Neutral-Neutral and Ion-Molecule Reactions

Detailed Theories

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Ab initio theories generally still out of reach,

but semi-quantitative models often feasible

Ingredients:

(i) potential energy surfaces (ab initio, model)

(ii) dynamics (classical, quantum, statistical)

(iii) sensitivity of observables on selected details

Stages of theory:

(i) capture

(ii) partitioning (forward-backward, various channels)

Low temperature aspects:

μK, mK, K, 10 – 30 K, 200 K, 300 K, (extrapolations from high T?)

10 – 30 K generally is "high" for quantum effects in translation
(tunneling and reflection) and in rotation (kT > B),
but low for vibrations

300 K is "low" for electron + molecule capture
(i.e. governed by quantum effects)

Capture rates for molecular species in r^{-4} and r^{-6} potentials

Quantum effects in translation?

Tunneling through centrifugal barriers?

(Dashevskaya, Maergoiz, Troe, Litvin, Nikitin,
J. Chem. Phys. 118, 7313 (2003))

Example: Ion + induced dipole, $V(r) = -q\alpha/2r^4$

$k_{cap}(T \rightarrow \infty) = k_{Langevin} = 2\pi q(\alpha/\mu)^{1/2}$

$k_{cap}(T \rightarrow 0) = 2 \times k_{Langevin}$

Where is the transition?

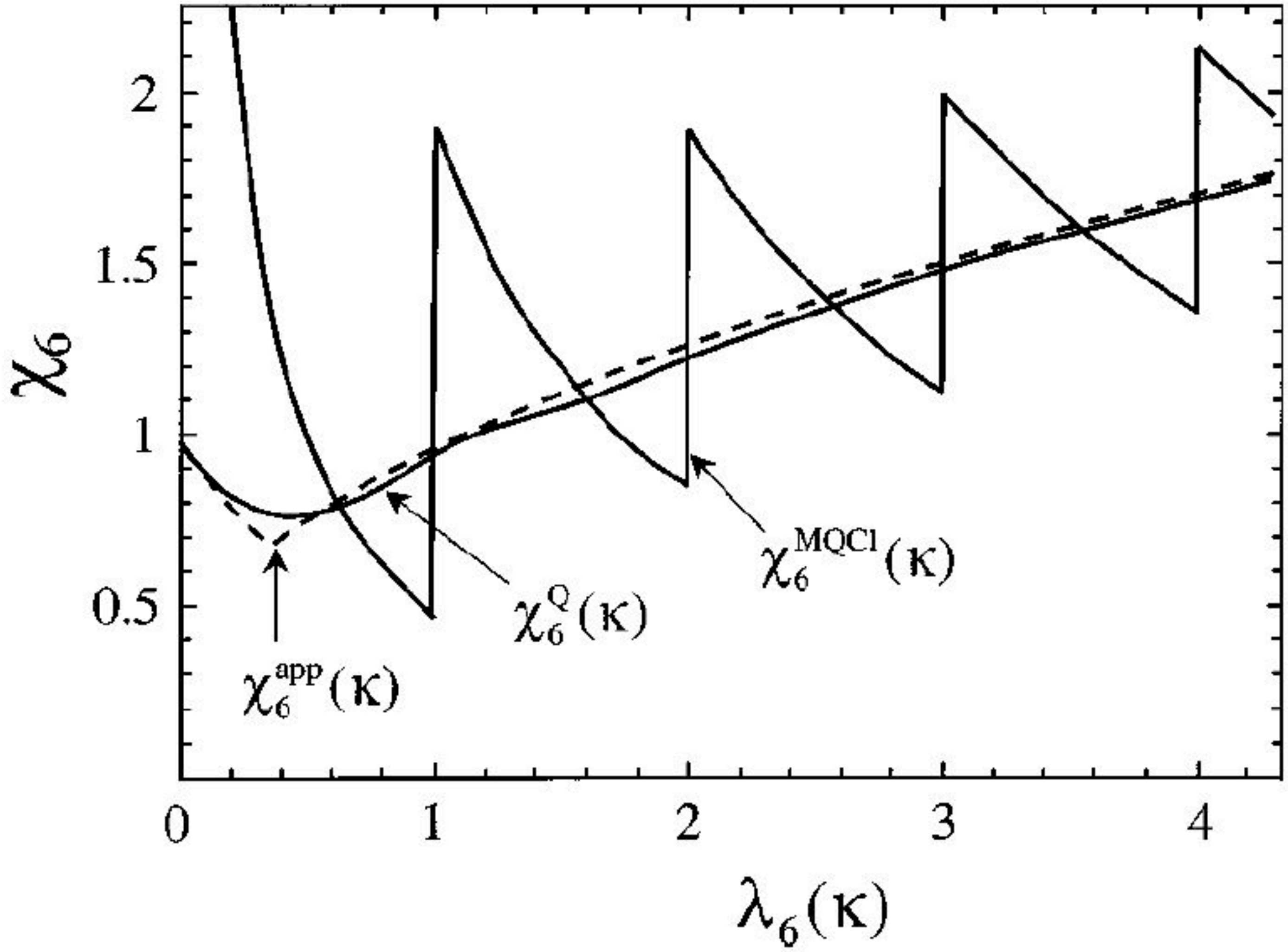
At $\theta_4 = (\alpha e^2\mu^2/\hbar^4)kT \approx 10^{-2}$

Much lower than expected for tunneling!

In the μK – mK range. Why?

