# Mobility of Ions in Gases

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Outline

1. Introduction to Ion mobility in gas

    Experiments

    Theory

2. Closed-shell systems

    Experimental results

    Quantal calculations

3. Open-shell systems

    Experimental results

    Classical calculations

4. Summary

# Swarm & Mobility

## Swarm method :

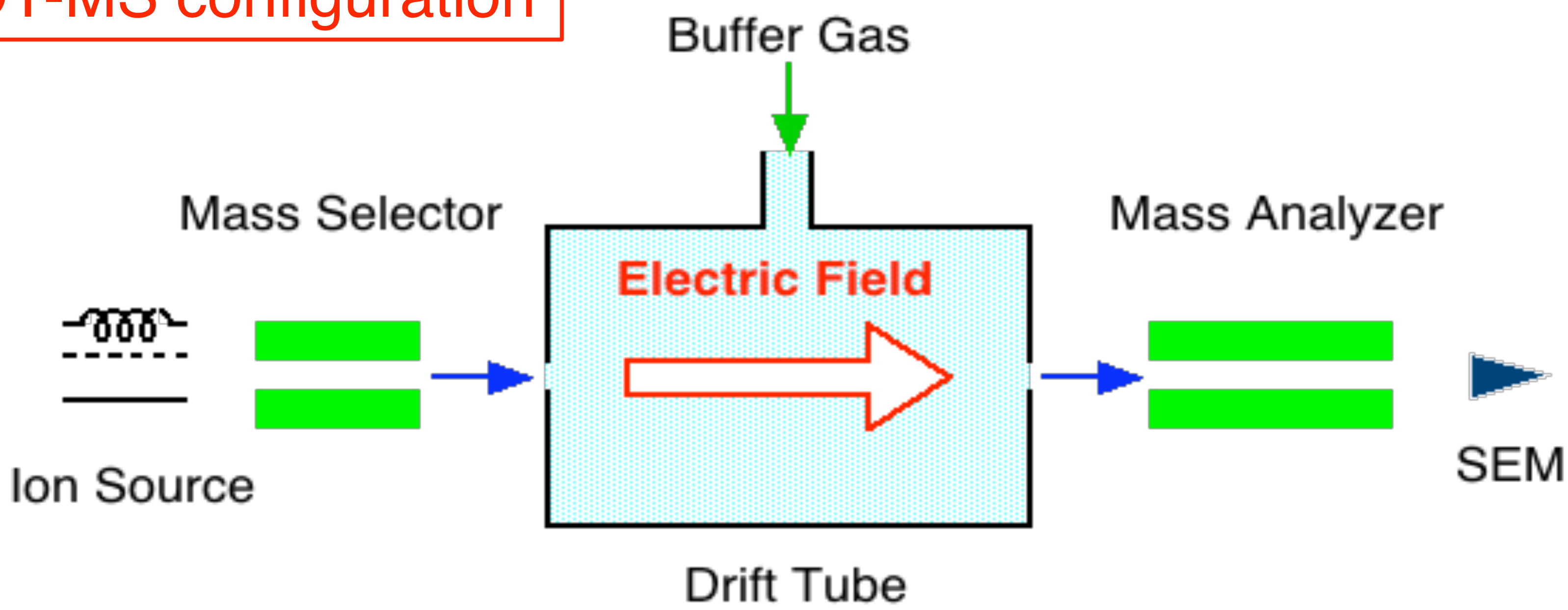
- long history since 19C
- extremely low energy collisions of ions / electrons

## Mobility :

- fundamental transport property
- very sensitive to the interaction potential
- recent application to cluster ions – size and structure
- depend on electronic states
  - historical works : $O^+$ and $O_2^+$
  - this work : $C^+$ and $N^+$

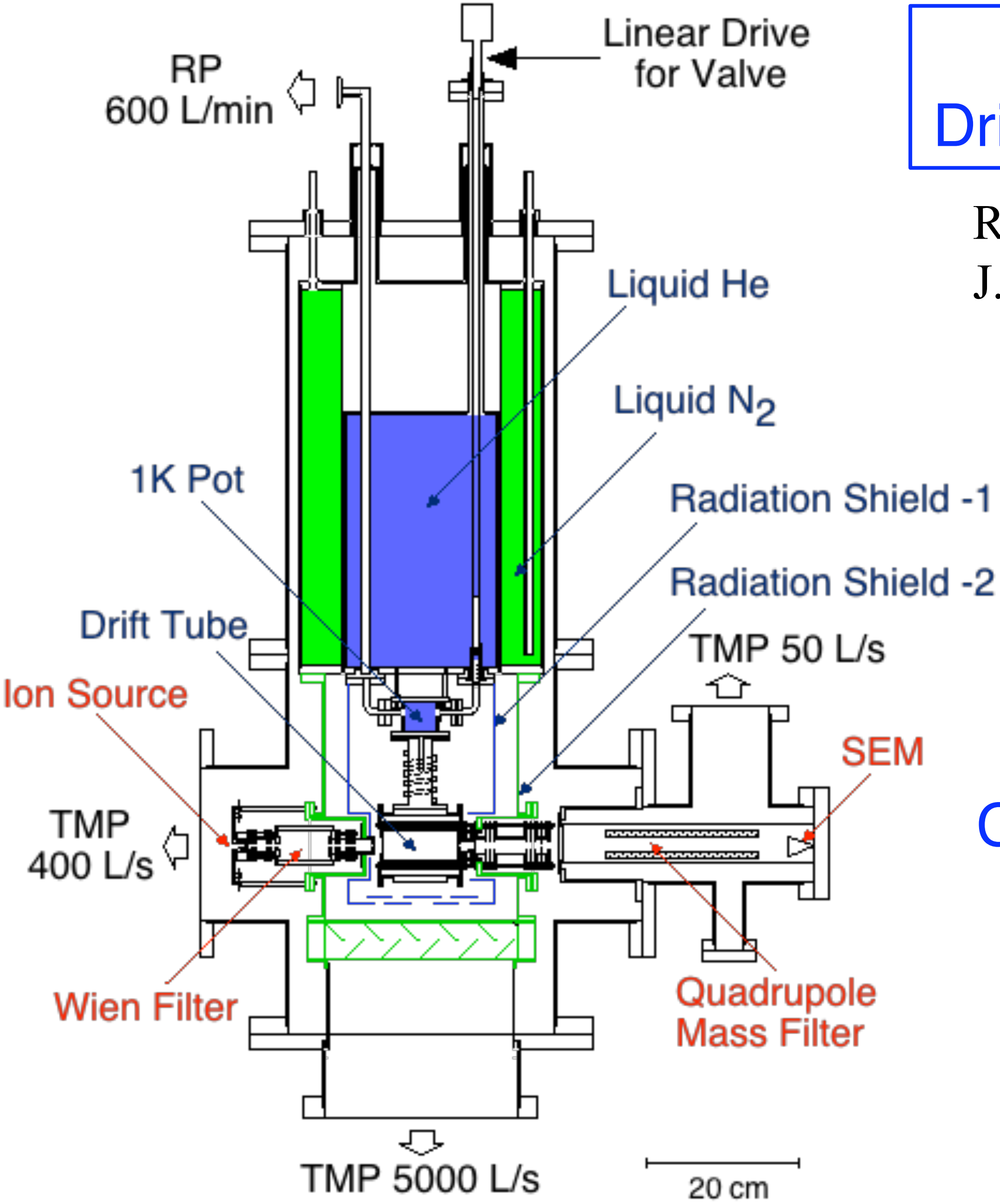
# Principle of Ion Swarm Experiments

MS-DT-MS configuration




Experimental parameters which determine the collision energy

*P* : gas pressure ( *N* : number density )
*E* : uniform electric field strength
*T* : gas temperature




## Very Low Temperature Drift Tube Mass Spectrometer

Rev. Sci. Instrum. **71** (2000) 2019.
J. Chem. Phys. **113** (2000) 1738.

