# New theory on electron-neutral sticking reactions

Jürgen Troe

University of Göttingen

$e^- + A \rightarrow A^-$ electron attachment

mechanism

| | | | |
|---|---|---|---|
| $e^- + A$ | $\rightarrow$ | $e^-A$ | (virtual) |
| $e^-A$ | $\rightarrow$ | $A^{-*}$ | (IVR) |
| $e^-A$ | $\rightarrow$ | $e^- + A^*$ | (VEX) |
| $A^{-*}$ | $\rightarrow$ | $e^- + A$ | (delayed) |
| $A^{-*}$ | $\rightarrow$ | $A^- + h\nu$ | (radiative) |
| $A^{-*} + M$ | $\rightarrow$ | $A^- + M$ | (collisional) |

$e^- + A \rightarrow B^- + C$ dissociative attachment

mechanism

| | | | |
|---|---|---|---|
| $e^- + A$ | $\rightarrow$ | $B^- + C$ | (direct) |
| $e^- + A$ | $\rightarrow$ | $A^{-*}$ | (complex-forming) |
| $A^{-*}$ | $\rightarrow$ | $B^- + C$ | (delayed) |
| $A^{-*}$ | $\rightarrow$ | $e^- + A$ | (delayed) |
| $A^{-*}$ | $\rightarrow$ | $A^- + h\nu$ | (radiative) |
| $A^{-*} + M$ | $\rightarrow$ | $A^- + M$ | (collisional) |

# electron capture theory

electron = quantum species

generally only s-waves important

Vogt-Wannier capture theory

(vs. resonance theory)

Klots-Hotop-Fabrikant formulae better

(analytical and accurate):

J. Troe, T. M. Miller, A. A. Viggiano

J. Chem. Phys. **127**, 244303, 244304 (2007)

E. I. Dashevskaya, I. Litvin, E. E. Nikitin, J. Troe

Phys. Chem. Chem. Phys. **10**, 1270 (2008)

# Ion-ion mutual neutralization

$$A^+ + B^- \rightarrow A + B$$

Landau-Zener-type curve crossing

splitting-transition probability

Olson-Grice-Herschbach-Smirnov

multidimensional

energy redistribution

J. C. Bopp, T. M. Miller, A. A. Viggiano

J. Chem. Phys. **129**, 074308 (2008)

# Quantum effects

(i) quantization of orbital angular momentum of relative motion (s-, p-, d-, … mK - μK)

(ii) quantization of rotational angular momentum ($kT \approx B$ = rotational constant of dipole, hydrides 1 – 10 K, non-hydrides < 1 K)

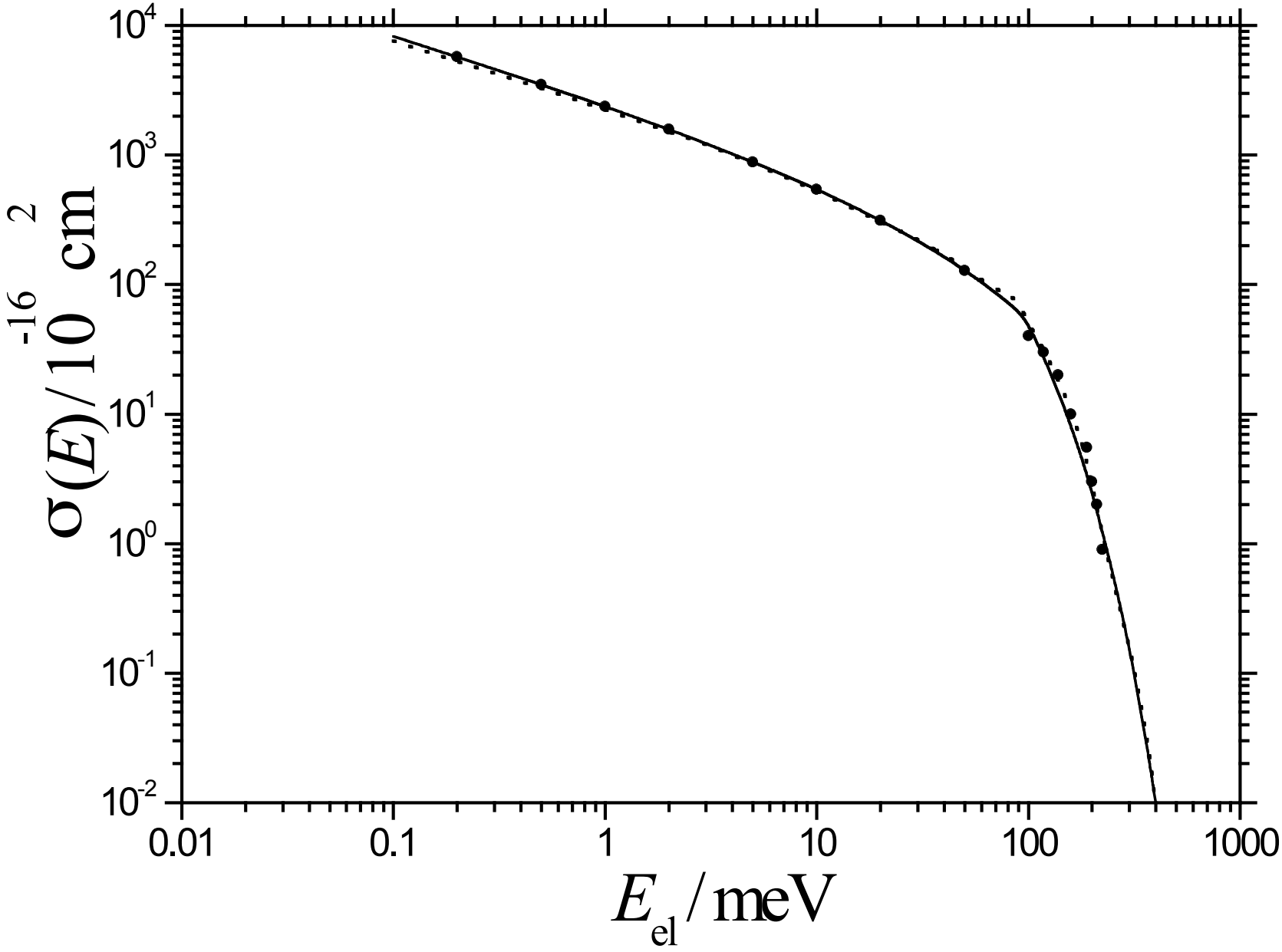
(iii) open electronic shells: coupling of rotational and electronic angular momentum (10 – 100 K)

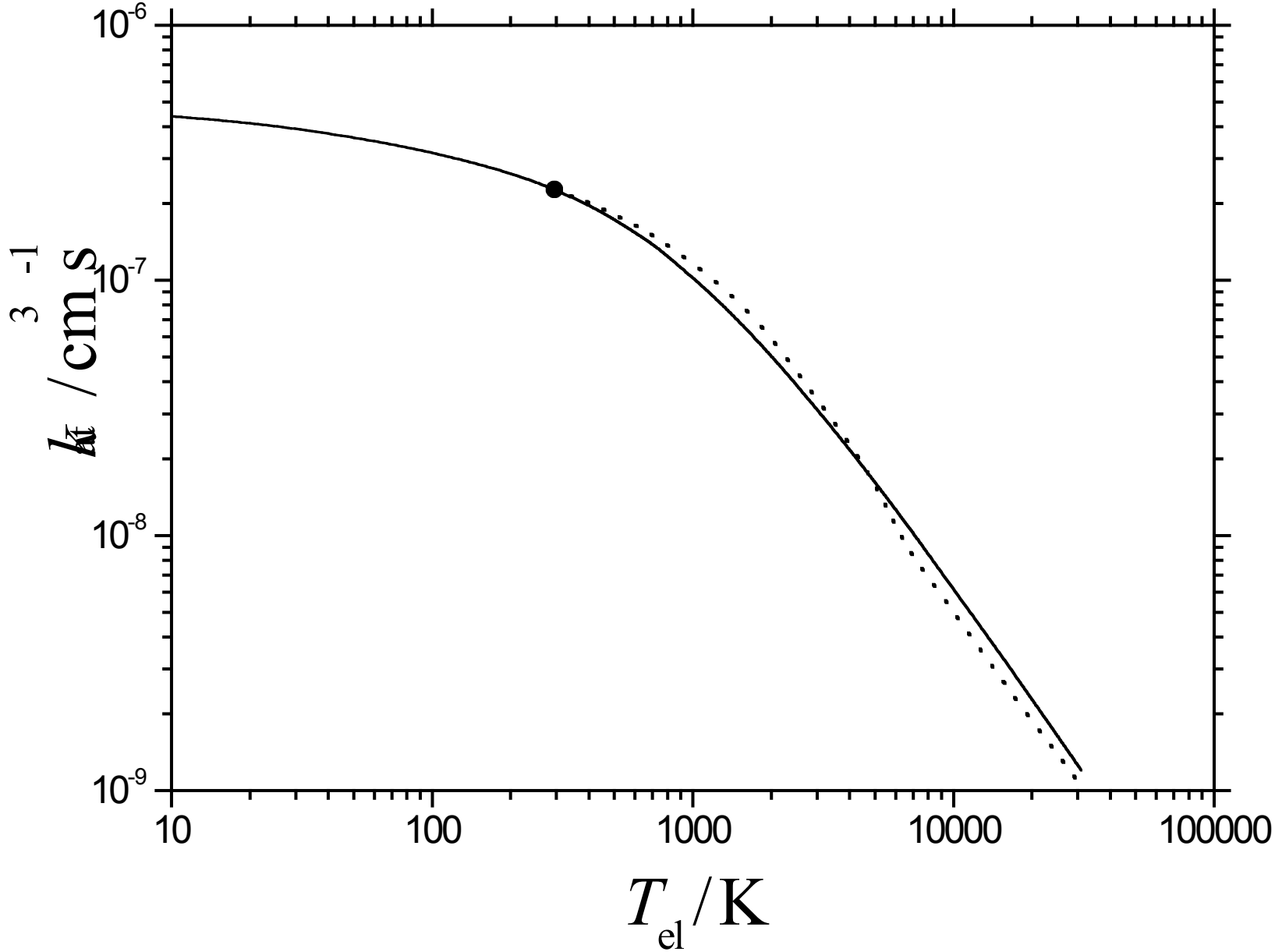
(iv) quantization of vibrations (high T, separable)