Because tunneling through and reflection over barriers

compensate except for s-waves ($l = 0$, central collisions)



Reduced rate coefficients $\chi_6^{\mathrm{Q}}(\kappa)$, $\chi_6^{\mathrm{app}}(\kappa)$, $\chi_6^{\mathrm{MQCl}}(\kappa)$ vs $\lambda_6(\kappa)$

Example: neutral-neutral capture, $V(r) = -C_6/r^6$

$k_{cap}(T \rightarrow 0) \approx 114\ \hbar^{1/2}\mu^{-3/4}C_6^{1/4}$

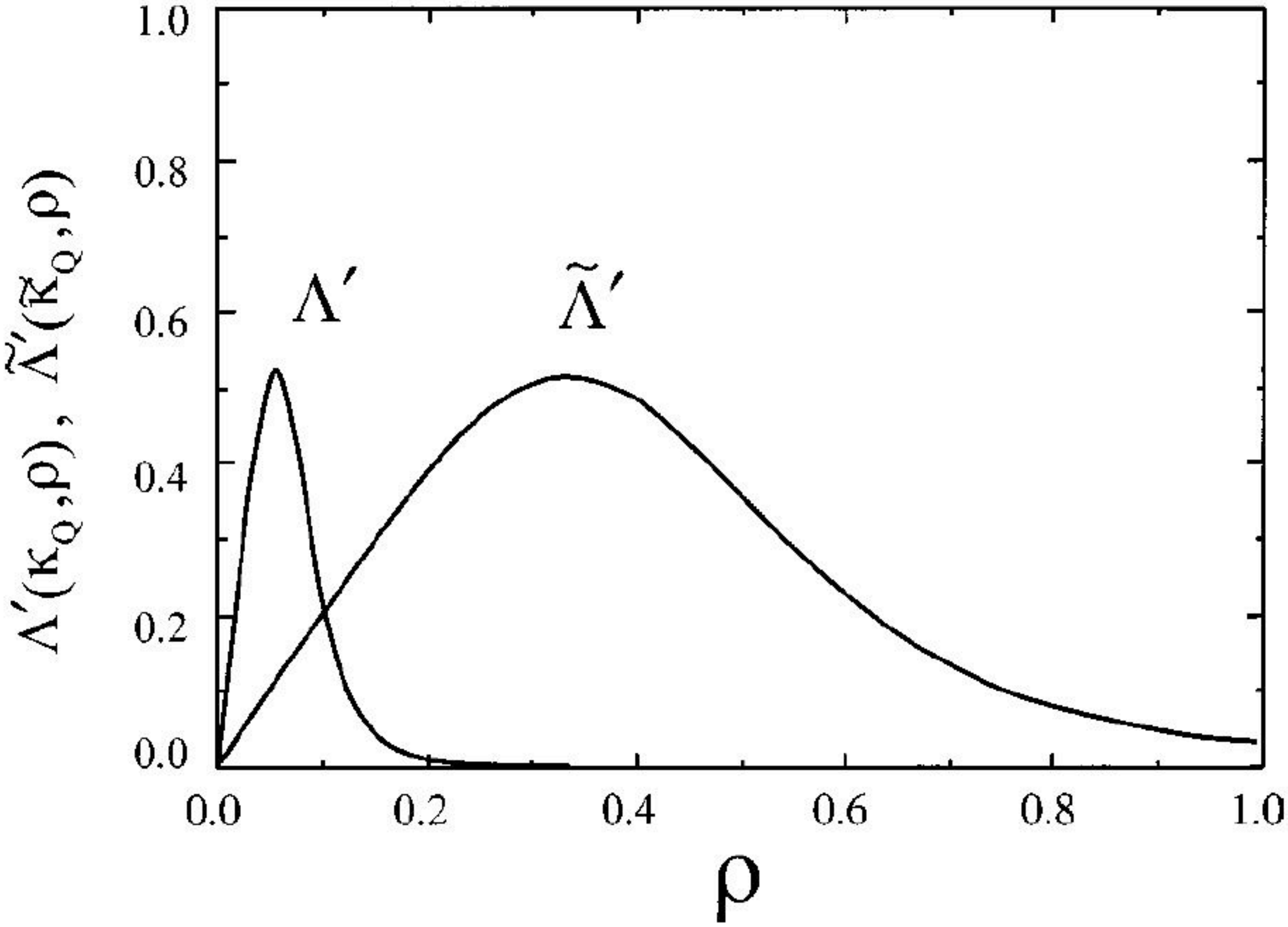
$k_{cap}(T \rightarrow \infty) \approx k_{cap}(T \rightarrow 0)\ 1.06\ \theta_6^{1/6}$

with $\theta_6 = (2C_6\mu^3/\hbar^6)^{1/2}\ kT$

Where is the transition?

At $\theta_6 \approx 10^{-2}$, i.e. again at very low T

General conclusion: relative motion can be treated classically, except for e^- + molecule



Test for quasiclassical criteria. Curve 1 corresponds to $\Lambda'(\kappa_Q,\rho)$ for $\kappa_Q = 150$, and curve 2 to $\tilde{\Lambda}'(\tilde{\kappa}_Q,\rho)$ for $\tilde{\kappa}_Q = 4$

Example: electron + polarizable molecule, $V = -e\alpha/2r^4)$
s-wave capture

Problem: capture is followed either by direct processes
or by IVR and anion break up

(Troe, Miller, Viggiano, J. Chem. Phys. 127, Dec 2007;
Dashevskaya, Litvin, Nikitin, Troe, PCCP, Dec 2007)