$P$ = 1 - 100 Pa

$E$ = 0.1 - 20 V/cm

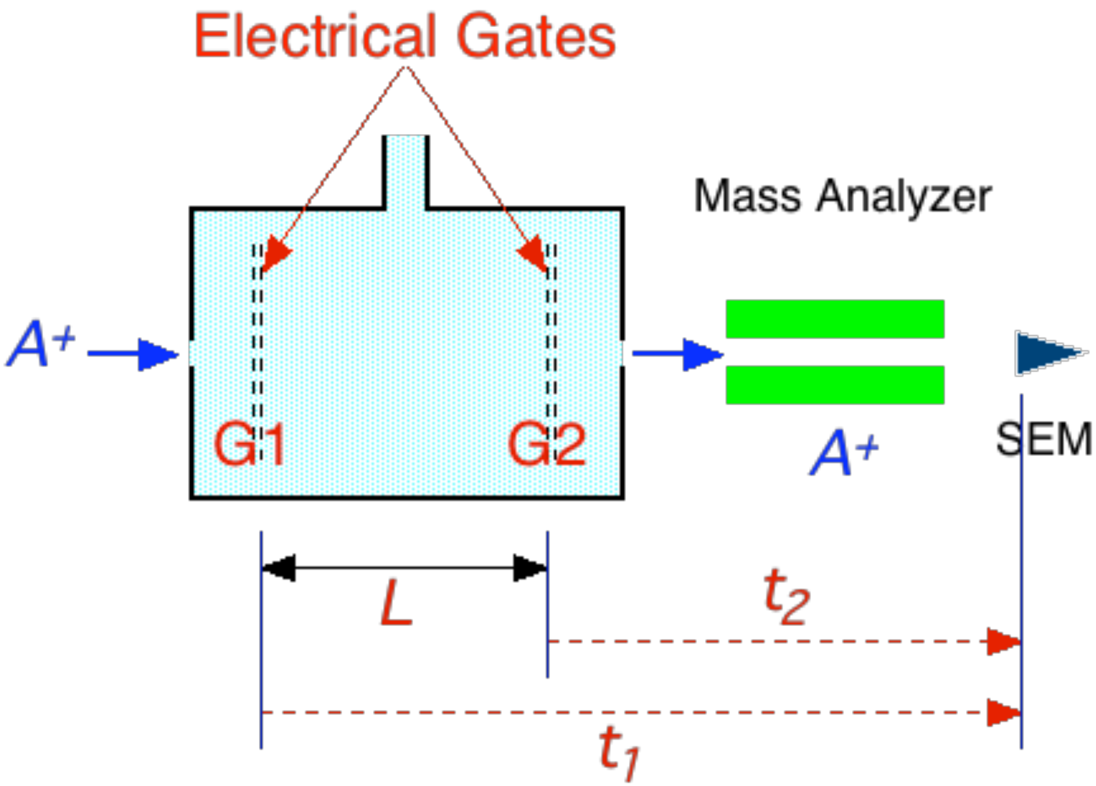
$T$ = 2.0 - 100 K

Cooling by liq. $N_2$ and liq. He

Mean collision energy

$$0.5 < \varepsilon \,/\, \text{meV} < 1000$$

# Drift velocity and Mobility of Ions




**Drift velocity :**

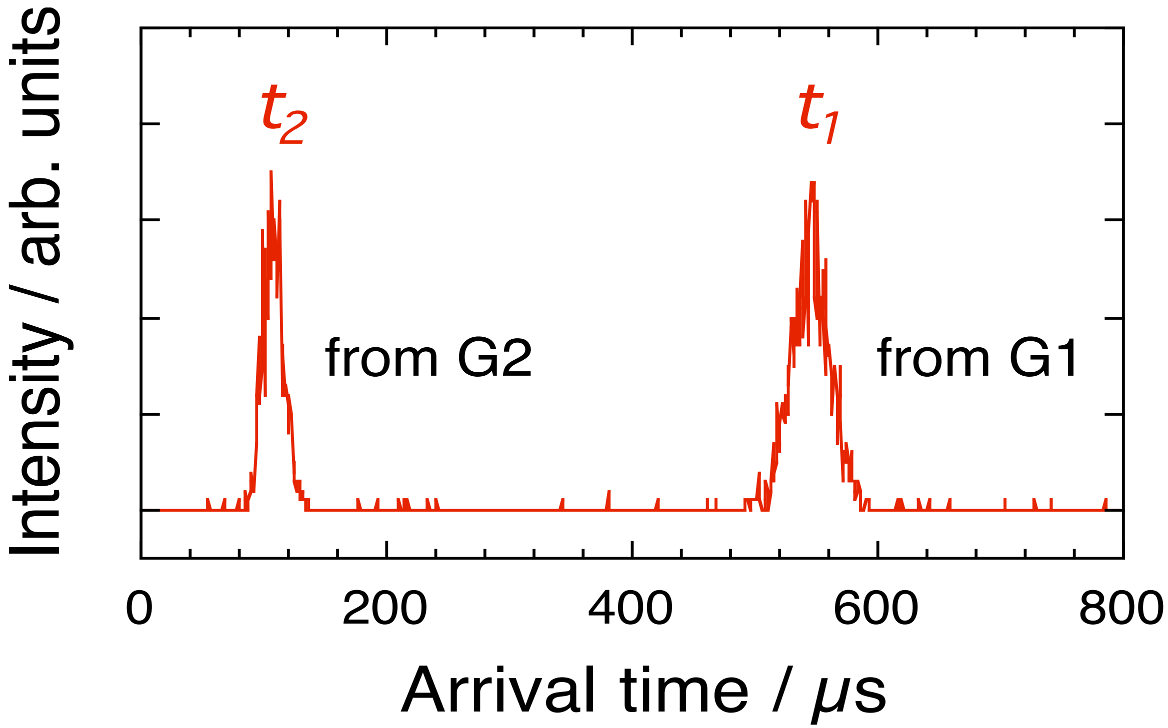
$$v_{\mathrm{d}} = \frac{L}{t_1 - t_2} = KE$$

**Reduced mobility :**

$$K_0 = \frac{v_{\mathrm{d}}}{E}\frac{N}{N_0} = K_0\left(\frac{E}{N}\right)$$

$N$ : number density, $N_0$ : Loschmidt number

# Typical Arrival Time Spectrum




He$^+$ in He, $P$ = 2.1 Pa, $E$ = 0.5 V/cm, $T$ = 4.3 K

$v_d$ = 214 m/s, $K_0$ = 24.4 cm$^2$V$^{-1}$s$^{-1}$

# Scaling of mobility (1)

reduced mobility $$K_0 = \frac{v_\mathrm{d}}{E}\frac{N}{N_0} = K_0(T, E/N)$$

$K_0$ generally does not depend on $P$.

mean collision energy $$\langle \varepsilon \rangle = \frac{3}{2}kT + \frac{1}{2}Mv_\mathrm{d}^2 = \frac{3}{2}kT_\mathrm{eff}$$

effective temperature $$T_\mathrm{eff} = T + \frac{1}{3k}Mv_\mathrm{d}^2$$

reduced mobility $$\boxed{K_0 \approx K_0(T_\mathrm{eff})}$$

# Scaling of mobility (2)

polarization potential

$$V_{\mathrm{pol}}(r) = -\frac{1}{4\pi\varepsilon_0}\cdot\frac{e^2\alpha_{\mathrm{d}}}{2r^4}$$

polarization limit

$$K_{\mathrm{pol}} \equiv K_0(E/N \to 0, T \to 0)$$

$$= \frac{13.853}{\sqrt{\alpha_{\mathrm{d}}\mu}} \quad \mathrm{cm^2V^{-1}s^{-1}}$$

$\alpha_{\mathrm{d}}$ : polarizability of gas in Å$^3$

$\mu$ : reduced mass in amu

normalized mobility ®

$$\frac{K_0}{K_{\mathrm{pol}}} \to 1 \quad (T_{\mathrm{eff}} \to 0\,\mathrm{K})$$

**in classical theory**

# Compilations of experimental data

E. A. Mason and his collaborators,

*Transport properties of gaseous ions over a wide energy range*

Atomic Data and Nuclear Data Tables,

| | |
|---|---|
| I | <u>17</u>, 177-210 (1976), |
| II | <u>22</u>, 179-217 (1978), |
| III | <u>31</u>, 113-151 (1984), |
| IV | <u>60</u>, 37-95 (1995). |

Available Mobilities of Singly Charged Monatomic Cations in Gases

| | $He$ | $Ne$ | $Ar$ | $Kr$ | $Xe$ | $H_2$ | $D_2$ | $N_2$ | $O_2$ | $NO$ | $CO$ | $CO_2$ | $CH_4$ | $HCl$ | $HBr$ | $HI$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H^+$ | III | I | | | | I | | | | | | | | | | |
| $D^+$ | III | I | | | | | I | | | | | | | | | |
| $He^+$ | IV | | | | | | | | | | | | | | | |
| $Li^+$ | IV | IV | IV | III | III | IV | I | IV | IV | | IV | IV | IV | IV | IV | IV |
| $C^+$ | IV | | | | | | | | | | I | | | | | |
| $N^+$ | IV | | IV | | | | | I | | | | | | | | |
| $O^+$ | IV | IV | IV | | | | | | | | | | | | | |
| $F^+$ | IV | | | | | | | | | | | | | | | |
| $Ne^+$ | IV | IV | III | | | | | | | | | | | | | |
| $Na^+$ | I | I | I | III | III | I | IV | | IV | | | I | IV | | | |
| $Si^+$ | III | | | | | | | | | | | | | | | |
| $S^+$ | III | | | | | | | | | | | | | | | |
| $Cl^+$ | IV | | | | | | | | | | | | | | | |
| $Ar^+$ | IV | III | III | | | | | | | | | | | | | |
| $K^+$ | IV | I | IV | II | II | I | I | I | I | I | I | I | II | | | |
| $Br^+$ | IV | | | | | | | | | | | | | | | |
| $Kr^+$ | IV | | II | II | | | | II | | | | | | | | |
| $Rb^+$ | I | I | I | II | II | II | | II | II | | | I | | | | |
| $I^+$ | IV | | | | | | | | | | | | | | | |
| $Xe^+$ | IV | III | III | | IV | | | | | | | | | | | |
| $Cs^+$ | II | II | II | II | II | II | | II | II | | II | II | | | | |
| $Ba^+$ | IV | | IV | | | | | | | | | | | | | |
| $Hg^+$ | I | I | I | | | | | | | | | | | | | |
| $Tl^+$ | III | III | III | III | III | | | | | | | | | | | |
| $U^+$ | I | | | | | | | | | | | | | | | |

**L. A. Vieland** and E. A. Mason (1995).

### Available Mobilities of Singly Charged Diatomic Cations in Gases

| | $He$ | $Ne$ | $Ar$ | $Kr$ | $N_2$ | $O_2$ | $NO$ | $CO$ | $CO_2$ | air |
|---|---|---|---|---|---|---|---|---|---|---|
| $H_2^+$ | I | | | | | | | | | |
| $HeH^+$ | II | | | | | | | | | |
| $He_2^+$ | III | | | | | | | | | |
| $CH^+$ | IV | | | | | | | | | |
| $CN^+$ | IV | | | | | | | | | |
| $CO^+$ | IV | III | III | | | | | I | | |
| $N_2^+$ | IV | III | III | III | IV | | | | | |
| $NO^+$ | I | | | | | | I | | IV | IV |
| $O_2^+$ | I | IV | I | III | | IV | | | IV | IV |
| $Ne_2^+$ | | IV | | | | | | | | |
| $ArH^+$ | I | | | | | | | | | |
| $Ar_2^+$ | | | III | | | | | | | |
| $Kr_2^+$ | | | | III | | | | | | |

### Available Mobilities of Singly Charged Polyatomic Cations in Gases

| | $He$ | $Ne$ | $Ar$ | $Kr$ | $Xe$ | $H_2$ | $D_2$ | $N_2$ | $O_2$ | $NO$ | $CO$ | $CO_2$ | $CH_4$ | $SF_6$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3^+$ | IV | | III | | | | | | | | | | | |
| $NH_3^+$ | I | | | | | | | | | | | | | |
| $H_3O^+$ | II | | IV | | | | | II | | | | | | |
| $H_2CN^+$ | IV | | | | | | | | | | | | | |
| $H_2O_2^+$ | I | | | | | | | | | | | | | |
| $N_2OH^+$ | I | | I | | | | | | | | | | | |
| $LiCO_2^+$ | | | | | | | | | | | | IV | | |
| $C_2N_2^+$ | IV | | | | | | | | | | | | | |
| $C_2O_2^+$ | | | | | | | | | | | I | | | |
| $N_4^+$ | IV | | | | | | | II | | | | | | |
| $N_2O_2^+$ | | | | | | | | | | I | | | | |
| $O_4^+$ | | | | | | | | | I | | | | | |
| $SF_3^+$ | | | | | | | | | | | | | | IV |
| $CH_4^+$ | III | | | | | | | | | | | | | |
| $NH_4^+$ | I | | | | | | | | | | | | | |
| $NOH_2O^+$ | I | | | | | | | | | | | | | |
| $SF_4^+$ | | | | | | | | | | | | | | IV |
| $CH_5^+$ | I | | | | | | | | | | | | IV | |
| $LiCH_4^+$ | | | | | | | | | | | | | IV | |
| $C_2H_3N^+$ | IV | | | | | | | | | | | | | |
| $CH_3O_2^+$ | I | | | | | | | | | | | | | |
| $CO_2CO_2^+$ | | | | | | | | | | | | IV | | |
| $C_2H_5^+$ | | | | | | | | | | | | | IV | |
| $CH_2CHOH^+$ | IV | | | | | | | | | | | | | |
| $CH_2OCH_2^+$ | IV | | | | | | | | | | | | | |
| $H_3OH_2O^+$ | II | | | | | | | II | | | | | | |
| $SF_5^+$ | | | | | | | | | | | | | | IV |
| $C_3H_5^+$ | | | | | | | | | | | | | IV | |
| $CH_3CHOH^+$ | IV | | | | | | | | | | | | | |
| $CH_3OCH_2^+$ | IV | | | | | | | | | | | | | |
| $S_2F_7^+$ | | | | | | | | | | | | | | IV |
| $H_3O(H_2O)_2^+$ | II | | | | | | | II | | | | | | |
| $C_3H_7^+$ | | | | | | | | | | | | | IV | |

## Available Mobilities of Singly Charged Triatomic Cations in Gases

| | He | Ne | Ar | $H_2$ | $D_2$ | $N_2$ | CO | $CO_2$ | $SF_6$ | air |
|---|---|---|---|---|---|---|---|---|---|---|
| $H_3^+$ | I | | | I | | | | | | |
| $D_3^+$ | | | | | I | | | | | |
| $CH_2^+$ | IV | | | | | | | | | |
| $NH_2^+$ | IV | | | | | | | | | |
| $H_2O^+$ | II | IV | IV | | | | | | | |
| $HCN^+$ | IV | | | | | | | | | |
| $COH^+$ | I | | I | | | | | | | |
| $N_2H^+$ | III | | III | | | II | | | | |
| $HO_2^+$ | I | | | | | | | | | |
| $LiCO^+$ | | | | | | | IV | | | |
| $LiN_2^+$ | | | | | | IV | | | | |
| $C_2N^+$ | IV | | | | | | | | | |
| $N_3^+$ | | | | | | I | | | | |
| $CO_2^+$ | IV | II | I | | | II | | IV | | |
| $N_2O^+$ | IV | II | IV | | | II | | | | |
| $NO_2^+$ | IV | | IV | | | III | | | | IV |
| $N_2Ar^+$ | IV | | | | | | | | | |
| $SF_2^+$ | | | | | | | | | IV | |
| $SO_2^+$ | IV | | IV | | | | | | | |