(v) classical range
(Su & Chesnavich, Troe, Maergoiz, Nikitin, Troe & Ushakov)

# Attachment mechanism

| | | |
|---|---|---|
| $e^- + SF_6 \rightarrow e^-SF_6$ | | "virtual" |
| $e^-SF_6 \rightarrow SF_6^- *$ | | IVR |
| $SF_6^- * \rightarrow ...$ | | |
| $e^- + SF_6 \rightarrow e^- + SF_6 *$ | | vib. exc. |


$10^4$
$10^3$
$10^2$
$10^1$
$10^0$
$10^{-1}$
$10^{-2}$
$\sigma(E)/10^{-16}$ cm$^2$
0.01
0.1
1
10
100
1000
$E_{el}$ / meV


$10^{-6}$
$10^{-7}$
$10^{-8}$
$10^{-9}$
$k_f$ / cm$^3$ s$^{-1}$
10
100
1000
10000
100000
$T_{el}$ / K

$\sigma(E_{el}, 300\ \mathrm{K}) \rightarrow k_{attach}\ (300\ \mathrm{K})$

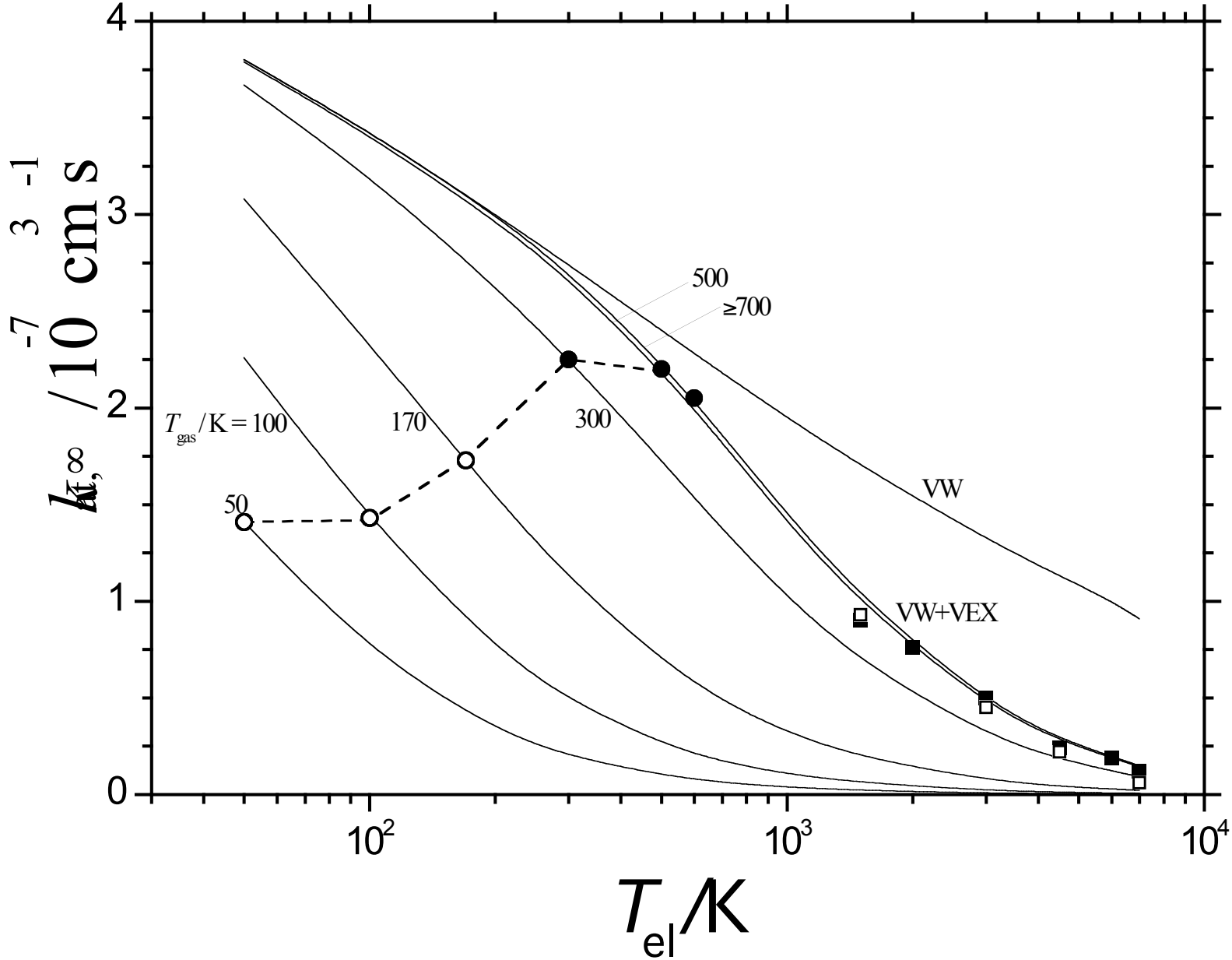
$k_{attach}\ (T_{gas})$ should decrease with $T_{gas}$ but it does not do that

$\Rightarrow k_{attach}(T_{el}, T_{gas})$

WHY?

IVR accelerates with increasing $T_{gas}$

IVR slows down with increasing $T_{el}$


4
3
2
1
0
$k_{T,8}$ /10$^{-7}$ cm$^3$ s$^{-1}$
$10^2$
$10^3$
$10^4$
$T_{el}$/K
500
≥700
VW
VW+VEX
$T_{gas}$/K = 100
170
300
50

Fate of $SF_6^{-}$ * ?