$k_{cap}(T \rightarrow 0) = 2 \times k_{Langevin}$

$k_{cap}(T \text{ large}) = (2\pi\theta)^{-1/2}$

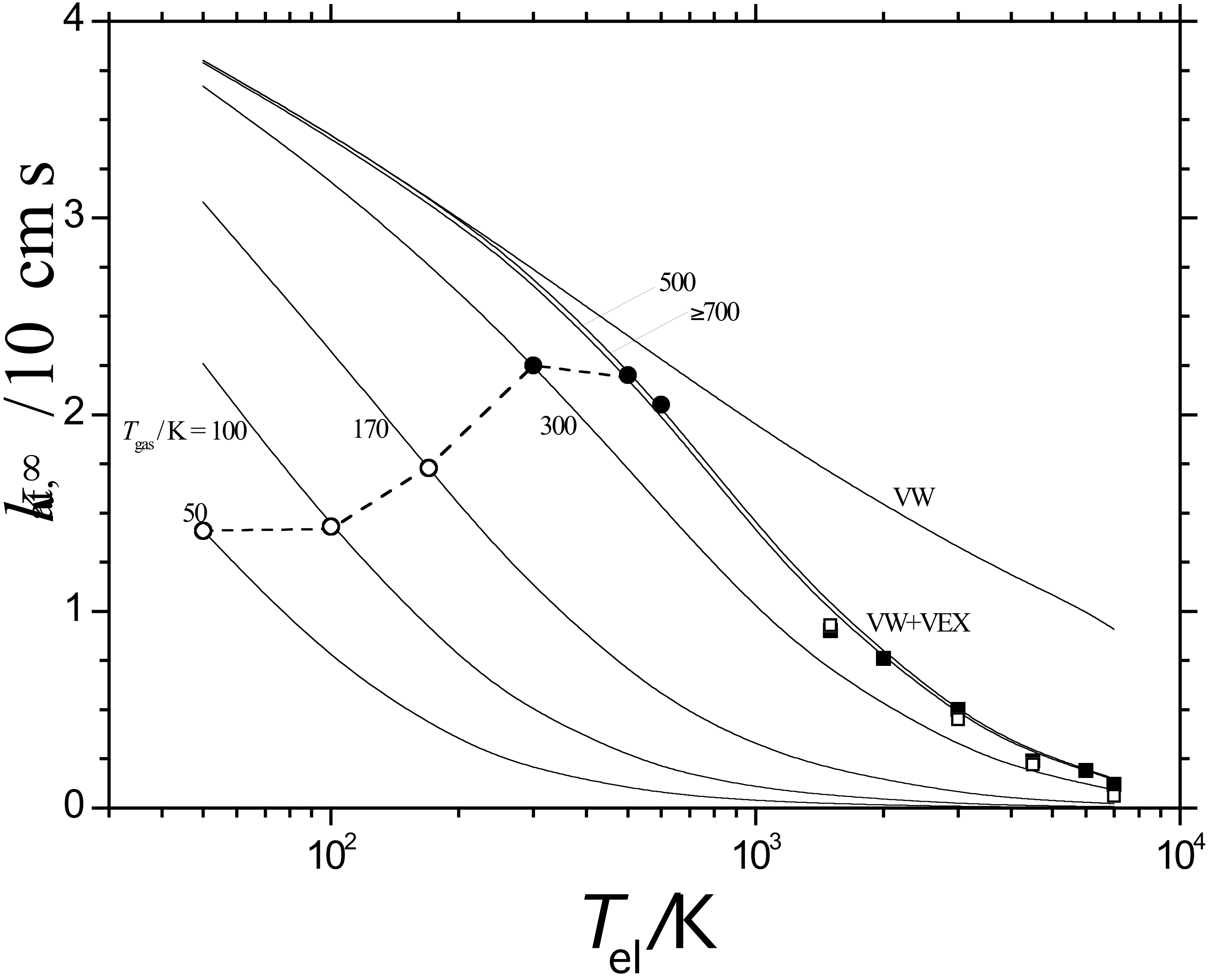
with $\theta = (e\mu/\hbar^2)^2 \alpha kT$

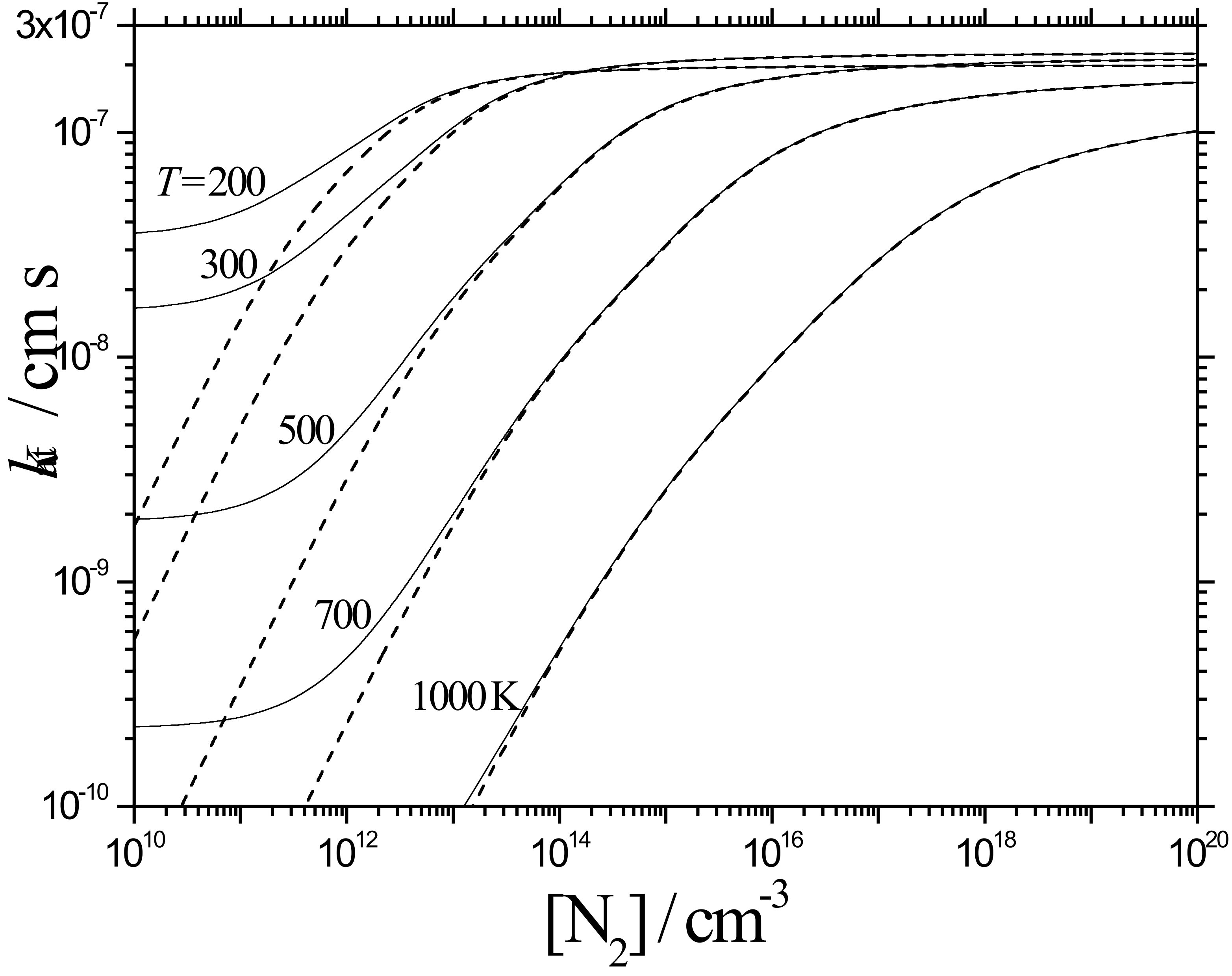
Examples: $e^- + SF_6 \rightarrow SF_6^{-*}$