## Available Mobilities of Doubly Charged Cations in Gases

| | He | Ne | Ar | Kr | Xe |
|---|---|---|---|---|---|
| $He^{2+}$ | II | | | | |
| $Ne^{2+}$ | III | II | | | |
| $Ar^{2+}$ | III | | II | | |
| $Kr^{2+}$ | IV | | | IV | |
| $Xe^{2+}$ | IV | III | | | II |
| $O^{2+}$ | IV | IV | | | |
| $Hg^{2+}$ | IV | | | | |
| $O_2^{2+}$ | IV | | IV | | |

## Available Mobilities of Singly Charged Anions in Gases

| | He | Ne | Ar | Kr | Xe | $H_2$ | $N_2$ | $O_2$ | $CO_2$ | $SF_6$ | air |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $H^-$ | I | | | | | I | | | | | |
| $O^-$ | IV | | | | | | | I | I | | IV |
| $F^-$ | IV | | II | II | II | | | | | IV | |
| $S^-$ | IV | | | | | | | | | | |
| $Cl^-$ | IV | II | II | II | II | | III | | | | IV |
| $Br^-$ | II | III | III | III | III | | | | | | |
| $I^-$ | II | | II | | | | | | | | |
| $OH^-$ | IV | | | | | | | | | | |
| $OD^-$ | IV | | | | | | | | | | |
| $O_2^-$ | IV | | | | | | | I | | | IV |
| $SH^-$ | IV | | | | | | | | | | |
| $S_2^-$ | IV | | | | | | | | | | |
| $NO_2^-$ | I | | | | | | III | | | | IV |
| $O_3^-$ | I | | I | | | | | I | | | IV |
| $C_2H_2^-$ | I | | | | | | | | | | |
| $CO_3^-$ | I | | I | | | | | I | I | | |
| $NO_3^-$ | | | | | | | III | | | | |
| $SO_2F^-$ | I | | | | | | | | | | |
| $SO_3^-$ | I | | | | | | | | | | |
| $CO_4^-$ | | | | | | | | I | | | |
| $SF_5^-$ | I | | | | | | | | | IV | |
| $SF_6^-$ | I | | | | | | | | | IV | |
| $SF_6SF_6^-$ | | | | | | | | | | IV | |
| $SF_6(SF_6)_2^-$ | | | | | | | | | | IV | |

# closed-shell systems

# Our works – Ion mobility in cooled He gas

## Atomic Ions :

$H^+$

$He^+$, $Ne^+$, $Ar^+$, $Kr^+$, $Xe^+$

$Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$

$C^+$, $N^+$, $O^+$

## Molecular Ions :

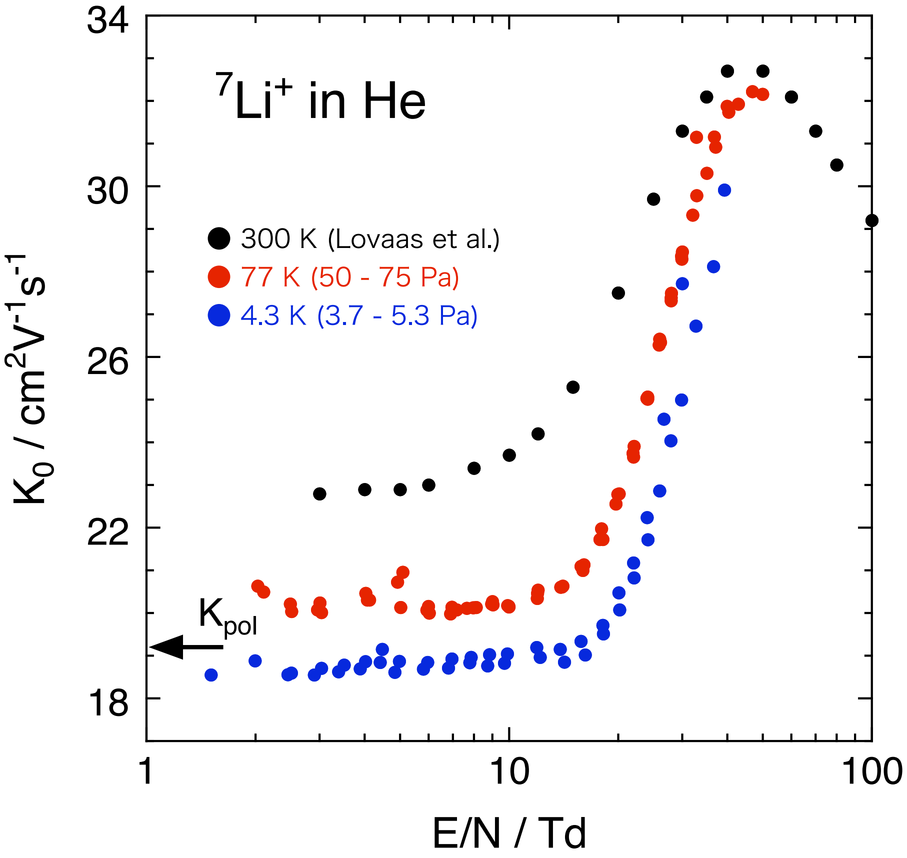
$N_2^+$, $O_2^+$, $CO^+$, $NO^+$, $CH^+$

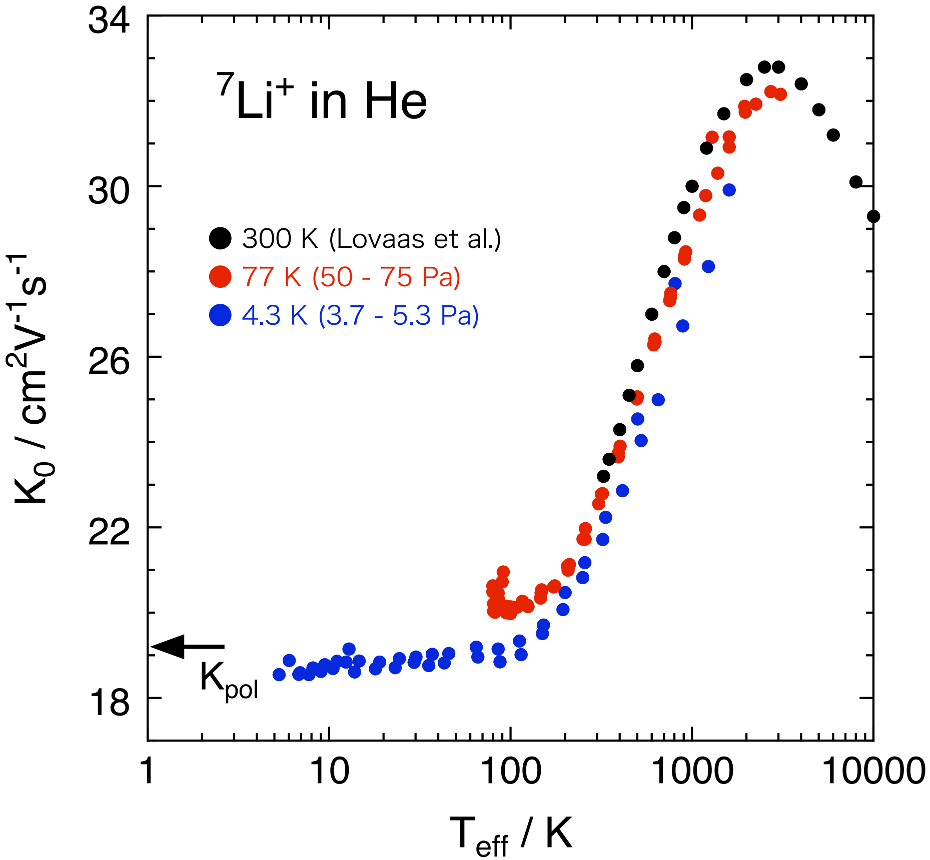
$CO_2^+$, $NO_2^+$, $CH_2^+$

$CH_3^+$

$CO_2^{2+}$

# Mobility of $Li^+$ in He at 4.3, 77, and 300 K




Scaling by $T_{eff}$ is sufficient to compile the mobility data measured at different gas temperatures.

# Two-temperature Theory of Ion Mobility

Mobility

$$K_0 = \frac{3e}{16N_0}\left(\frac{2\pi}{\mu k T_{\mathrm{eff}}}\right)^{1/2} \frac{1+\alpha}{\Omega^{(1,1)}(T_{\mathrm{eff}})}$$

Effective temp.

$$T_{\mathrm{eff}} = T + \frac{1}{3k} M v_{\mathrm{d}}^2 (1+\beta)$$

Collision integral

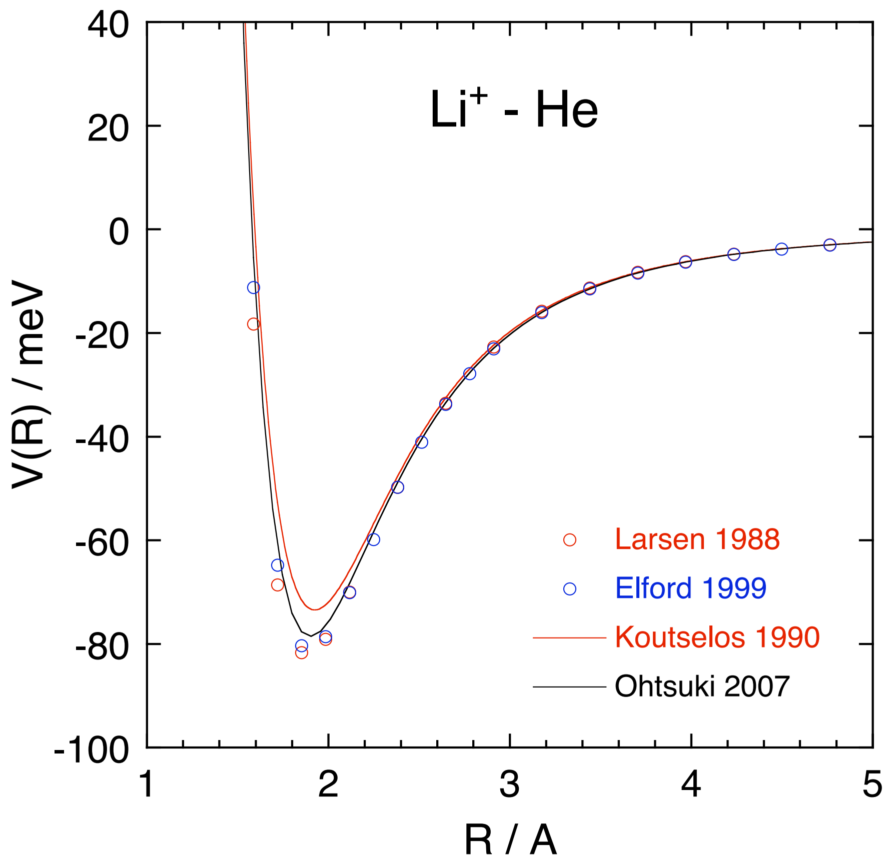
$$\Omega^{(1,1)}(T_{\mathrm{eff}}) = \frac{1}{2(kT_{\mathrm{eff}})^3} \int_0^\infty Q^{(1)}(\varepsilon) \exp\left(-\frac{\varepsilon}{kT_{\mathrm{eff}}}\right) \varepsilon^2 \mathrm{d}\varepsilon$$