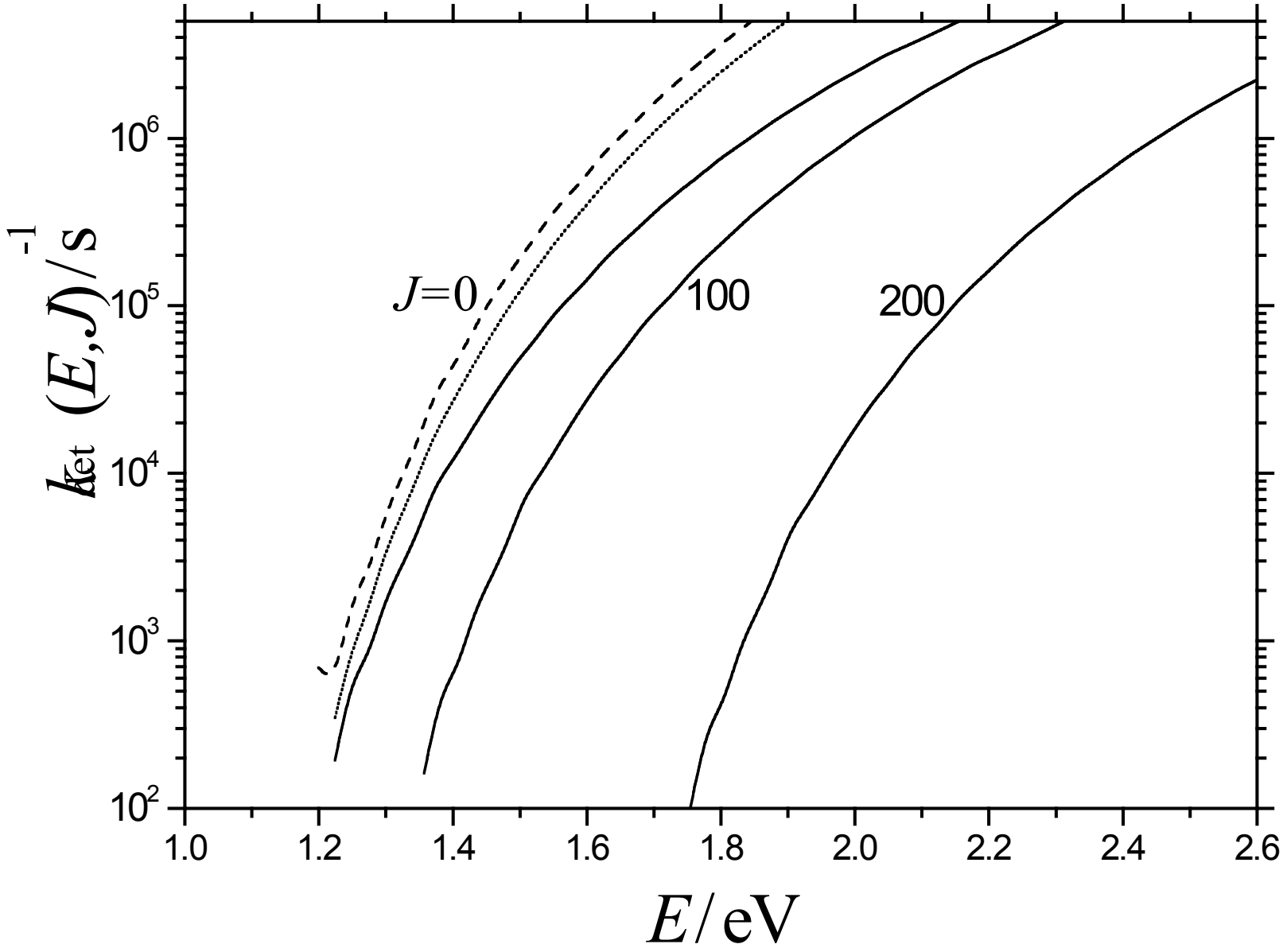
detection before decay

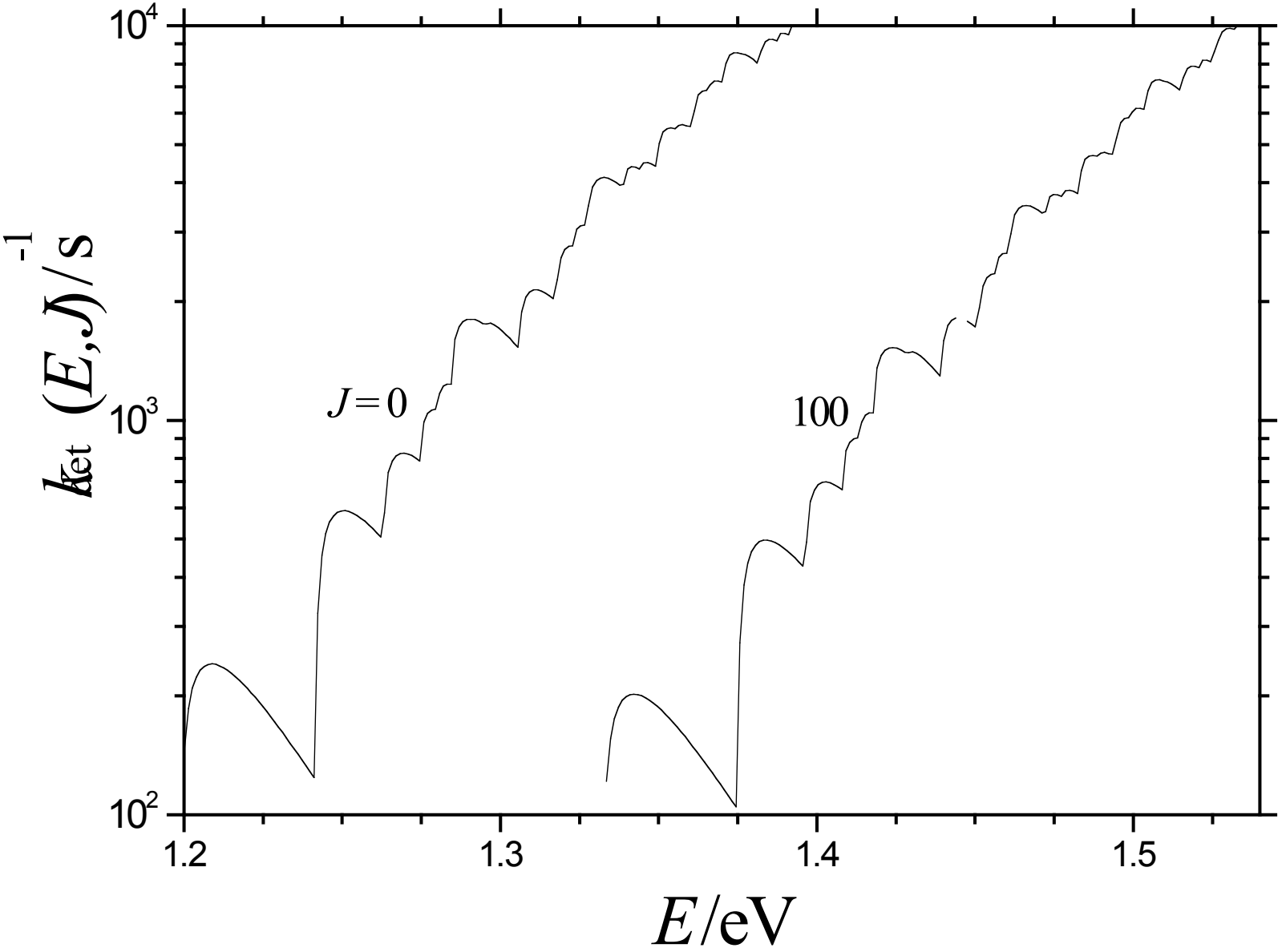
autodetachment: lifetime?

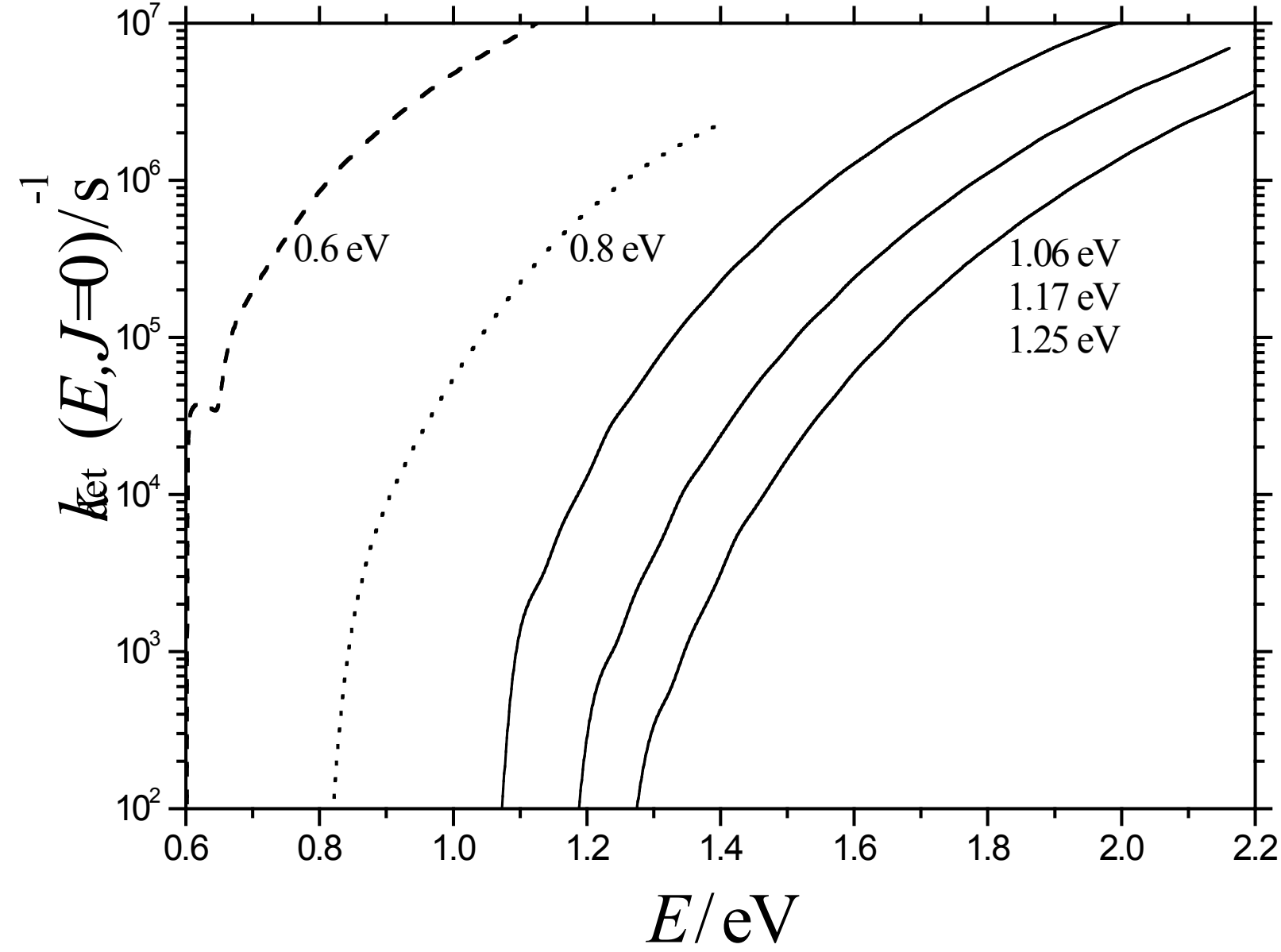
radiative stabilization?