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

$\rightarrow SF_6^- + h\nu$

$\xrightarrow{[M]} SF_6 + M$


k_{t,∞} α /10^{-7} cm^3 s^{-1}
4
3
2
1
0
10^2
10^3
10^4
T_el/K
T_gas/K = 100
170
300
500
≥700
50
VW
VW+VEX


3x10^-7
10^-7
10^-8
10^-9
10^-10
10^10
10^12
10^14
10^16
10^18
10^20
T=200
300
500
700
1000 K
k / cm^3 s^-1
[N_2] / cm^-3

Example: Ion neutralizations ($V \propto r^{-1}$)

$A^- + K^+ \rightarrow A + K$

$H^+ + H^-$	$k(300\ K) = 4 \times 10^{-7}\ cm^3\ s^{-1}$
$N^+ + O^-$	2.9×10^{-7}
$O^+ + O^-$	2.8×10^{-7}

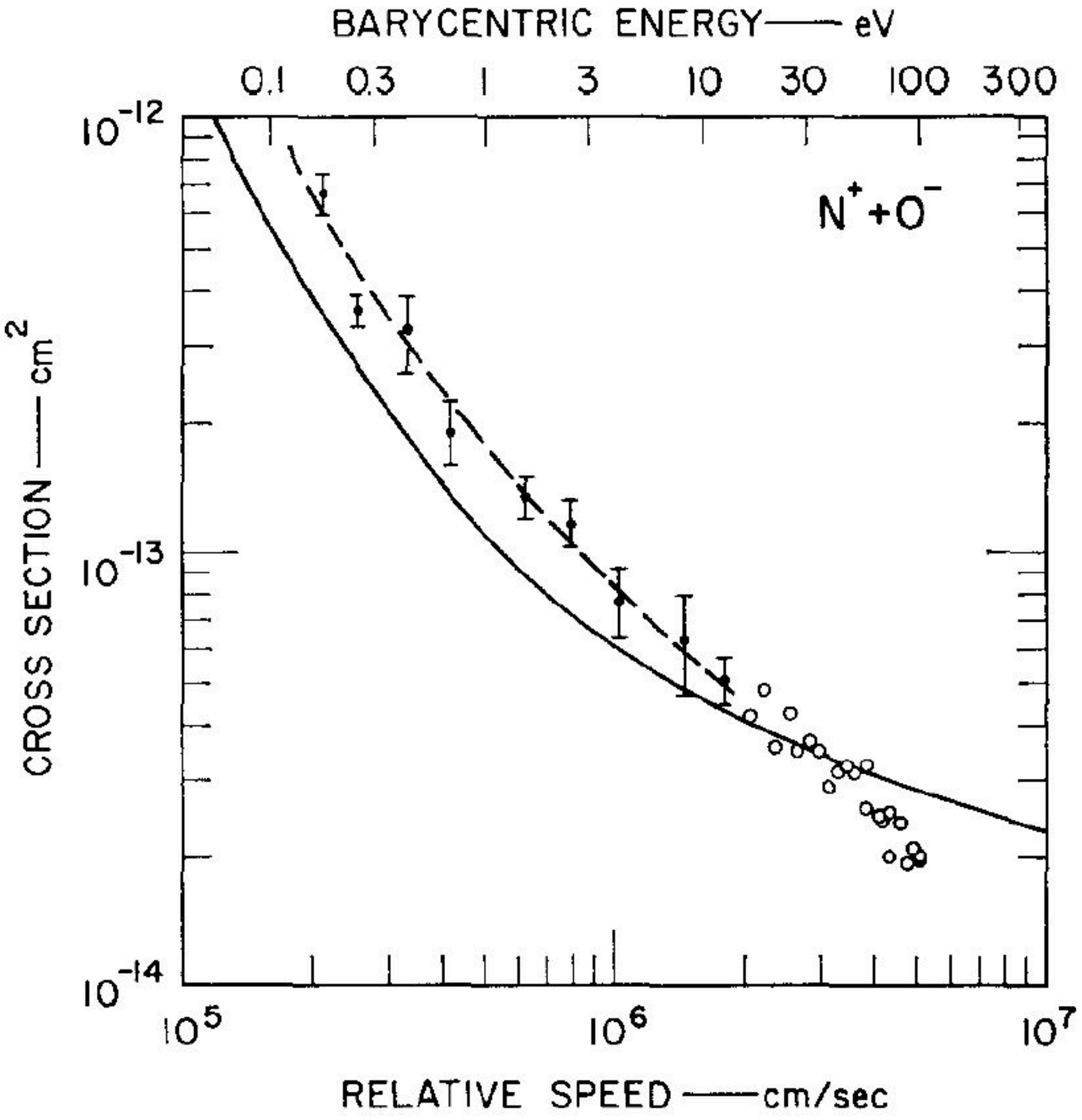
$\sigma \rightarrow E^{-2}$ for low energy