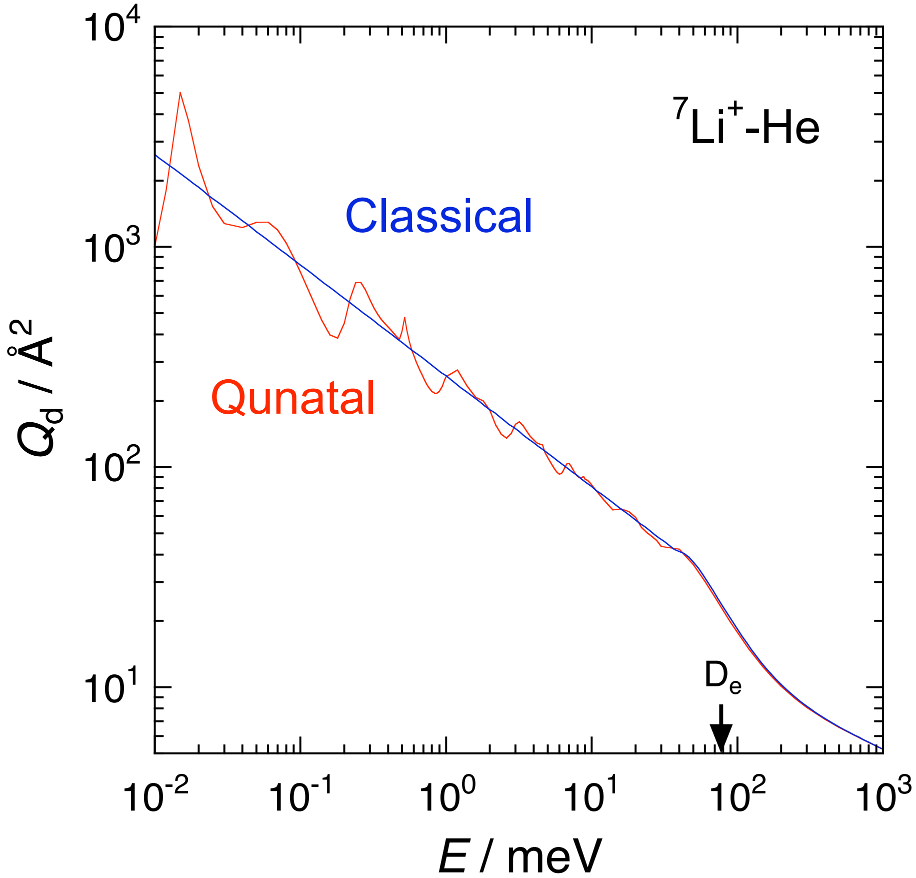
Momentum transfer cross section

$$Q^{(1)}(\varepsilon) = \frac{4\pi}{\kappa^2} \sum_{l=0}^{\infty} (l+1) \sin^2\left(\eta_l - \eta_{l+1}\right)$$

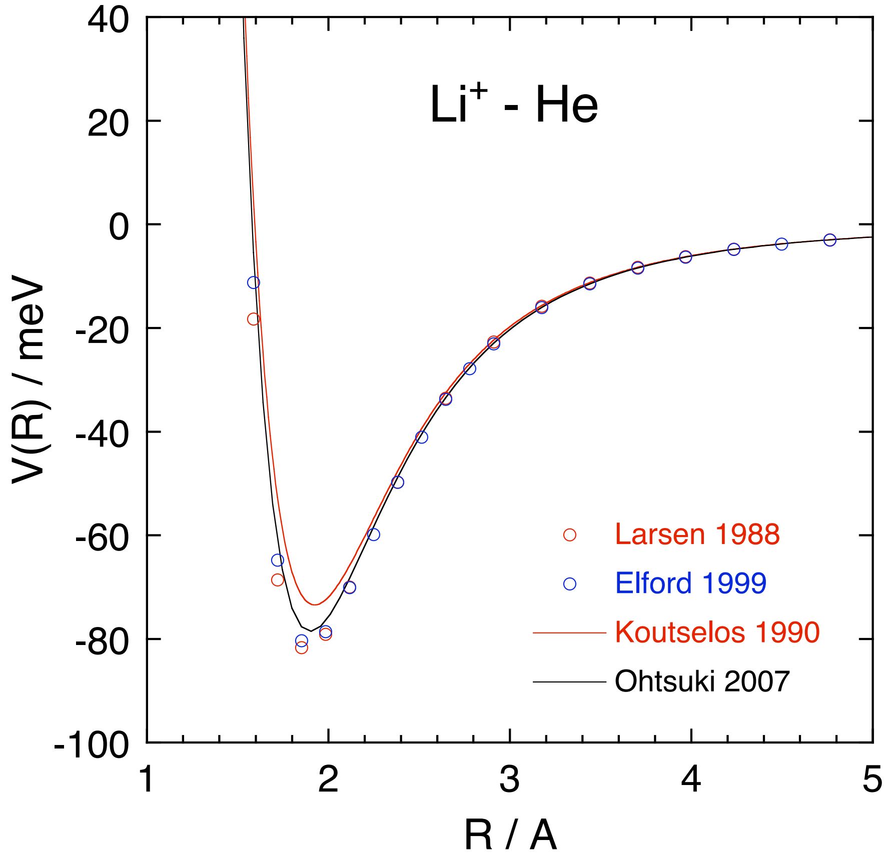
$\kappa = \sqrt{2\mu\varepsilon}/\hbar$ $\eta_l$ : **phase shift**

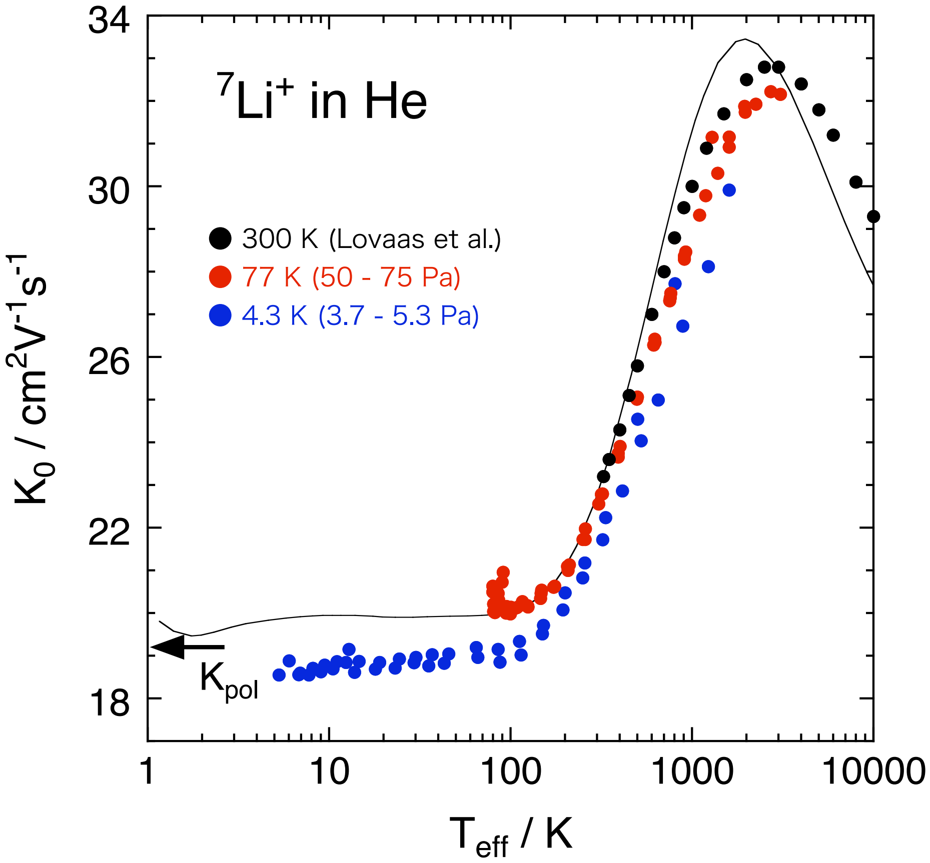
# Potential curve and MTCS of Li⁺ in He



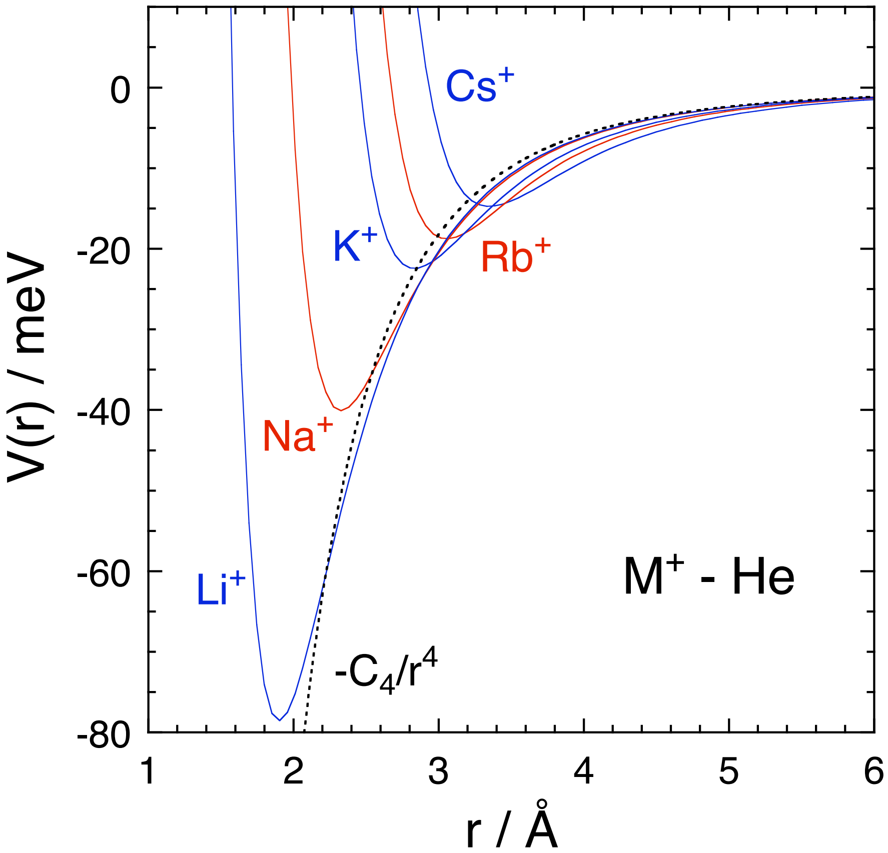
# Potential curve and Mobility of $Li^+$ in He