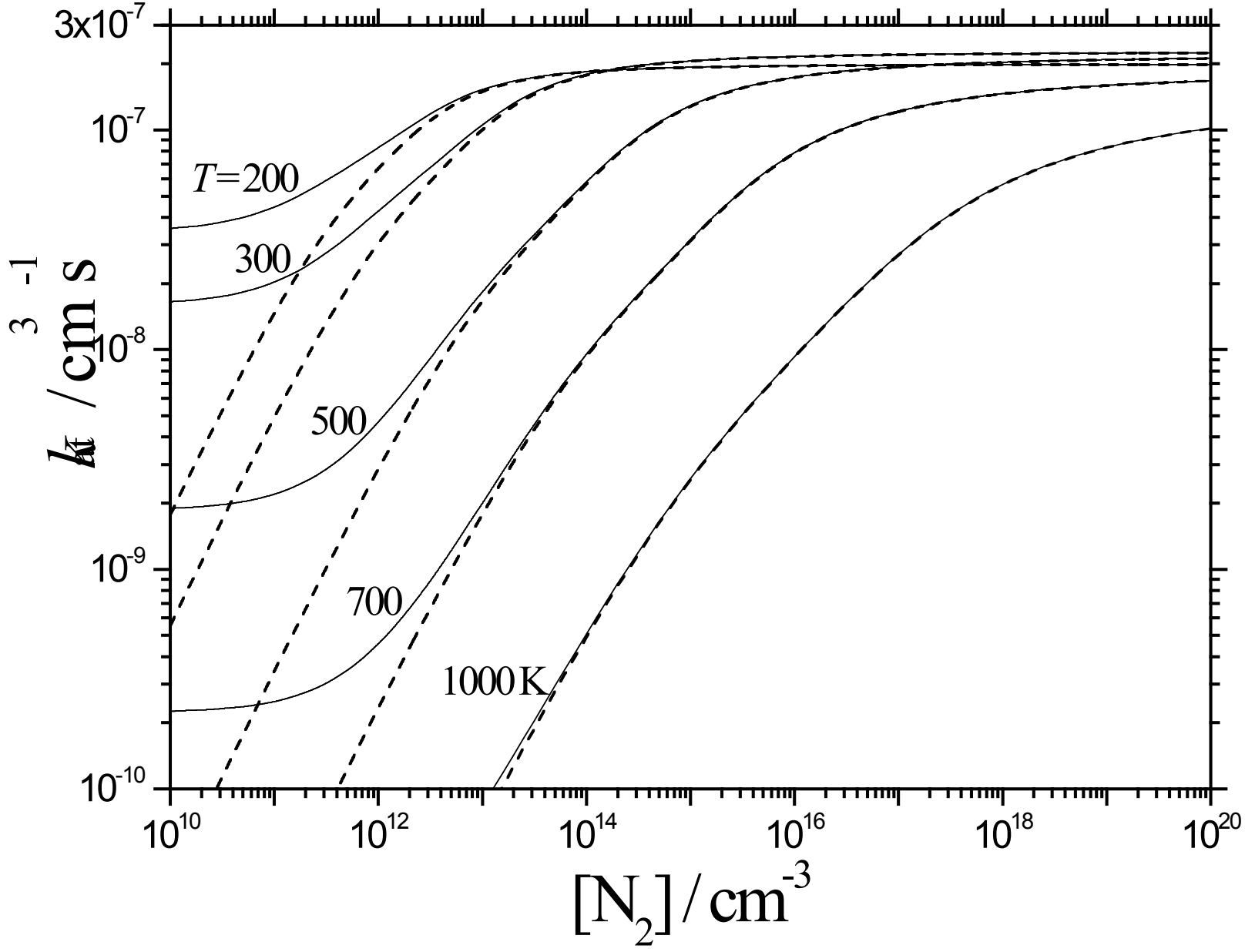
Kinetic modelling:

$\sigma_{attach}\,(E_{el}, E_{vib}) \Leftrightarrow k_{detach}\,(E_{total}, T_{gas})$


$k_{et}(E,J)/s^{-1}$
$10^6$
$10^5$
$10^4$
$10^3$
$10^2$
$J=0$
100
200
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
$E/eV$


$10^4$
$10^3$
$10^2$
$k_{et}(E,J)/s^{-1}$
$J=0$
100
1.2
1.3
1.4
1.5
$E$/eV


$10^7$
$10^6$
$10^5$
$10^4$
$10^3$
$10^2$
$k_{et}\ (E,J=0)/\mathrm{s}^{-1}$
0.6 eV
0.8 eV
1.06 eV
1.17 eV
1.25 eV
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
$E$/ eV


3x10-7
10-7
10-8
10-9
10-10
T=200
300
500
700
1000 K
k1 / cm3 s-1
10^10
10^12
10^14
10^16
10^18
10^20
[N2] / cm-3

## Dissociative attachment

$e^- + SF_6 \rightarrow SF_6^{-*}$

$SF_6^{-*} + M \rightarrow SF_6^- + M$

$SF_6^{-*} \rightarrow SF_5^- + F$

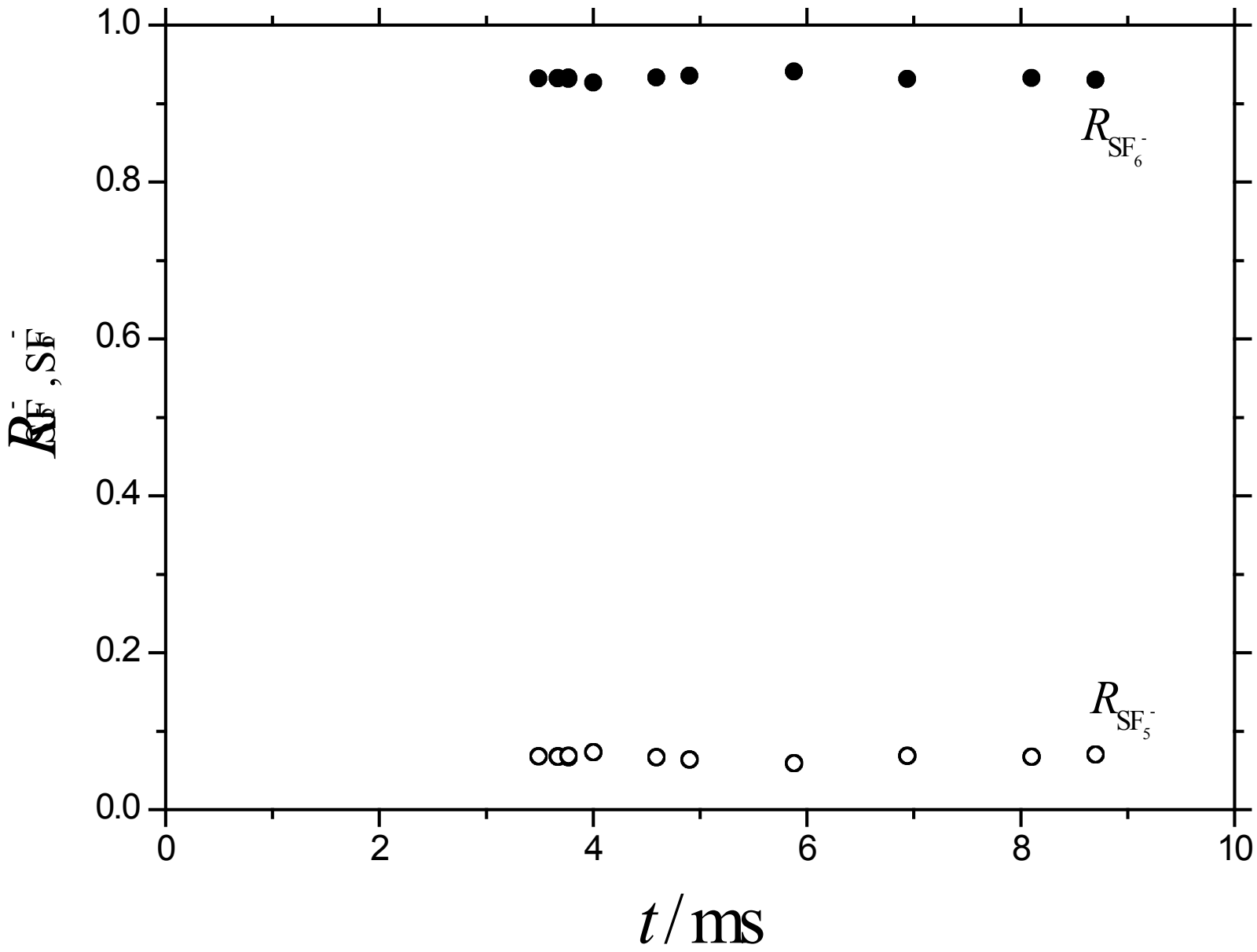
chemical activation system (fast)

