,\pm2)(2,\pm2)]$	$64\pi/1225$
$A[(0,\pm1)(0,0)(2,\mp1)]$	$3\pi/500$
$A[(0,\pm1)(2,0)(2,\mp1)]$	$27\pi/4900$
$A[(0,\pm1)(2,\pm1)(2,0)]$	$27\pi/4900$
$A[(0,\pm1)(2,\pm1)(0,0)]$	$3\pi/500$
$A[(0,\pm1)(2,\mp1)(2,\mp2)]$	$81\pi/2450$
$A[(0,\pm1)(2,\pm2)(2,\pm1)]$	$81\pi/2450$
$A[(\pm1,\pm1)(0,0)(2,\pm2)]$	$27\pi/16000$
$A[(\pm1,\pm1)(2,0)(2,\pm2)]$	$81\pi/3136$
$A[(\pm1,\pm1)(2,\pm1)(2,\mp1)]$	$81\pi/78400$
$A[(\pm1,\pm1)(2,\pm2)(2,0)]$	$243\pi/39200$
$A[(\pm1,\pm1)(2,\pm2)(2,0)]$	$27\pi/16000$
$A[(\pm1,\mp1)(0,0)(2,0)]$	$81\pi/8000$
$A[(\pm1,\mp1)(2,0)(0,0)]$	$81\pi/8000$
$A[(\pm1,\mp1)(2,0)(2,0)]$	$81\pi/19600$
$A[(\pm1,\mp1)(2,\pm1)(2,\pm1)]$	$81\pi/78400$
$A[(\pm1,\mp1)(2,\pm2)(2,\pm2)]$	$81\pi/19600$

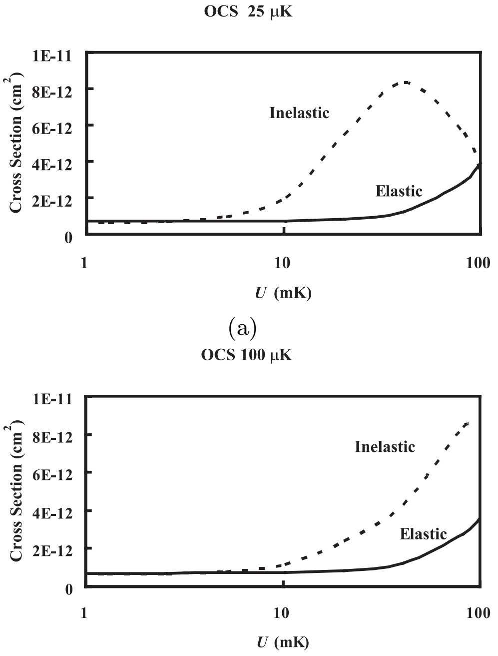
In the case of molecules in the $^1\Pi$ state, the effective adiabatic potential should be taken into account to avoid the crossing of an attractive channel and a repulsive channel [10]. This crossing happens when

$$\frac{\langle a\,|\mu|\,b\rangle\,\langle c\,|\mu|\,d\rangle}{4\pi\varepsilon_0 r^3}\approx\Delta \quad (19)$$

where $\langle a\,|\mu|\,b\rangle$ and $\langle c\,|\mu|\,d\rangle$ are the matrix elements of the molecular dipole moment. Generally the matrix elements of the dipole moment are smaller than the permanent dipole moment (μ). Δ is the energy gap between the different quantum energy states: it is determined by the Λ-splitting for the molecules in the $^1\Pi$ state. For molecules in the $^1\Sigma$ state, Δ is determined by the energy gap between different rotational states. The parameter

$$\eta(r)=\frac{\mu^2}{4\pi\varepsilon_0 r^3hB} \quad (20)$$

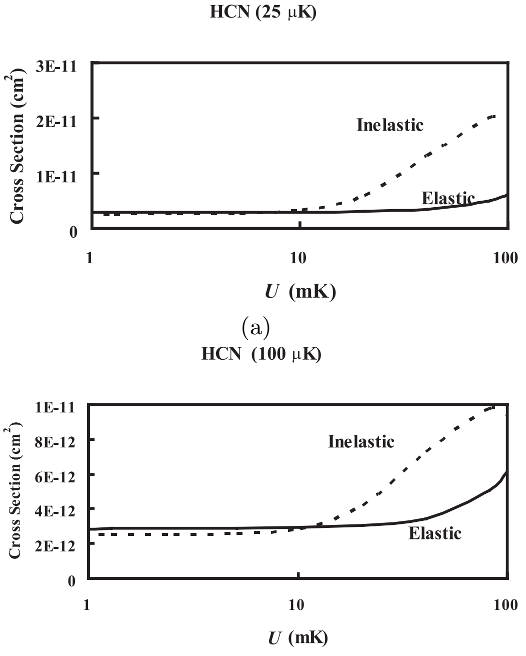
is considered taking $r=1/k$. When the molecular temperature is less than 100 μK, $\eta(k)$ is less than 10^{-3} for OCS ($\mu=0.71$ D, $B=6.09$ GHz) and HCN ($\mu=2.94$ D, $B=43.4$ GHz) molecules. The influence of the effective adiabatic potential is thus negligible in the case of molecules in the $^1\Sigma$ state.