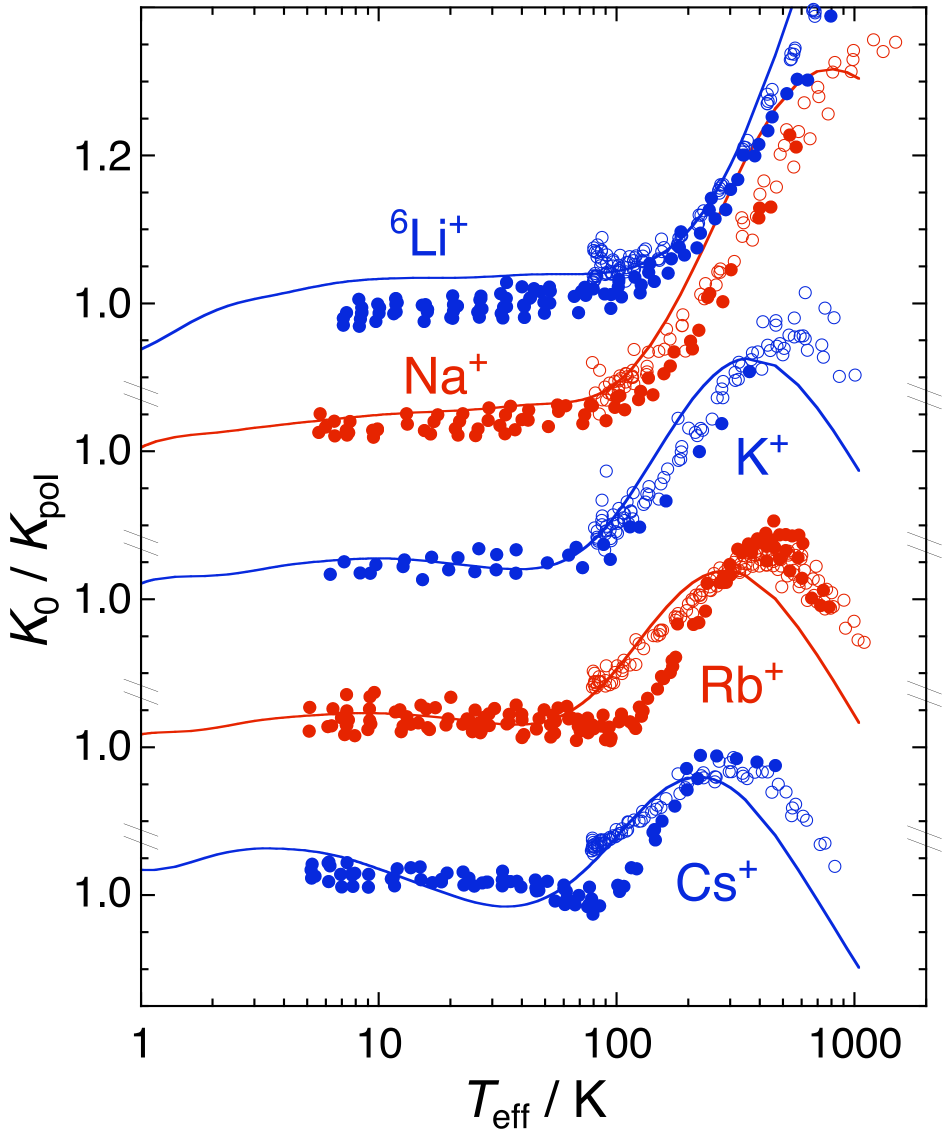


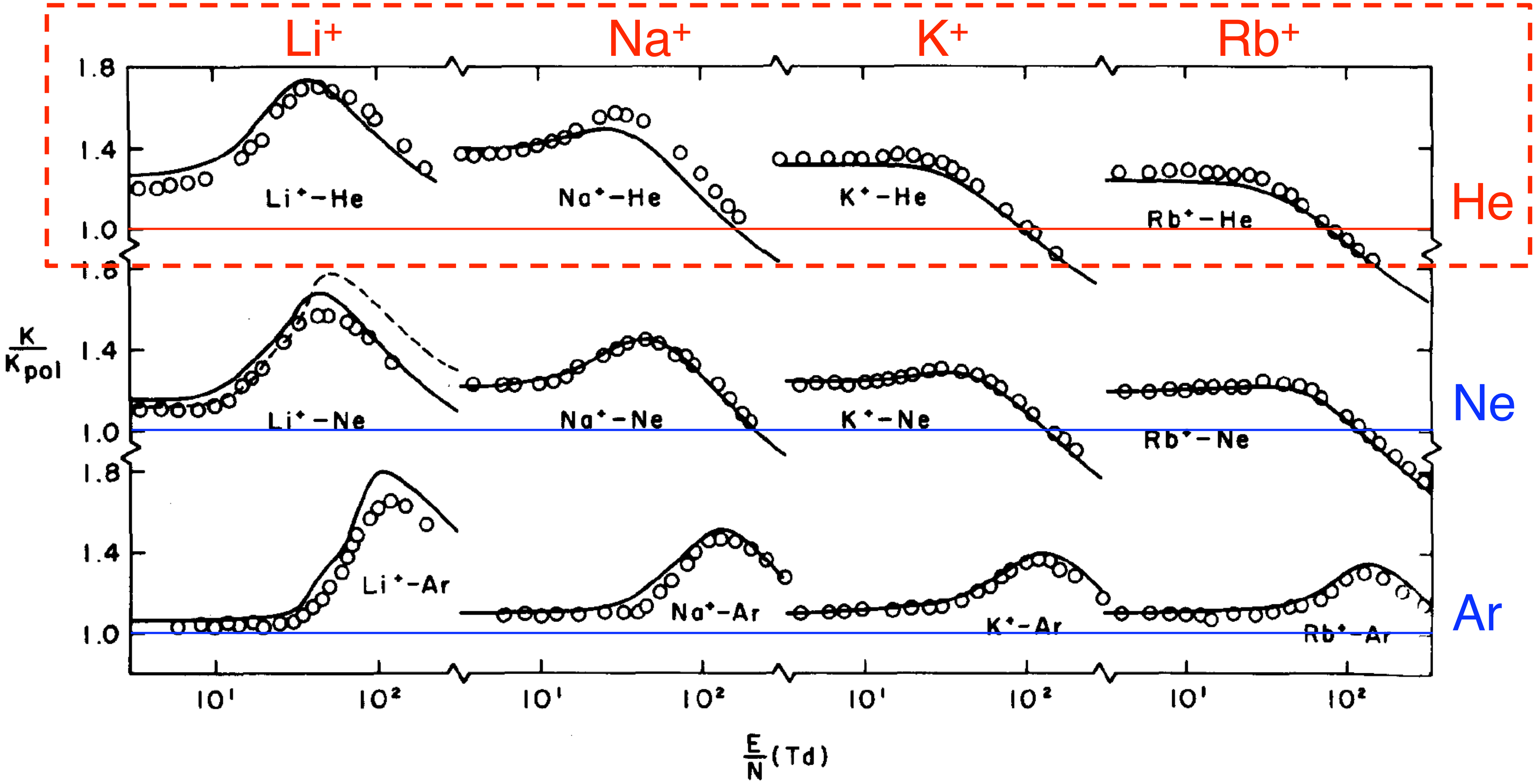

Accurate potential gives good agreement between the experiment value and the theoretical calculation.

# $K_0 / K_{pol}$ of five alkali ions in He



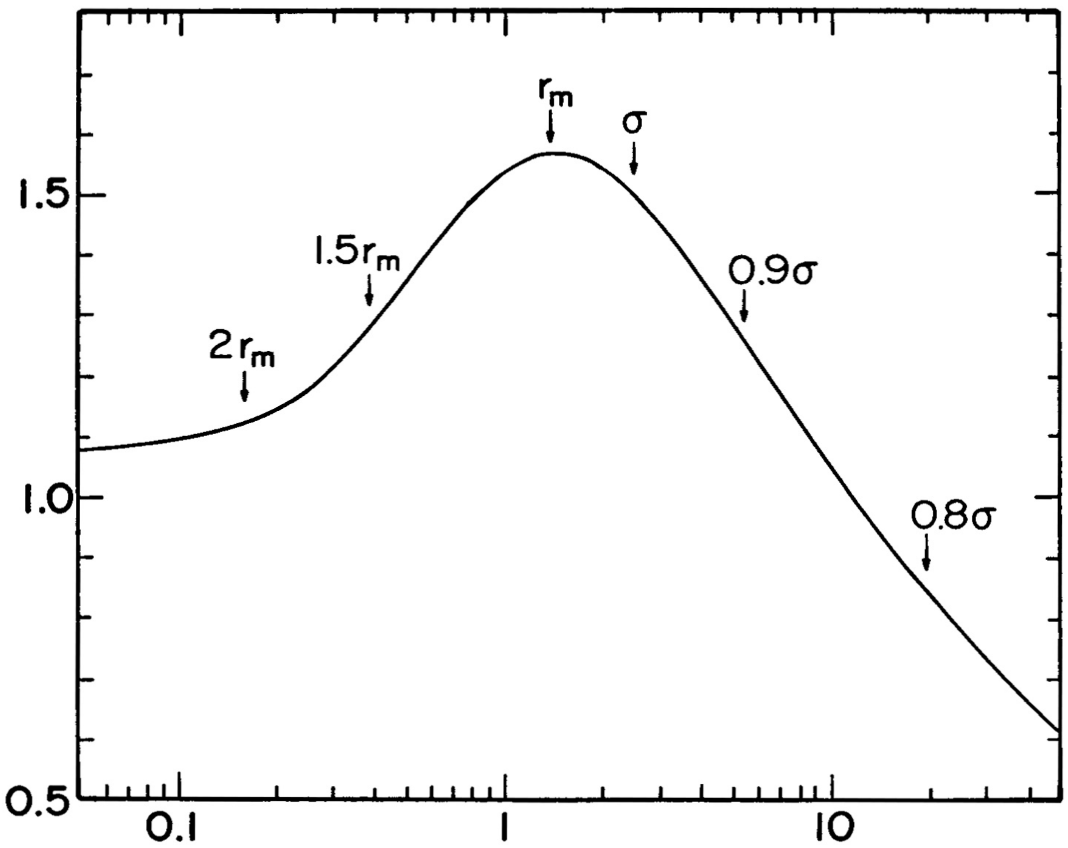



# Historical works in Georgia Institute of Technology @ room temperature




I. R. Gatland *et al.*, J. Chem. Phys. 66 (1977) 537.

# Generalized ion mobility curve




$$\frac{K_0}{K_{pol}}$$

$$T^* = \frac{kT_{eff}}{\text{(potential depth)}}$$

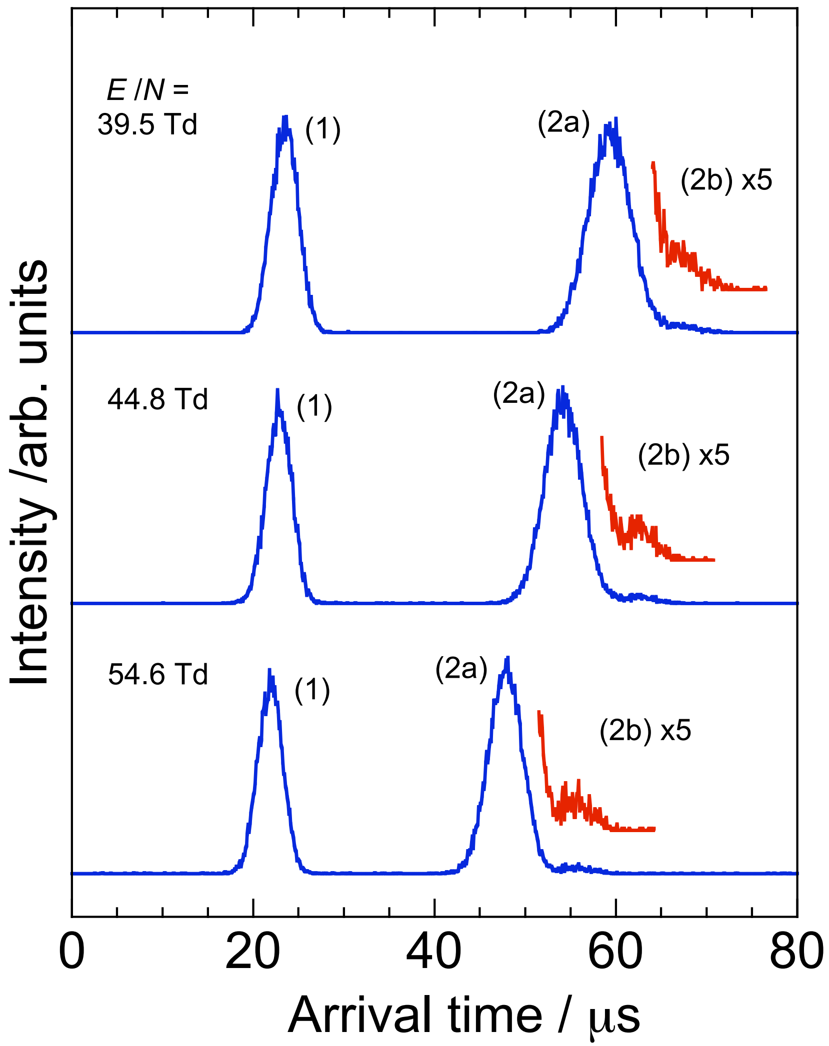
# open-shell systems

# Meta-stable States of Atomic Ions

| Ion | Configuration | Energy | Fraction* | Source gas |
|---|---|---|---|---|
| $C^+(^2P^o)$ | $2s^22p$ | G.S. | 94 % | $CH_4$ |
| $C^+(^4P)$ | $2s2p^2$ | 5.3 eV | 6 % | |
| $N^+(^3P)$ | $2s^22p^2$ | G.S. | 88 % | $N_2$ |
| $N^+(^1D)$ | $2s^22p^2$ | 1.9 eV | 12 % | |
| $N^+(^1S)$ | $2s^22p^2$ | 4.1 eV | - | |
| $O^+(^4S^o)$ | $2s^22p^3$ | G.S. | 65 % | $O_2$ |
| $O^+(^2D^o)$ | $2s^22p^3$ | 3.3 eV | 15 % | |
| $O^+(^2P^o)$ | $2s^22p^3$ | 5.0 eV | 20 % | |

*electron impact of 70 eV, Enos *et al*., J. Phys B **25** (1992) 4021.