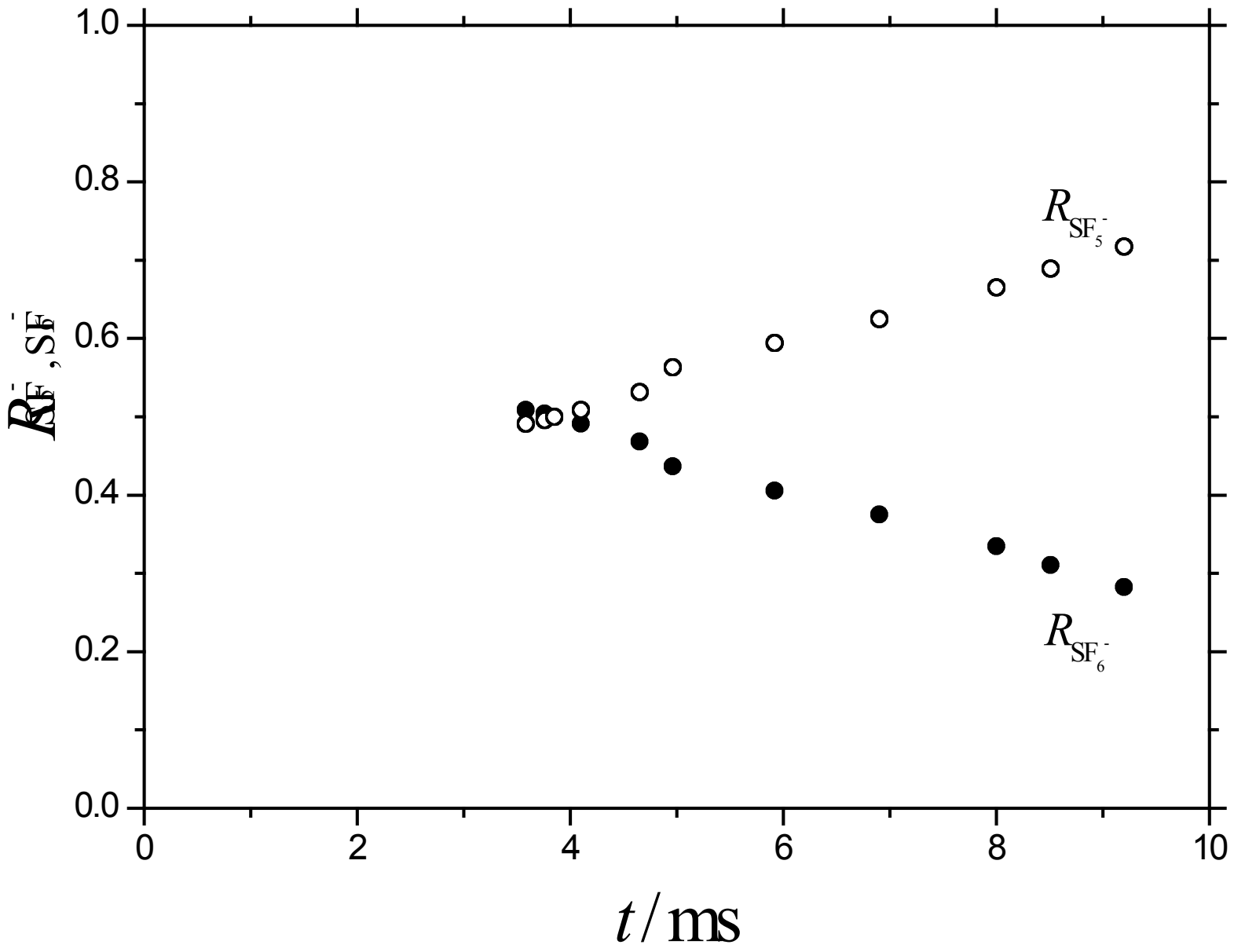
$SF_6^- + M \rightarrow SF_6^{-*} + M$

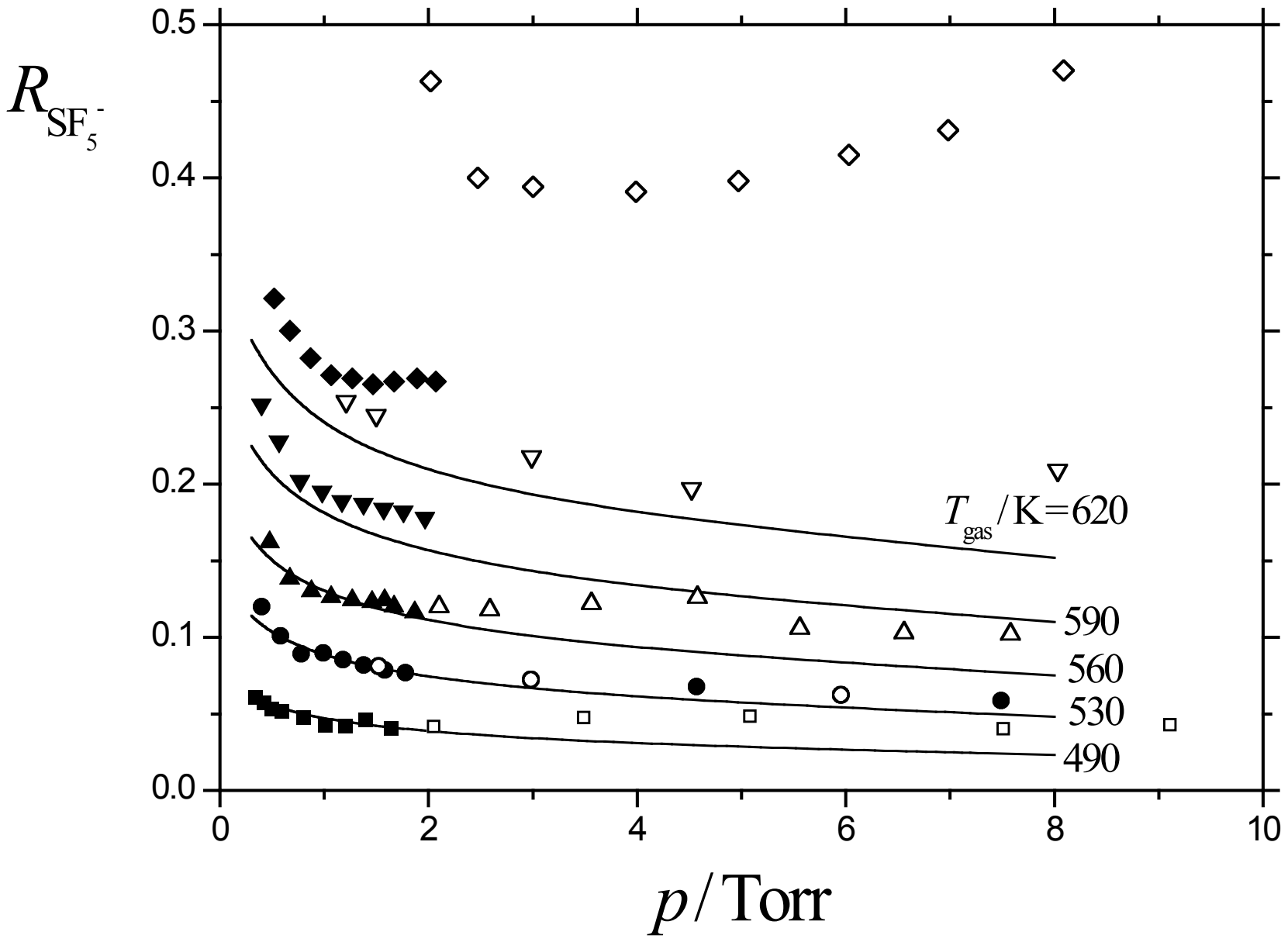
$SF_6^{-*} \rightarrow SF_5^- + F$

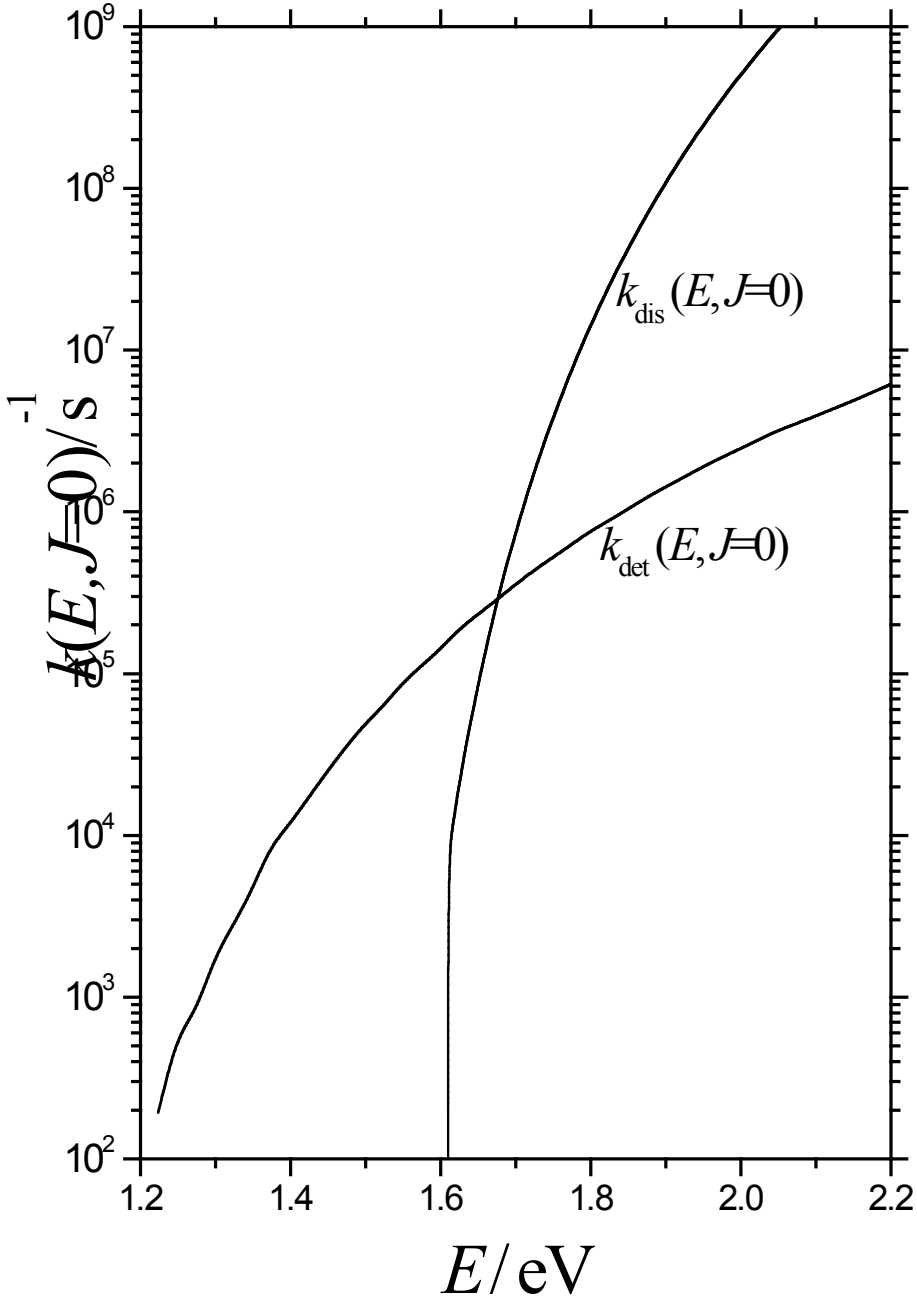
thermal dissociation (slow)