(a)

(b)

Fig. 1. Cross-sections of elastic (solid line) and inelastic (dotted line) collisions of OCS molecules as a function of the electrostatic potential of trapped molecules (U), where the temperature is 25 μK and 100 μK.



(a)

(b)

Fig. 2. Cross-sections of elastic (solid line) and inelastic (dotted line) collisions of HCN molecules as a function of the electrostatic potential of trapped molecules (U), where the temperatures is 25 μK and 100 μK.

3 Calculation results

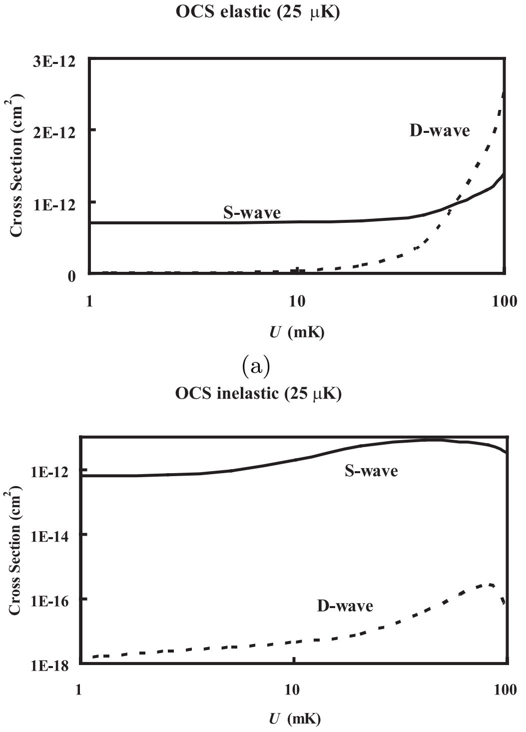
We calculated the elastic and inelastic collision cross-sections of OCS and HCN molecules with $U < 100$ mK ($E < 32$ kV/cm for OCS and $E < 20$ kV/cm for HCN). With this electric field range, $\mu E \ll hB$ holds and equations (7–16) are valid.

The elastic (σ_{elastic}) and inelastic ($\sigma_{\text{inelastic}}$) collision cross-sections of OCS and HCN molecules are shown as functions of U in Figures 1 and 2. The molecular temperature (T) was taken as 25 and 100 μK. In any case, $\sigma_{\text{inelastic}} > \sigma_{\text{elastic}}$ for 10 mK $< U <$ 100 mK because G_{02} increases as β becomes larger, while the molecular energy is lower than the height of the D-wave centrifugal barrier in the exit channel [14]. And σ_{elastic} increases drastically for 50 mK $< U$, because the contribution of D-wave scattering (Fig. 3) becomes significant. The contribution of D-wave scattering in an inelastic collision is negligibly small compared with that of S-wave scattering for $U \leq 100$ mK (Fig. 3). This is because G_{20} and G_{22} decrease as β becomes larger.

Figure 4 shows the values of

$$R = \frac{\sigma_{\text{loss}}}{\sigma_{\text{elastic}}} \tag{21}$$

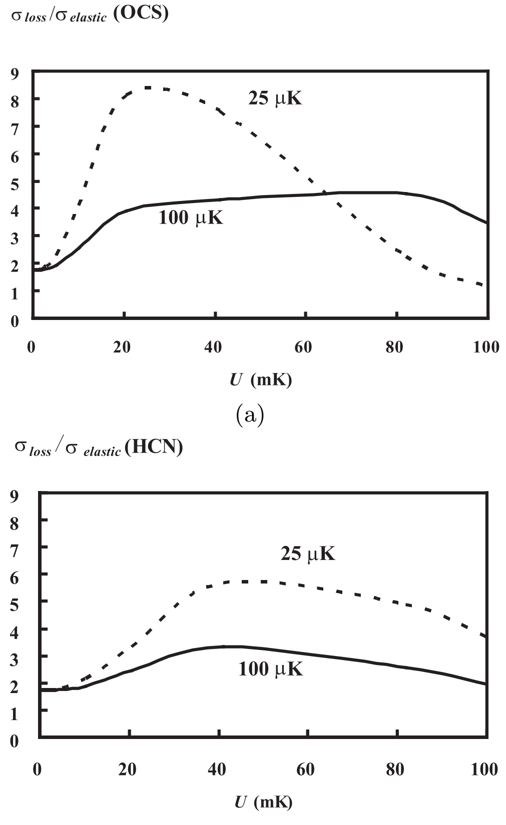
for OCS and HCN molecules as function of U. To attain the BEC state with molecules, R is should be small so that a high evaporative cooling effect can be obtained while maintaining a low inelastic collision rate. Actually R is maximum at a certain value of U (20–50 mK).