$k = \langle \sigma \cdot v \rangle \rightarrow k \propto T^{-3/2}$

$k(T \rightarrow 0) = ?$

divergence removed by short range repulsion

little known



$N^+ + O^-$ cross sections. The averaged data of Aberth and Peterson[5] are illustrated by the dashed line, and the unaveraged data (above 10 eV there are insufficient data for averaging) are shown by open circles. The theoretical calculation is given by the solid line.

Example: electron + dipolar molecule (anisotropic potential)

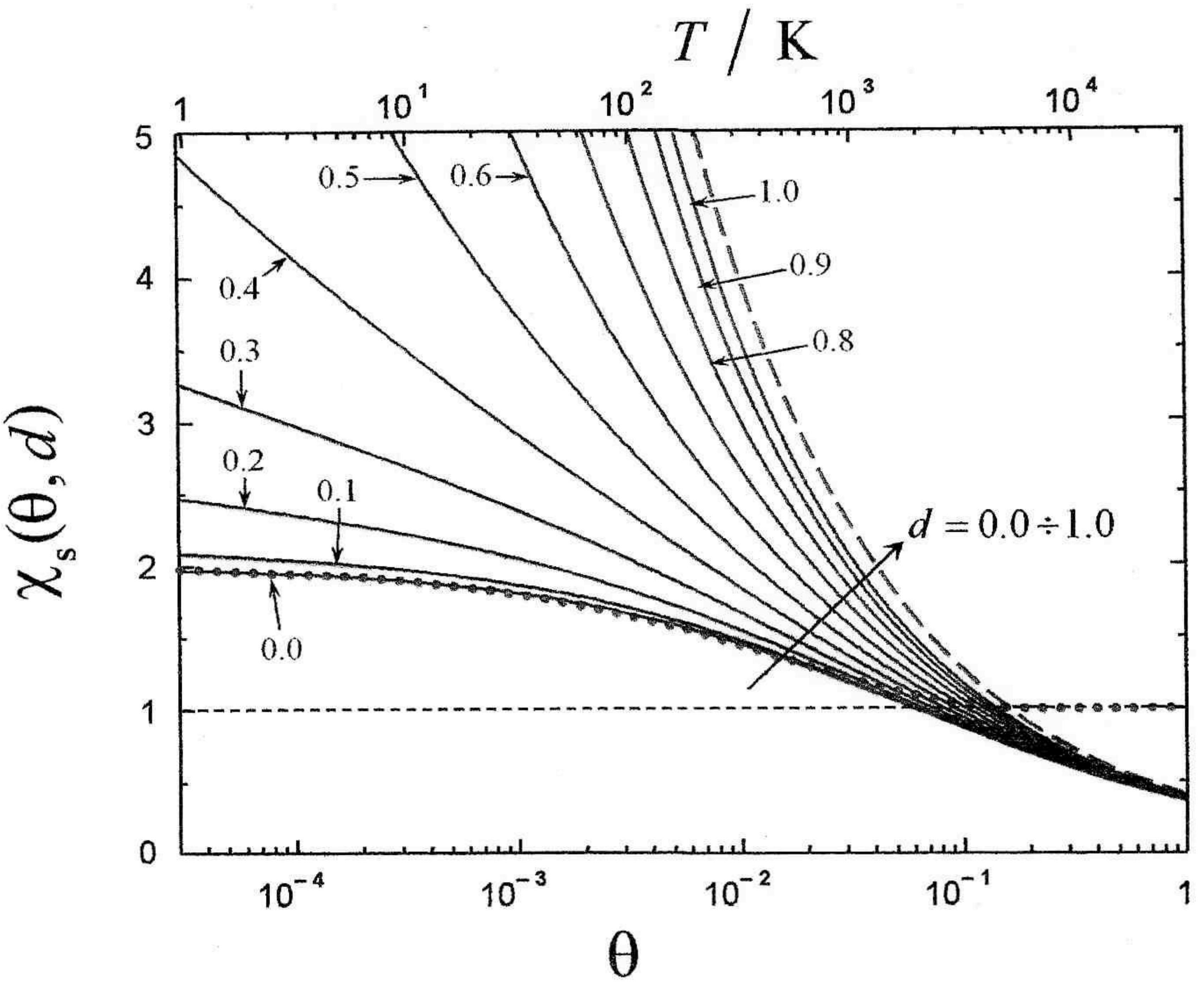
solution of angular Schrödinger equation, after that

solution of radial Schrödinger equation

(Dashevskaya, Litvin, Nikitin, Troe, PCCP Dec 2007)

$k(T \rightarrow 0) = ?$

divergence removed by short range repulsion



T / K
1
10^1
10^2
10^3
10^4
5
4
3
2
1
0
0.5
0.6
1.0
0.9
0.8
0.4
0.3
0.2
0.1
0.0
d = 0.0 ÷ 1.0
χ_s(θ, d)
10^-4
10^-3
10^-2
10^-1
1
θ

Example: Ion-dipole capture (anisotropic)

Anisotropy → hindered rotor motion classical or quantized?