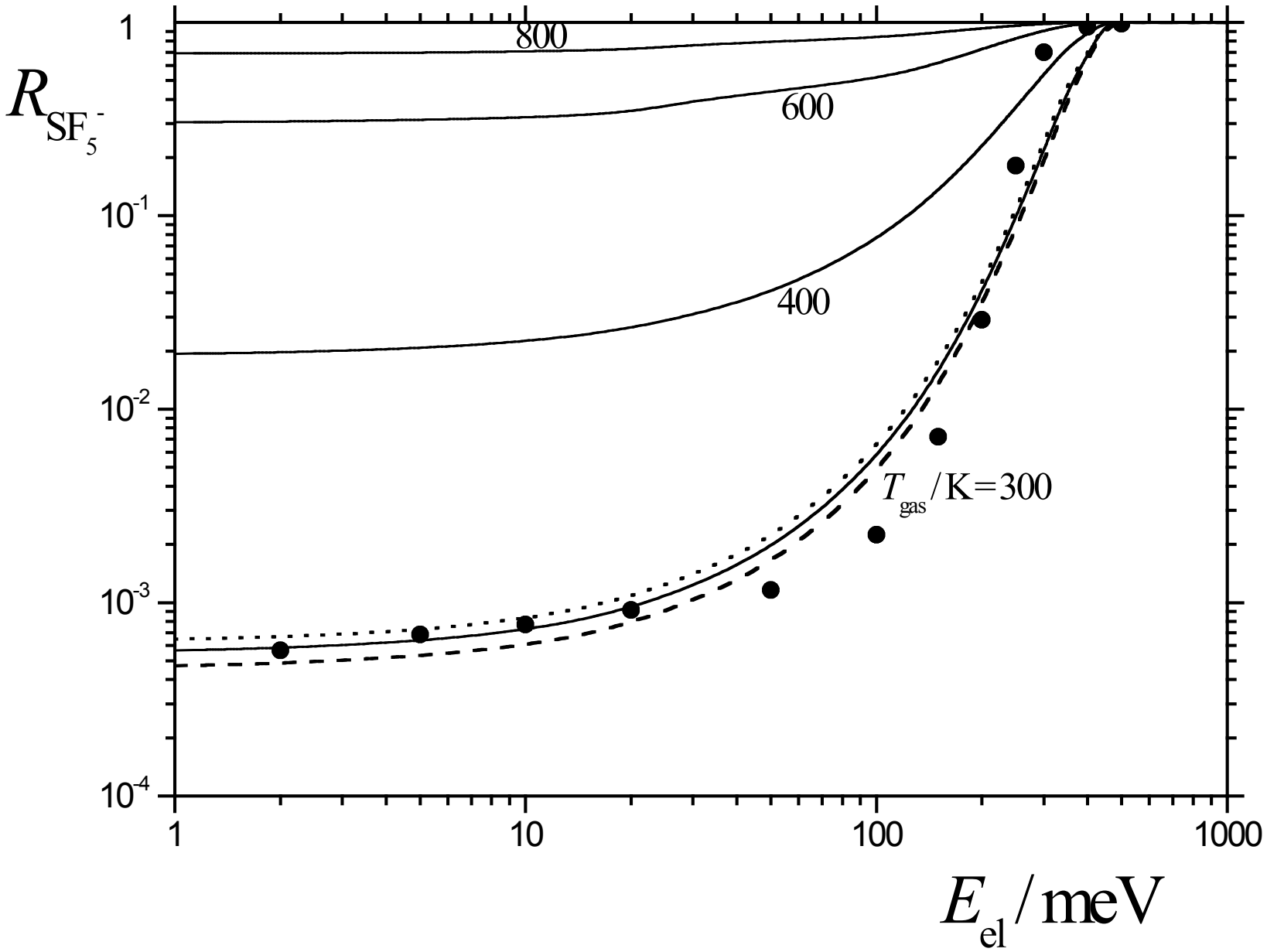
FALP studies at AFRL

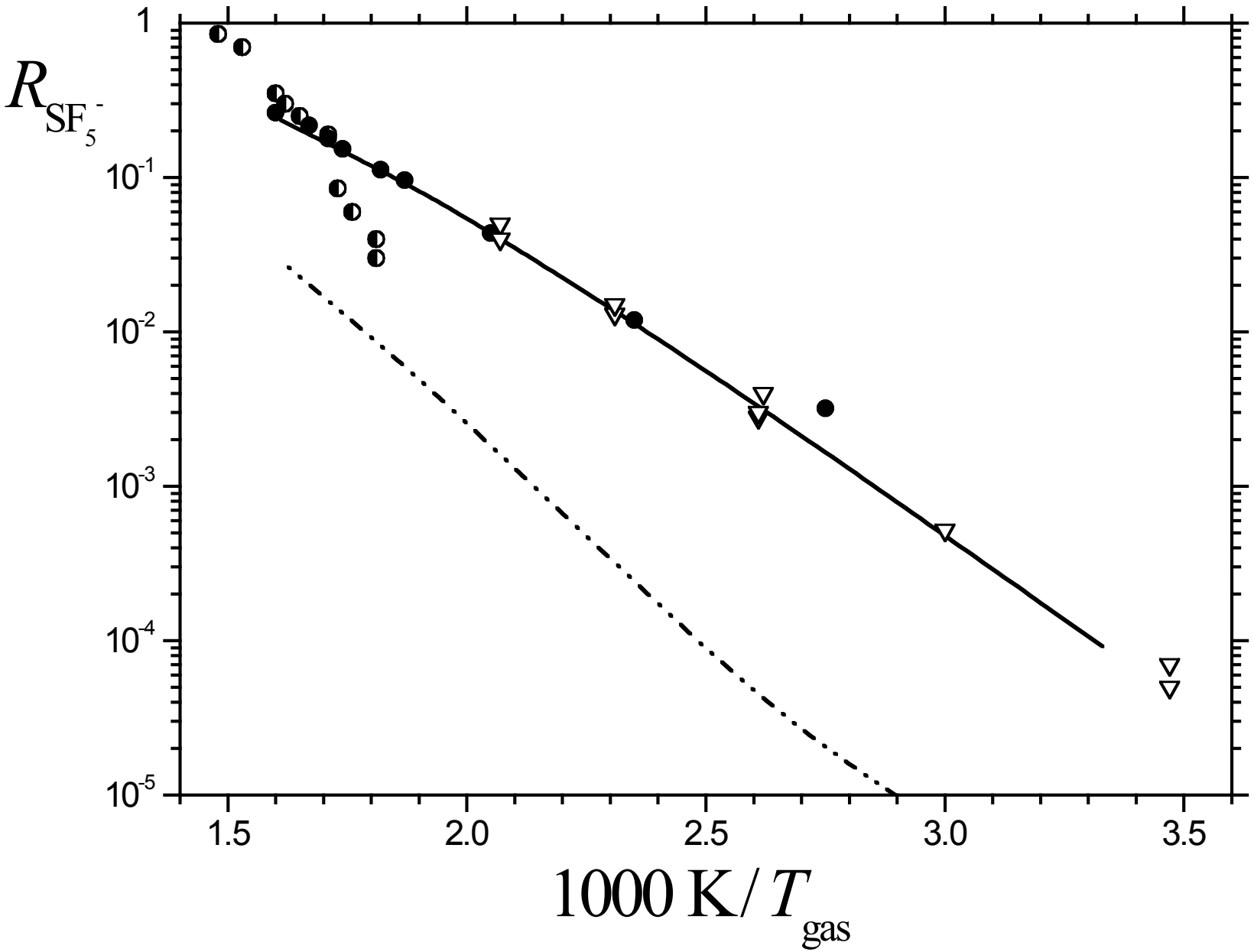

1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
$R_{SF_6^-}$
$R_{SF_5^-}$