(a)

(b)

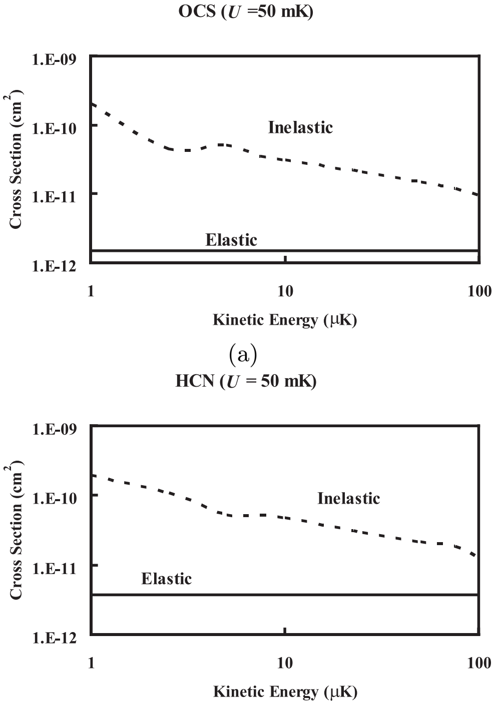
Fig. 3. The contributions of the S- and D-waves to the elastic and inelastic collision cross-sections of OCS molecules as a function of the electrostatic potential energy of the trapped molecules (U), where the temperature is 25 μK.



(a)

(b)

Fig. 4. $R = \sigma_{\text{loss}}/\sigma_{\text{elastic}}$ of OCS and HCN molecules as a function of the electrostatic potential energy of trapped molecules (U), where the temperature is 25 μK (dotted line) and 100 μK (solid line).



(a)

(b)

Fig. 5. Cross-sections of elastic (solid line) and inelastic (dotted line) collisions of OCS and HCN molecules as a function of the molecular kinetic energy (T) with a fixed value of the electrostatic potential energy ($U = 50$ mK).

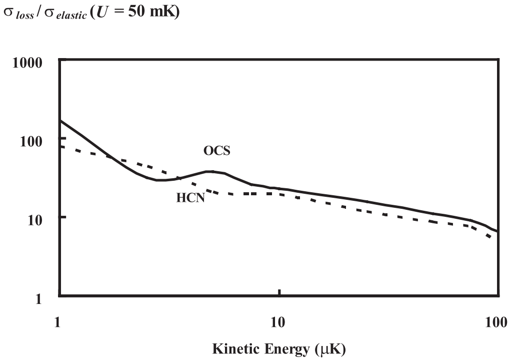


Fig. 6. $R = \sigma_{\text{loss}}/\sigma_{\text{elastic}}$ of OCS (solid line) and HCN (dotted line) molecules as a function of the molecular kinetic energy (T) with a fixed value of the electrostatic potential energy ($U = 50$ mK).

The calculation also considers the dependence of the collision cross-sections on the molecular temperature (T). Figure 5 shows σ_{elastic} and $\sigma_{\text{inelastic}}$ as a function of T for OCS and HCN molecules. As given by the Wigner law, $\sigma_{\text{inelastic}}$ is proportional to $T^{-1/2}$ and σ_{elastic} is constant [14]. Figure 6 shows R as a function of T for OCS and HCN molecules taking $U = 50$ mK. Also R is roughly proportional to $T^{-1/2}$.

4 Conclusion

Considering the contributions of S- and D-wave scatterings, we calculated the elastic and inelastic collision cross-sections of linear polar molecules ($^1\Sigma$ state) in the $(J, M) = (1, 0)$ state at ultra-low temperatures. We thus found that the significance of the D-wave scattering under elastic collisions increases as the electric field strength becomes higher, while it is negligibly small in inelastic collisions.

As mentioned above, the calculated is performed using DWBA taking S- and D-waves into account. For OCS and HCN molecules, this treatment is reasonable because of $DUk \ll 1$. However, this treatment is not valid for molecules with larger values of D (NaCl molecules, for example). The S-wave scattering cross-section can be in maximum π/k^2, while it can be obtained as a larger value using DWBA. In this case S-wave scattering cross-section is actually in the order of π/k^2. We must also consider incident partial waves with $L \geq 4$. In such cases, it is expected to be easier to get lower values of R, because the scattering of partial incident waves with $L \geq 2$ can be significant only for the elastic collision (see Fig. 3). Reference [6] shows that when the relative velocity is 8.5 m/s, R decreases as D increases.

With ultra low temperature, the dependence of R on the electric field strength is quite different from that with higher temperature ($T > 100$ mK) [6]. With high temperature, R decreases monotonously as the electric field strength becomes higher. However with ultra low temperature, R becomes maximum with a certain value of electric field strength. As T decreases, R becomes higher, so it is found to be difficult to get ultra-low temperature with the evaporative cooling of molecules in the $(J, M) = (1, 0)$ state. Bohn mentioned that the collision loss rate is high for molecules in the $^1\Pi$ state [9]. The evaporative cooling seems possible for molecules in $J = 0$ state (this is a high-field seeking state), as the collisional transition to higher rotational states is not possible when $k_BT \ll hB$. To be able to trap molecules in high-field seeking states, Bethlem *et al.* have developed a synchrotron storage ring [15].

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