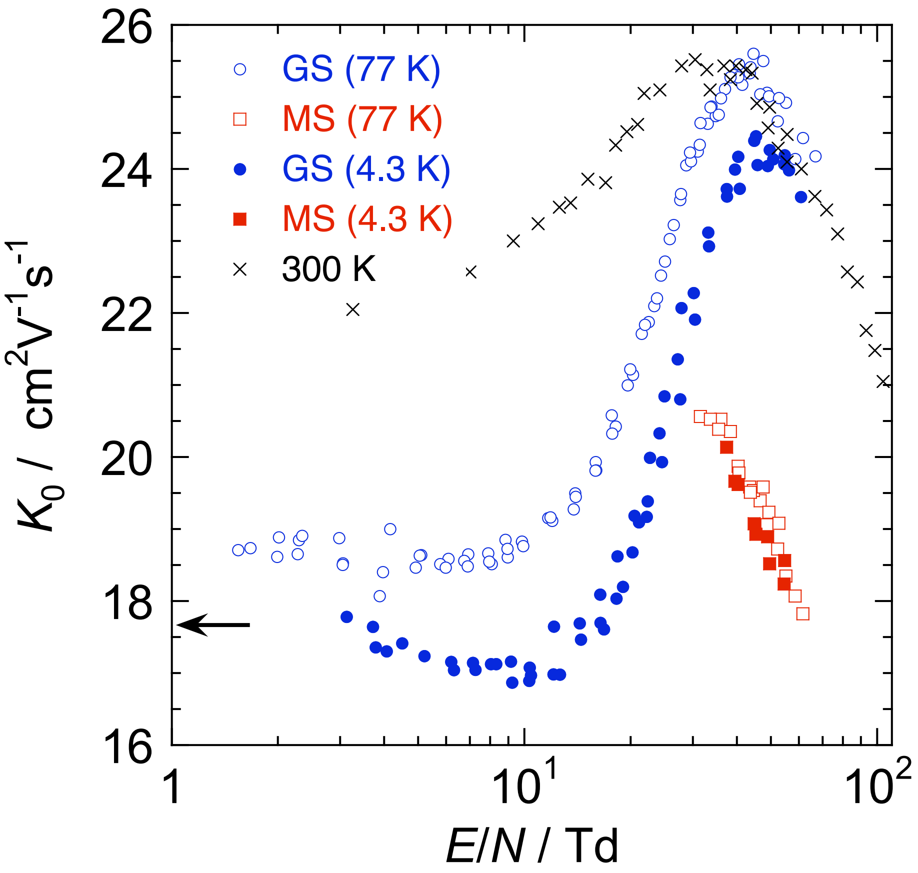
# Arrival spectra of $C^+$ in He at 4.3 K

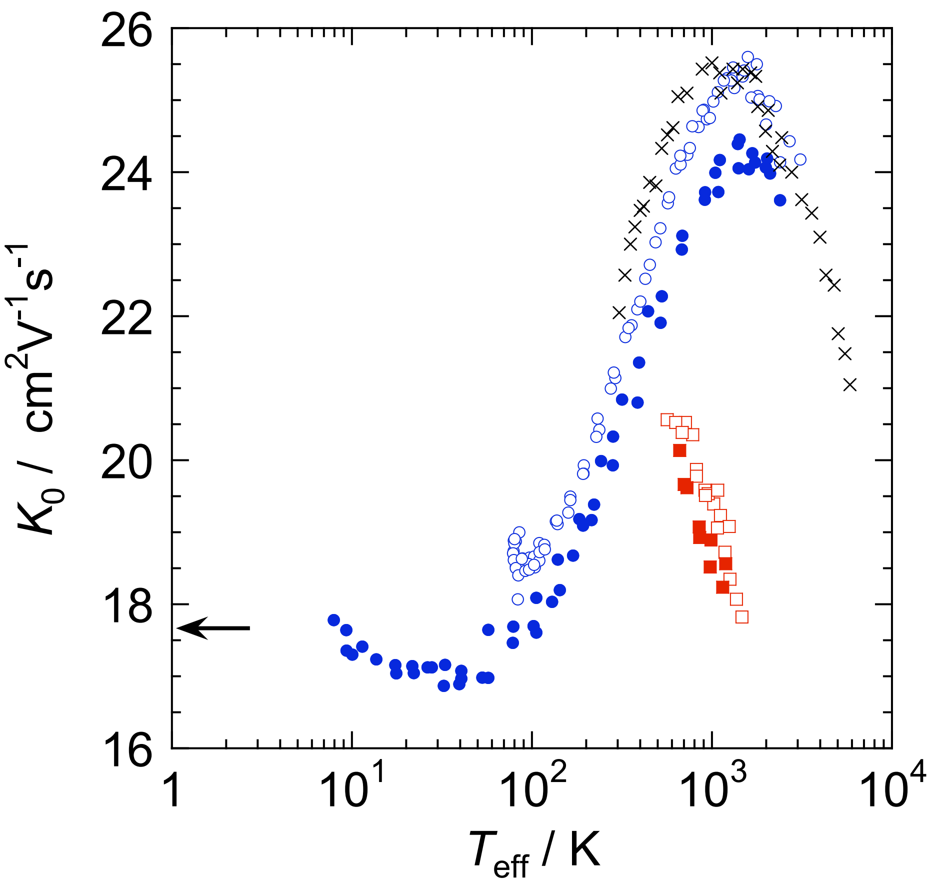



| | Fraction | Identification |
|---|---|---|
| (2a) | 98 % | G.S. ($^2P$) |
| (2b) | 2 - 3 % | M.S. ($^4P$) |

S. Matoba *et al*. J. Phys. B **41** 145205.

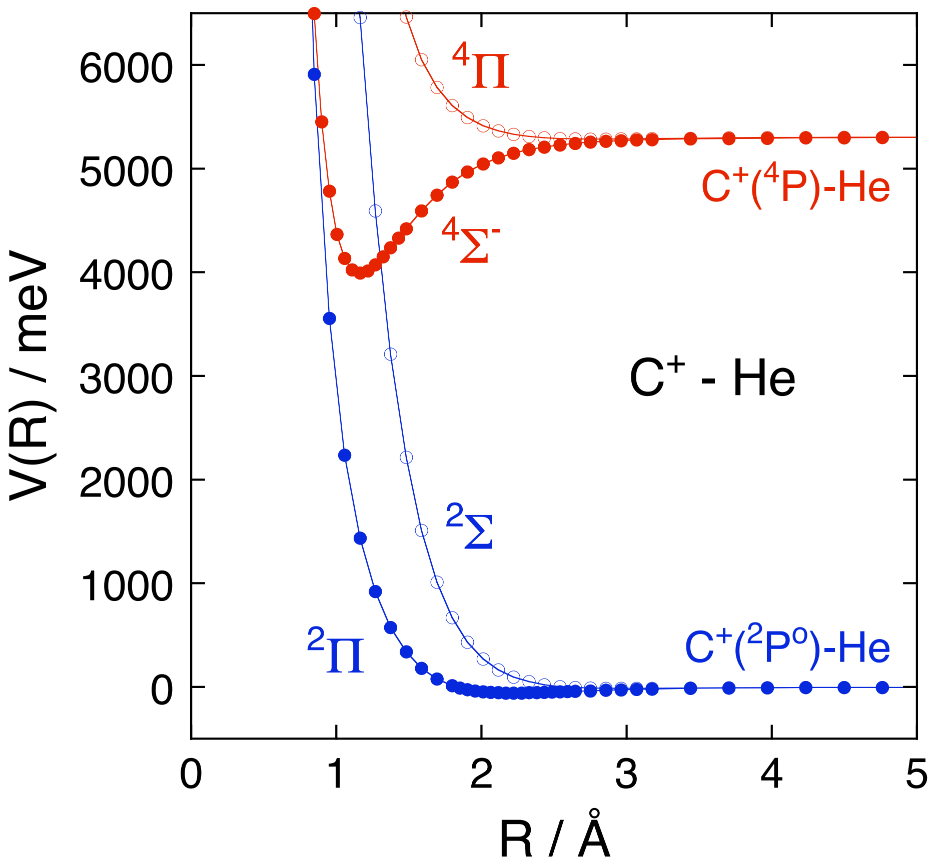
# Mobility of $C^+$ in He at 4.3, 77, and 300 K




S. Matoba *et al*. J. Phys. B **41** 145205.

# ab initio potentials and cross sections




Approximated cross sections

$$Q \approx \frac{g_a Q_a + g_b Q_b}{g_a + g_b}$$

$g_i$ : multiplicity of the state $i$

$\Sigma$ : $g = 1$

$\Pi$ : $g = 2$

$\Delta$ : $g = 2$

As $Q_i$ , we used the classical cross sections.



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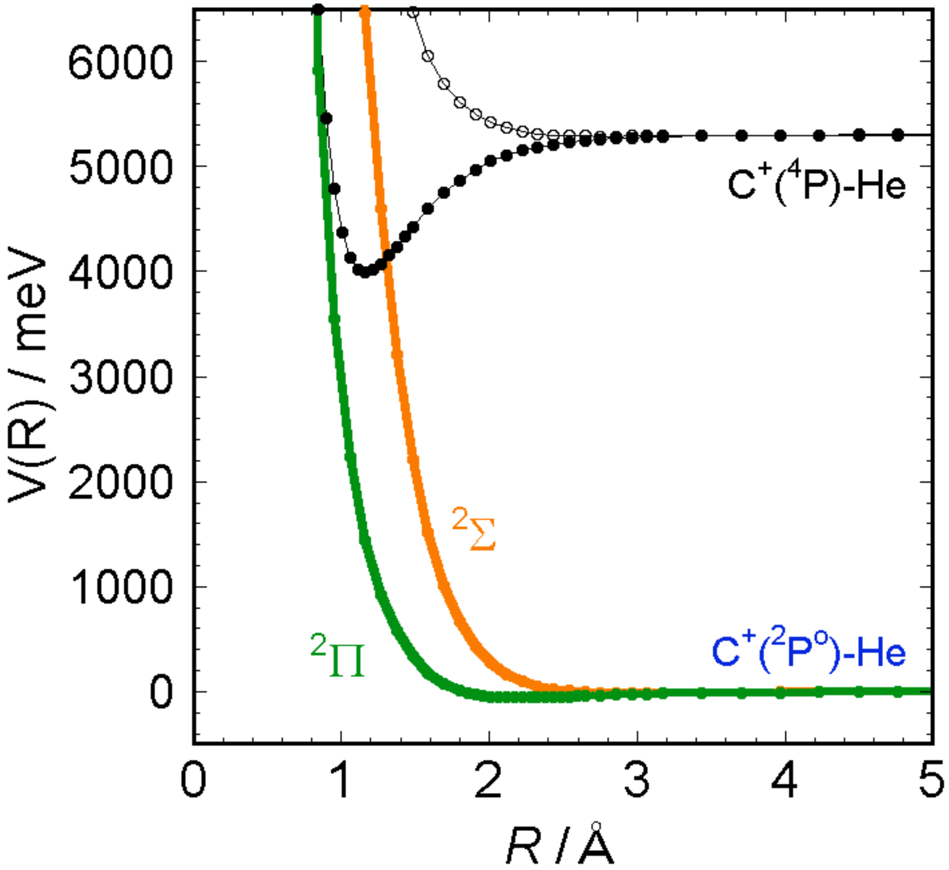
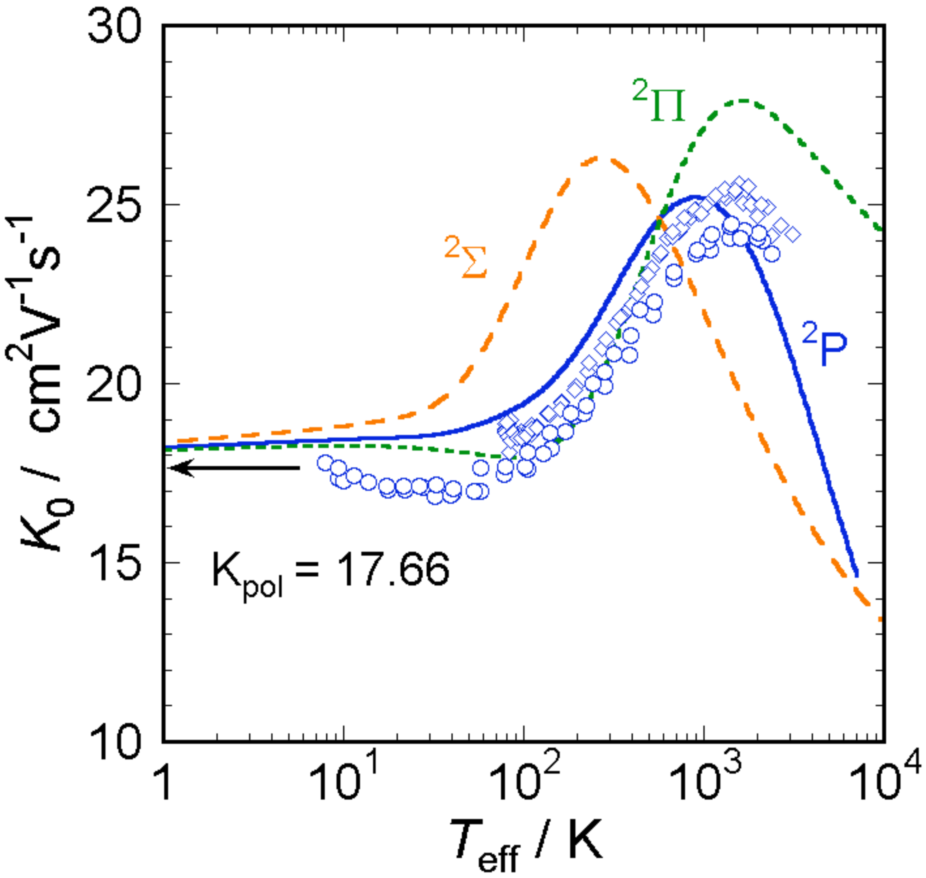
# Calculation for the ground state $C^+(^2P)$