$R_{SF_6^-}, R_{SF_5^-}$
$t$/ms

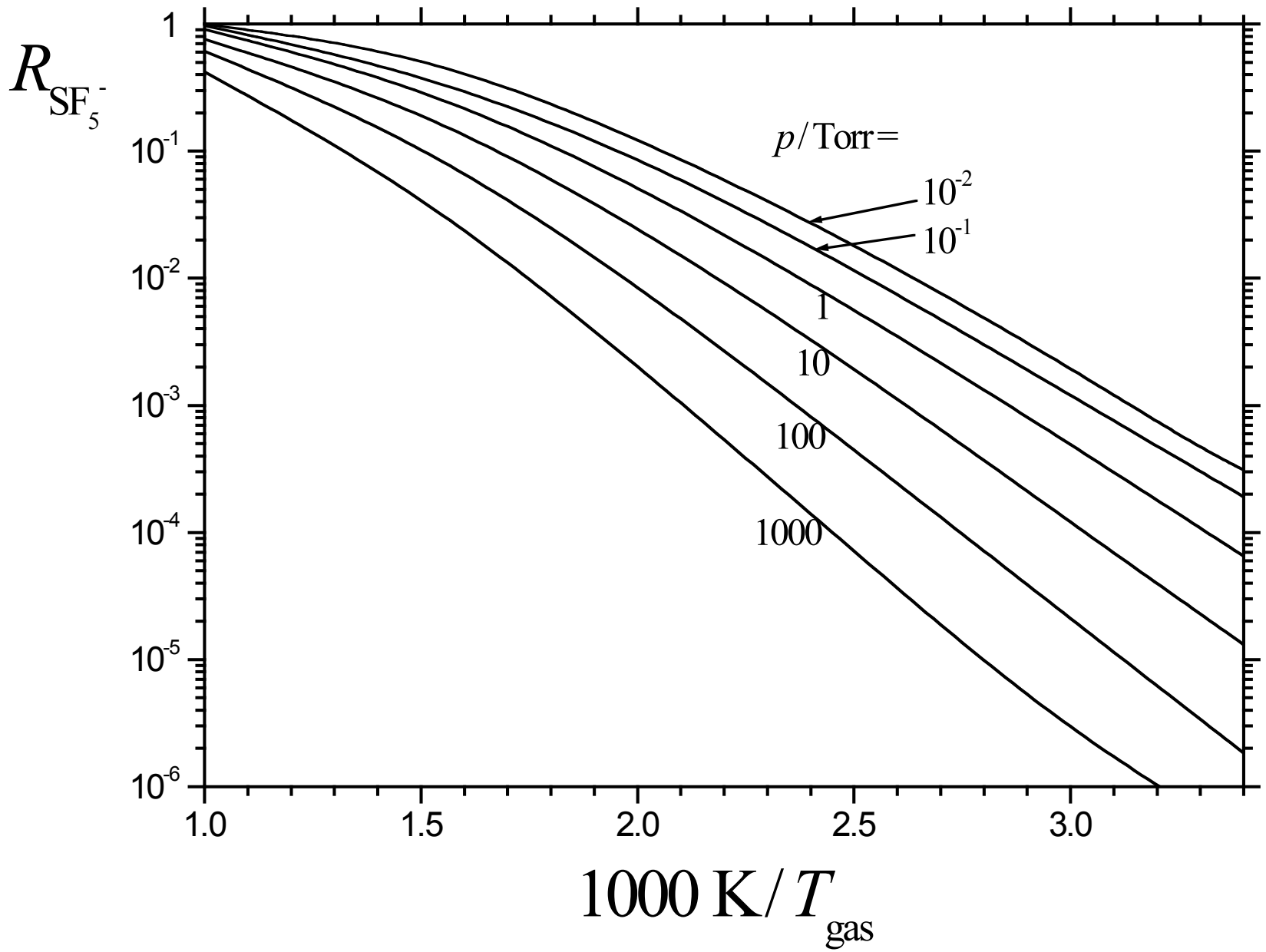

1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
$R_{SF_5^-}$
$R_{SF_6^-}$
$R_{SF_5^-}, R_{SF_6^-}$
$t$ / ms