SACM (quantized) gives the answer

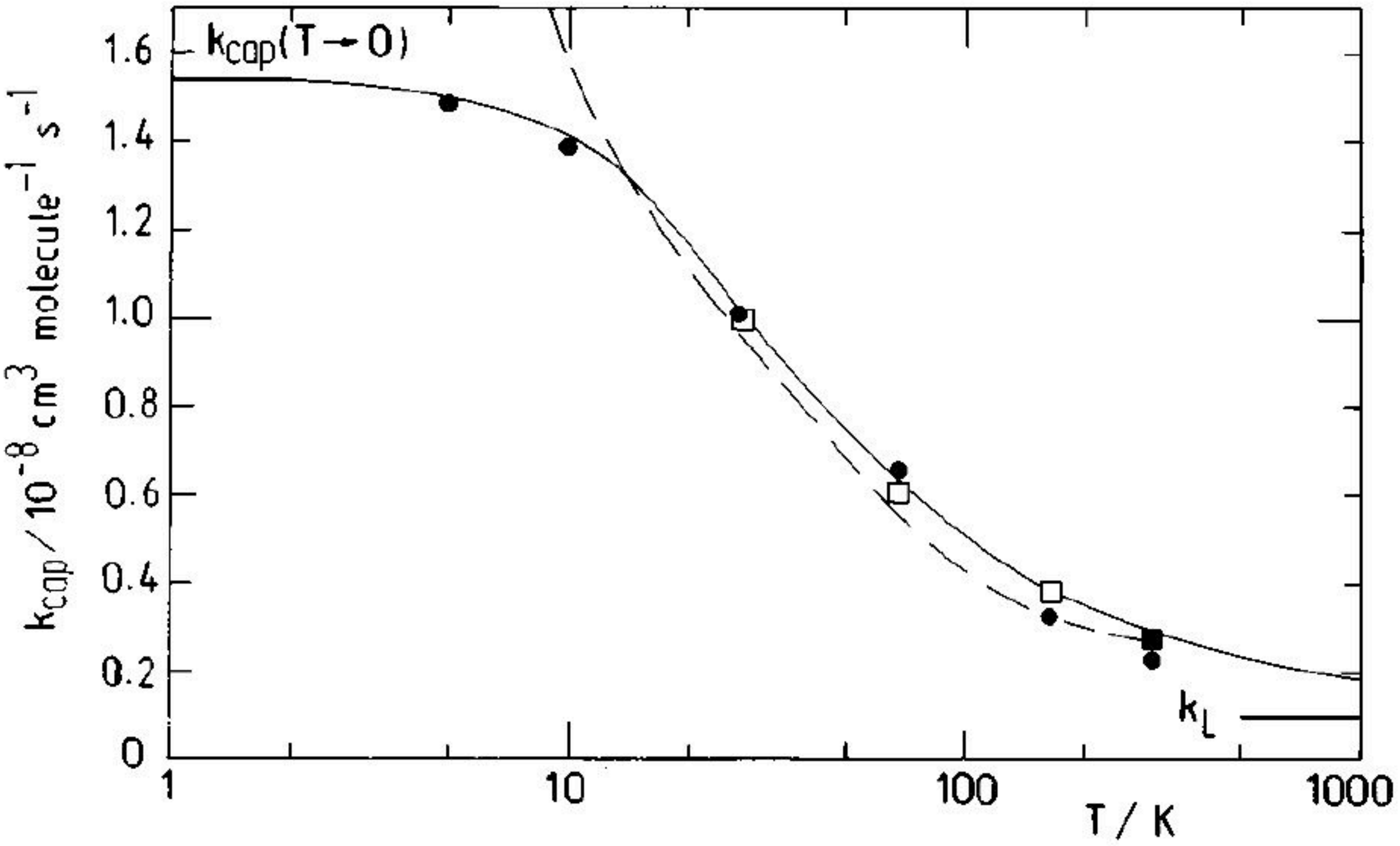
SACM: ACCSA, perturbed rotor etc. all special, but inaccurate, cases