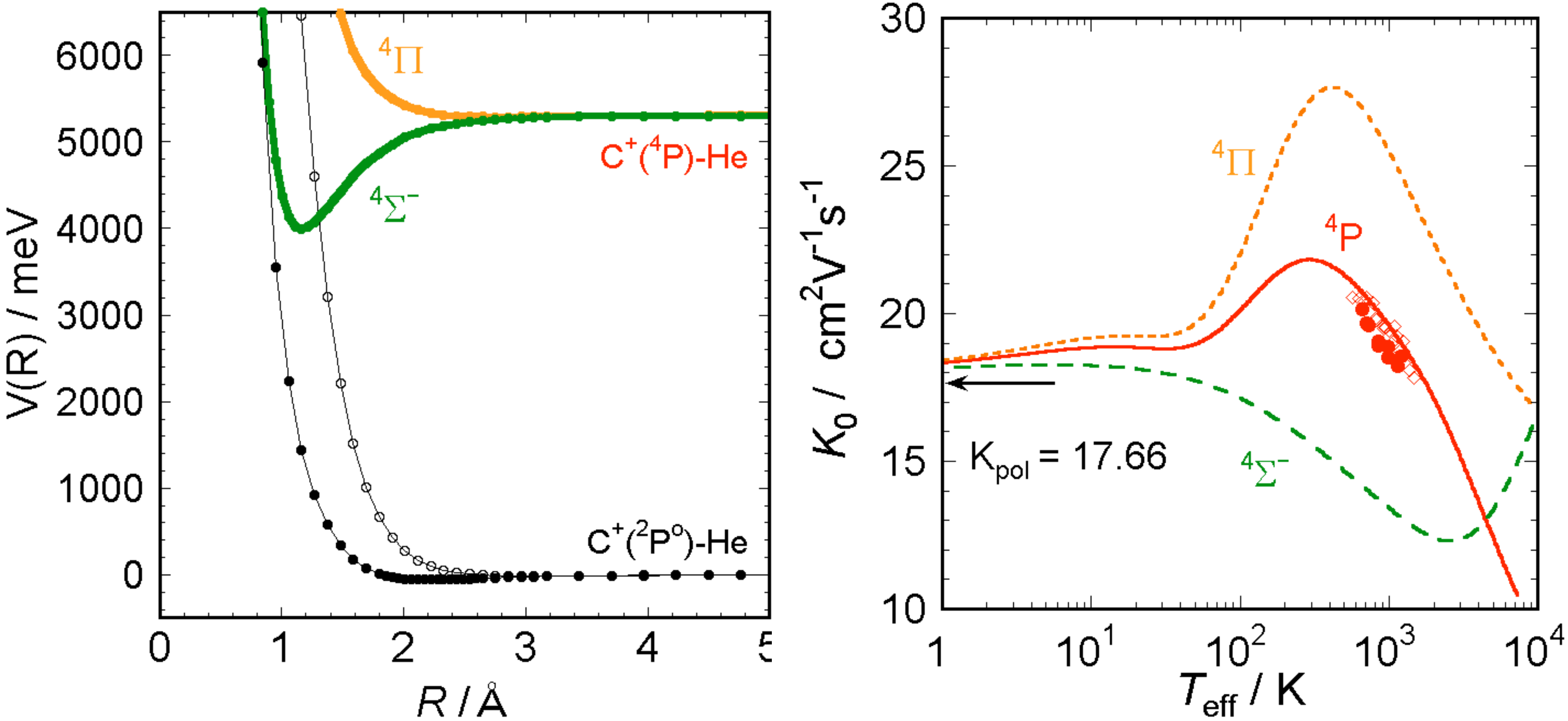




Calculation with only one potential can not reproduce the measured mobility.



S. Matoba *et al*. J. Phys. B **41** 145205.

# Calculation for the matastable state $C^+(^4P)$

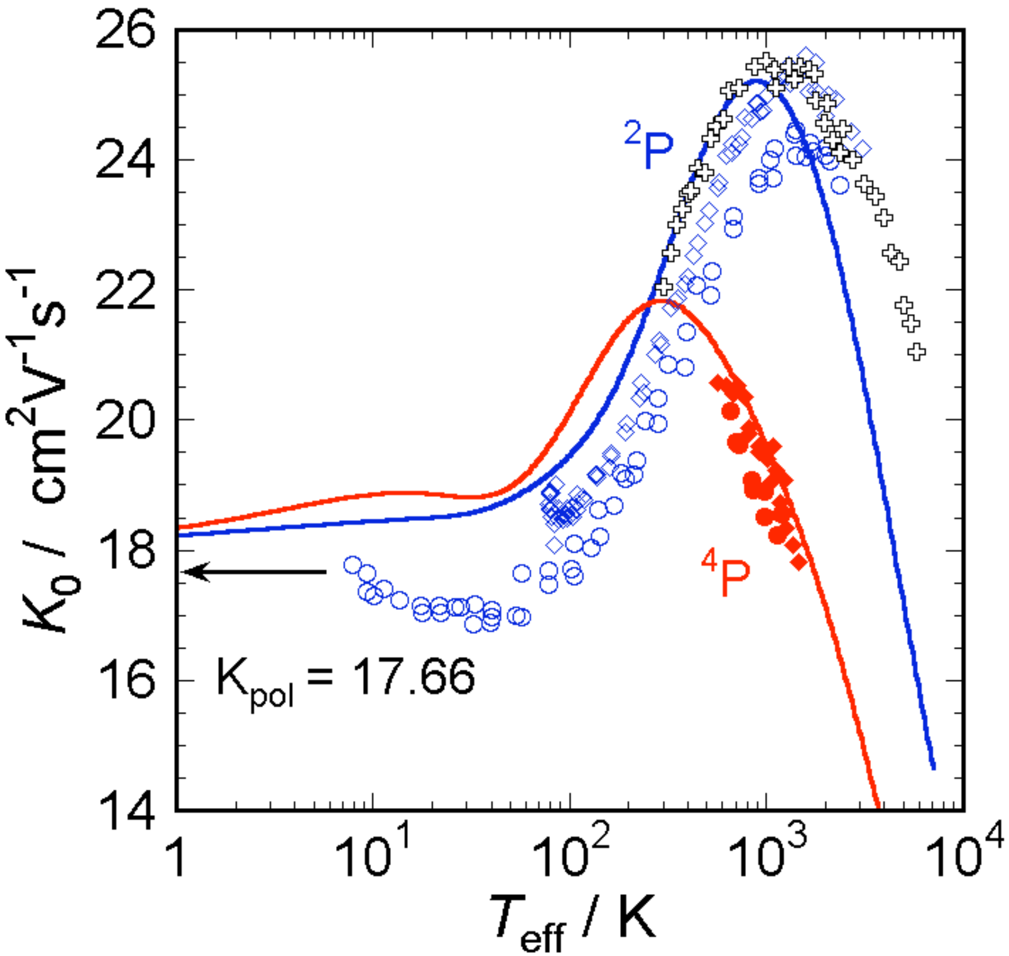



Calculation with two potentials reproduces the experiment even though the interaction between two states is neglected.



S. Matoba *et al*. J. Phys. B **41** 145205.

# Mobility of C($^2$P) and C$^+$($^4$P) in He



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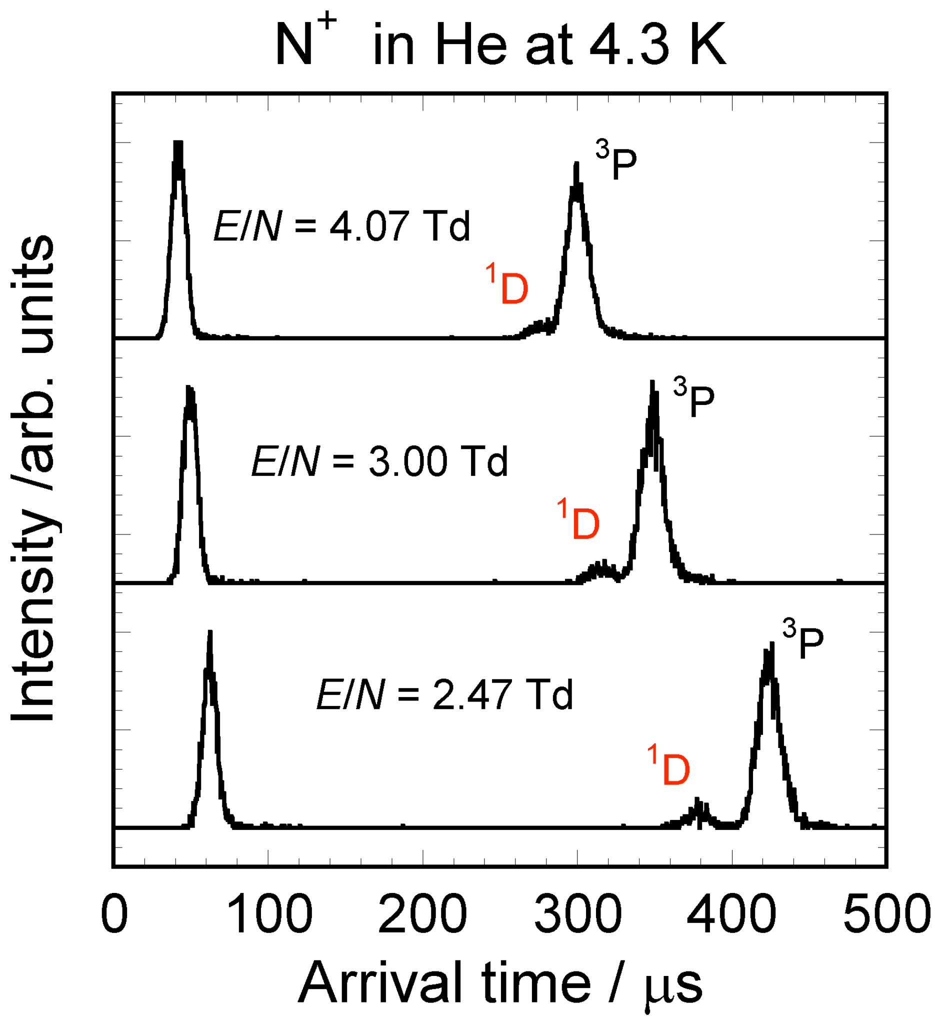
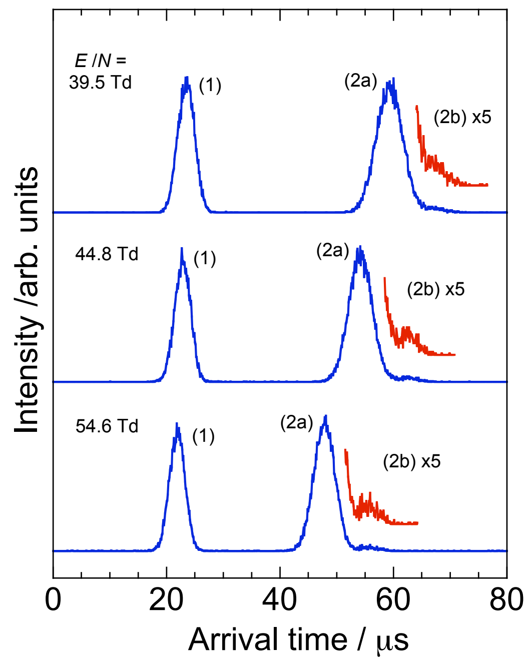
# Arrival spectra of $N^+$ in He at 4.3 K