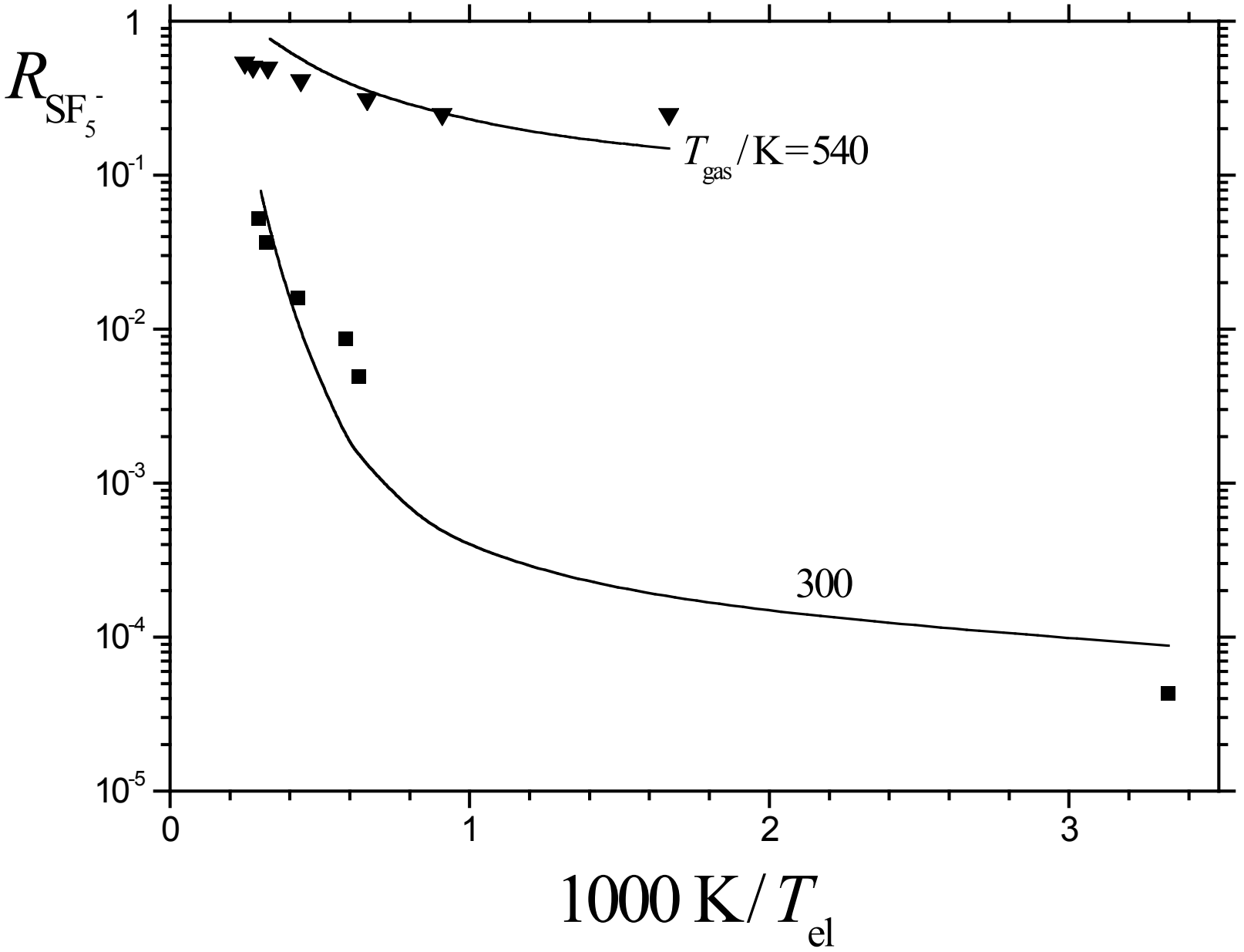

$R_{SF_5^-}$
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
$p$/Torr
$T_{gas}$/K=620
590
560
530
490

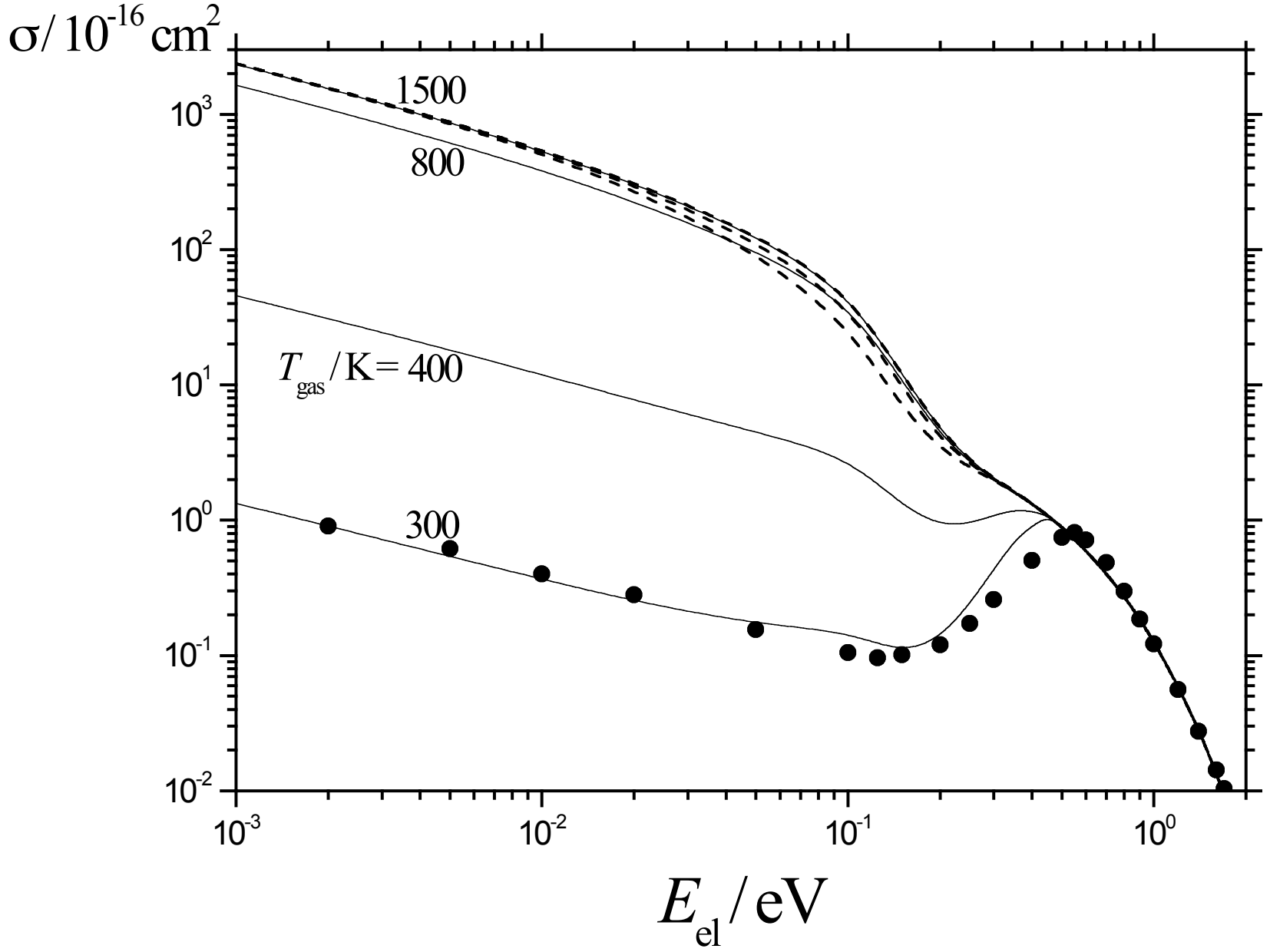

$10^9$
$10^8$
$10^7$
$10^6$
$10^5$
$10^4$
$10^3$
$10^2$
$k(E,J=0)/\mathrm{s}^{-1}$
$k_{\mathrm{dis}}(E,J=0)$
$k_{\mathrm{det}}(E,J=0)$
1.2
1.4
1.6
1.8
2.0
2.2
$E/\mathrm{eV}$


$R_{SF_5^-}$
1
$10^{-1}$
$10^{-2}$
$10^{-3}$
$10^{-4}$
800
600
400
$T_{gas}$/K=300
1
10
100
1000
$E_{el}$/meV


$R_{SF_5^-}$
1
$10^{-1}$
$10^{-2}$
$10^{-3}$
$10^{-4}$
$10^{-5}$
1.5
2.0
2.5
3.0
3.5
1000 K/ $T_{gas}$


$R_{SF_5^-}$
1
$10^{-1}$
$10^{-2}$
$10^{-3}$
$10^{-4}$
$10^{-5}$
$10^{-6}$
$p$/Torr=
$10^{-2}$
$10^{-1}$
1
10
100
1000
1.0
1.5
2.0
2.5
3.0
1000 K/ $T_{gas}$


$R_{SF_5^-}$
1
$10^{-1}$
$10^{-2}$
$10^{-3}$
$10^{-4}$
$10^{-5}$
0
1
2
3
$T_{gas}$/K=540
300
1000 K/$T_{el}$


σ/ 10^-16 cm^2
1500
800
T_gas / K= 400
300
10^3
10^2
10^1
10^0
10^-1
10^-2
10^-3
10^-2
10^-1
10^0
E_el / eV

From thermal attachment and detachment rates via third law analysis to a reliable electron affinity of $SF_6^-$ :

$$EA = 1.20\ (\pm 0.05)\ eV$$

From dissociative attachment yields at $E_{el}$ ($T_{gas}$ = 300 K) $\rightarrow$ 0 and at $T_{el} = T_{gas}$ from 300 $\rightarrow$ 600 K to a reliable dissociation energy of $SF_6^-$ :

$$E_0(SF_6^- \rightarrow SF_5^- + F) = 1.61\ (\pm 0.05)\ eV$$