$k(T \rightarrow 0) = k_{\text{Langevin}}\,(1 + \mu_D^2/3\alpha B)^{1/2}$

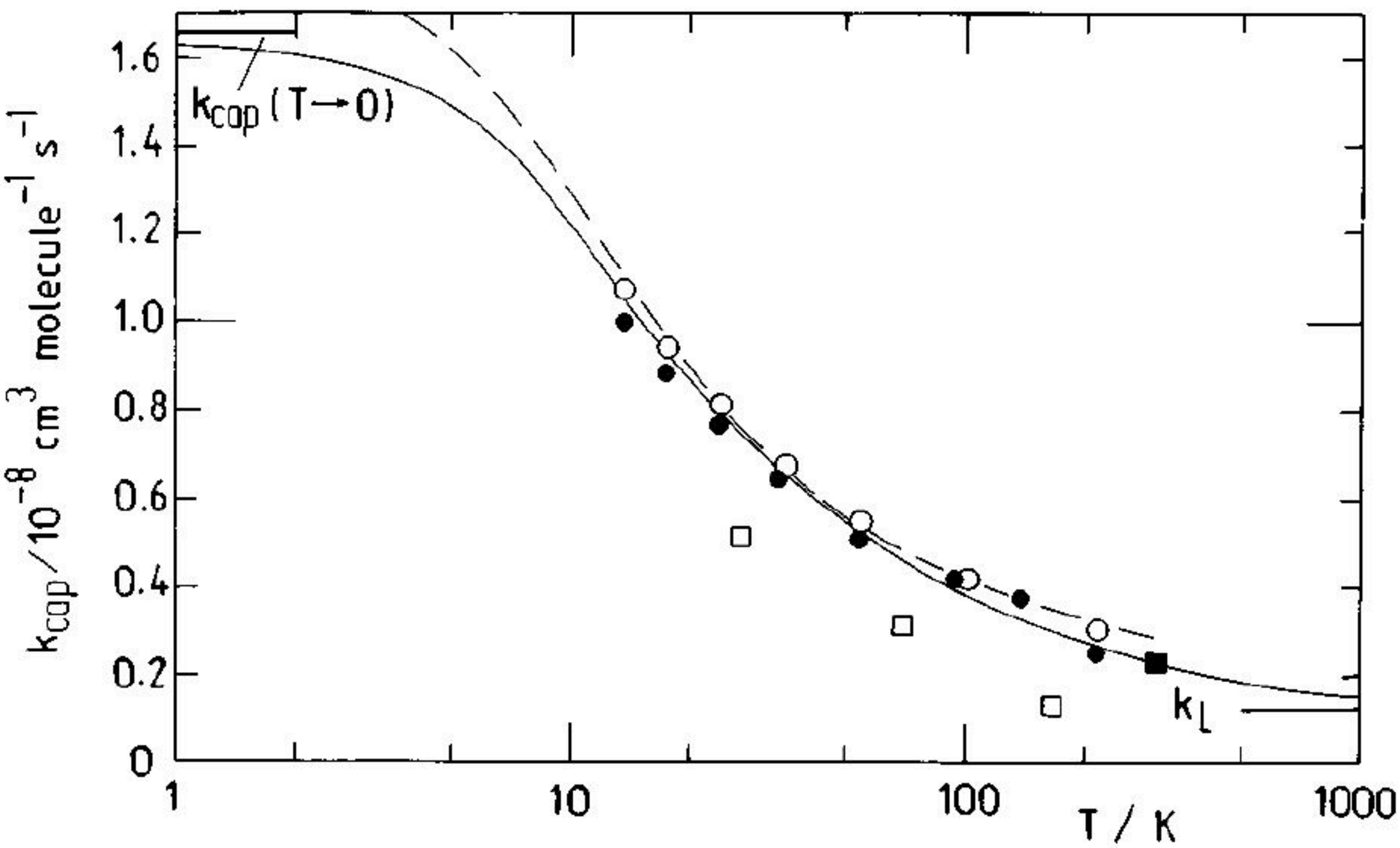
(Troe, J. Chem. Phys. 87, 2773 (1987); 105, 6249 (1996))

Quantum effects of rotor at $kT \leq B$

Classical capture at higher temperatures:
adiabatic – nonadiabatic – sudden
(heavy species light)



Thermal rate constants for capture by N^+ of H_2O. (Full line: SACM symmetric top treatment of this work; ●: SACM asymmetric top treatment from Ref. 27; dashed line: ACCSA treatment from Ref. 47; □: experiments from Ref. 44; ■: experiments from Refs. 45 and 46.)



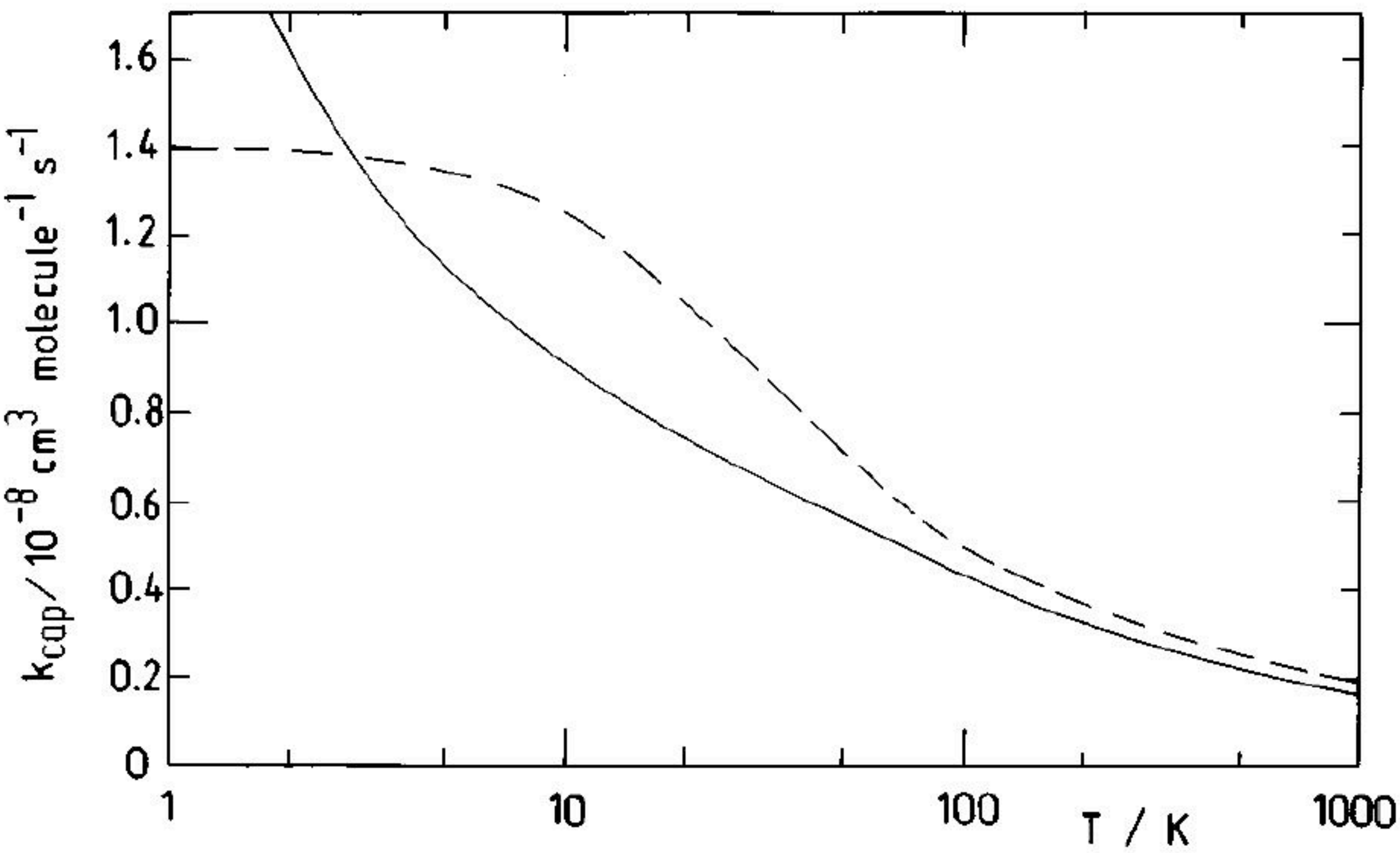
Thermal rate constants for capture by N^+ of NH_3. (Full line: SACM treatment of this work; dashed line: ACCSA treatment of Ref. 47; ●: perturbed rotational state method of Ref. 18; ○: adiabatic invariance method of Ref. 21; □ and ■: experiments of Refs. 44–46.)