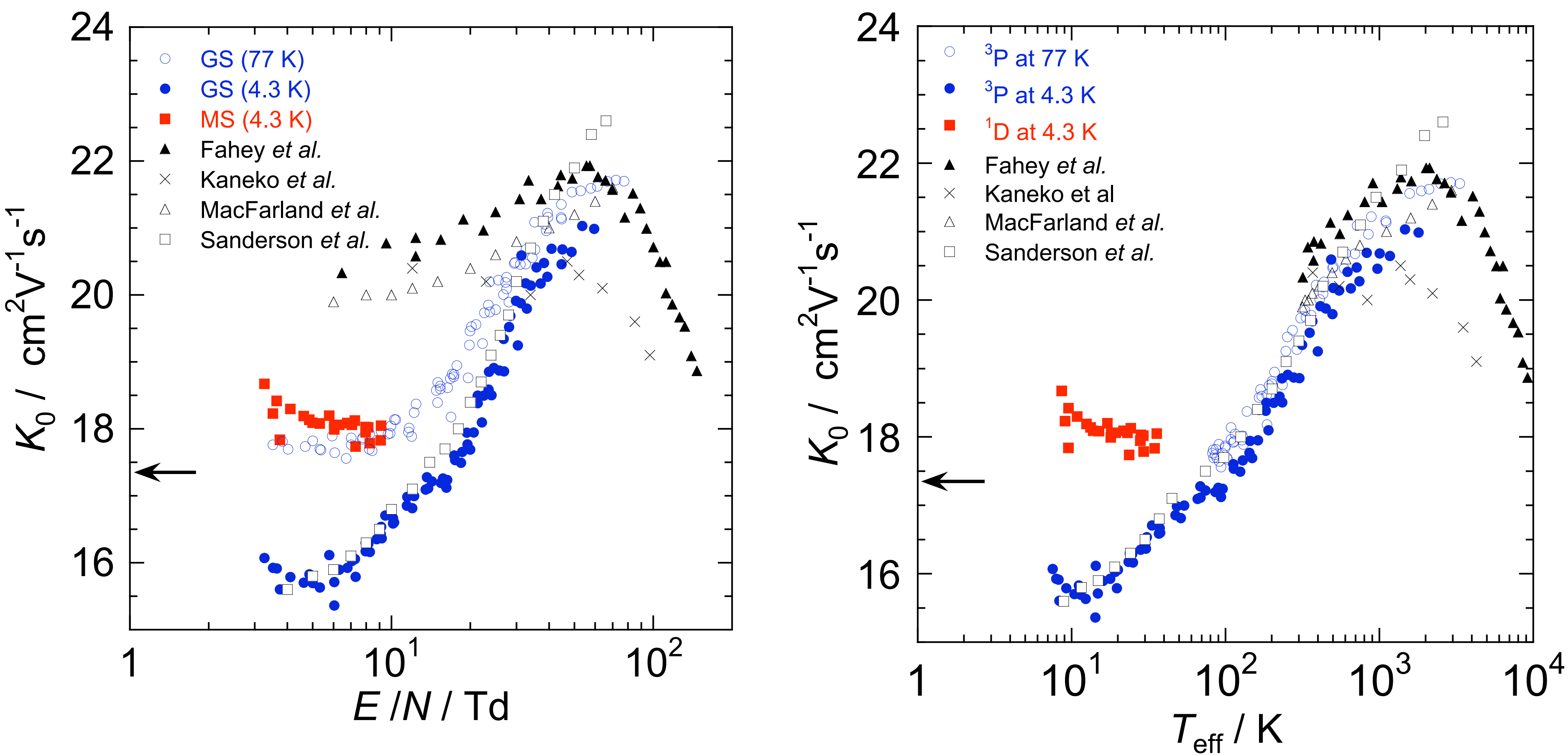



| | This work | Eos et al. |
|---|---|---|
| G.S. ($^3P$) | 72-95% | 88% |
| M.S. ($^1D$) | 5-28% | 12% |



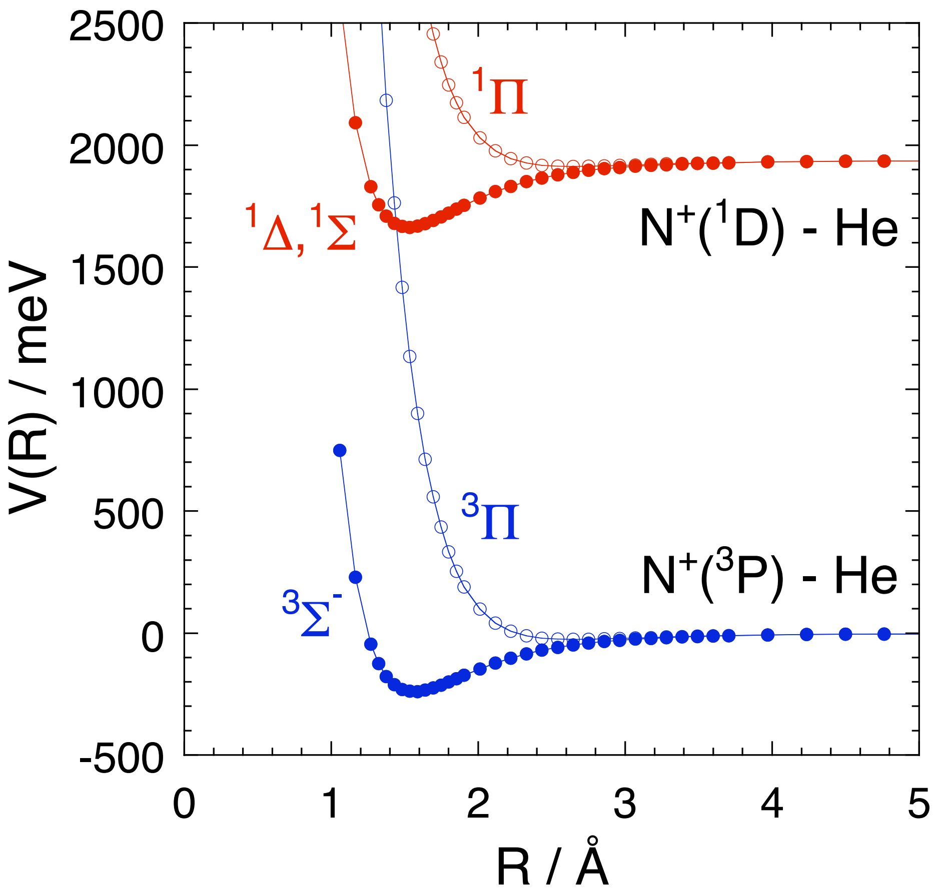

$C^+$/He

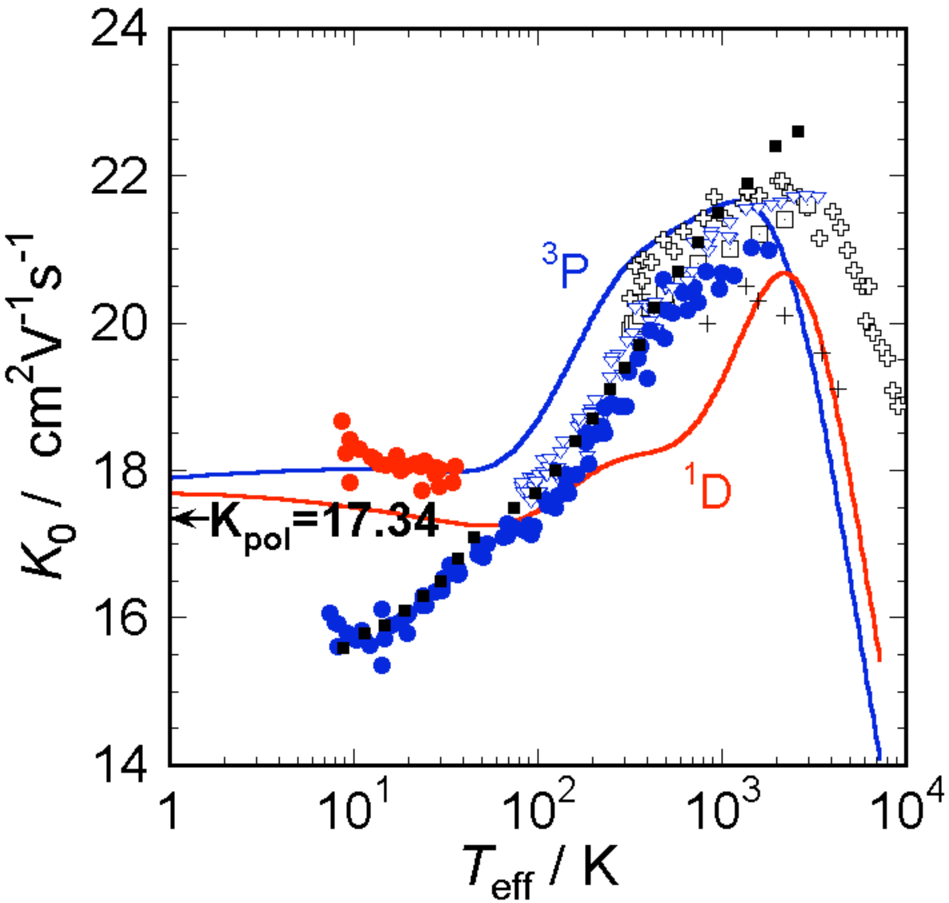
# Mobility of $N^+$ in He at 4.3, 77, and 300 K




$K_0(\text{MS}) > K_{pol} > K_0(\text{GS})$ in $N^+$/He

# Potential curves and Mobility of $N^+$ in He




Mobility of $^1D$ state can be explained, but that of $^3P$ is not.

# Summary

Close-shell systems : **Alkali ions**

- We measured the mobility of five alkali ions in cooled He.
- The results are explained by the calculation with qunantal cross sections taking account one molecular state.

Open-shell systems : **$C^+$ and $N^+$ ions**

1. We measured the mobility of ions in the ground and excited (metastable) states
2. The calculation with classical cross sections concerning two molecular states can explain the experimental results on $C^+(^4P$ and $^2P)$ and $N^+(^1D)$ in He.
3. Mobility of **$N^+(^3P)$** cannot be explained by our calculation. This is an **open question**.

*Do you need mobility data ?*