Example: ion + open shell species

quantum effects reach up to higher temperatures ($kT \approx 3\ B$)

(Clary, Troe, …)

$k(T \rightarrow 0) = ?$



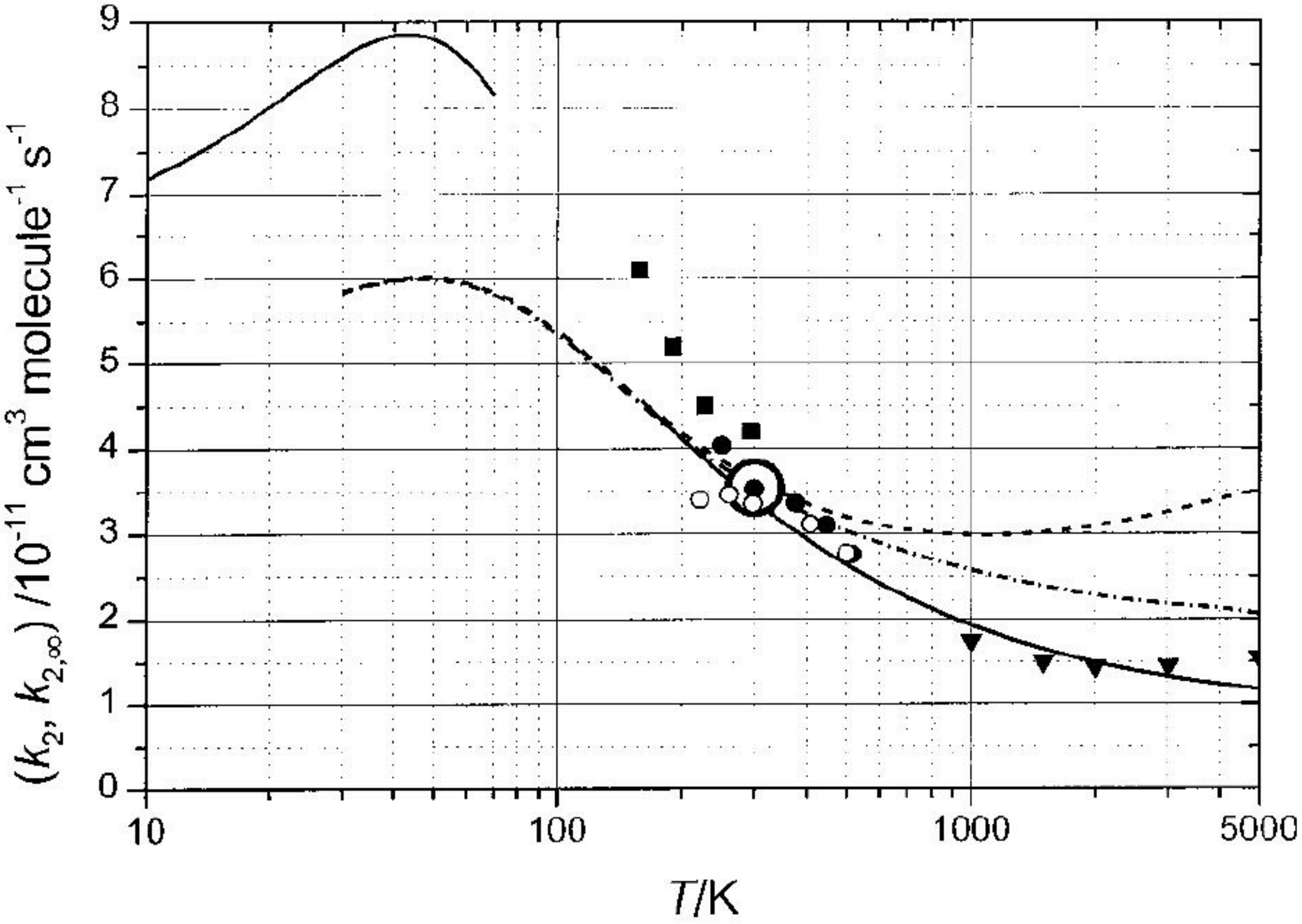
Thermal rate constants for capture by C^+ of OH. [Full line: SACM treatment of this work and of Ref. 28, and analytical SACM representation by Eqs. (7.3) and (7.4) for $C^+ + OH(^2\Pi)$; dashed line: the same for hypothetical $C^+ + OH(^1\Sigma)$; numerical results tabulated in Ref. 49.]

For astrophysical applications mostly classical trajectory
calculations sufficient
(adiabatic – nonadiabatic – sudden)

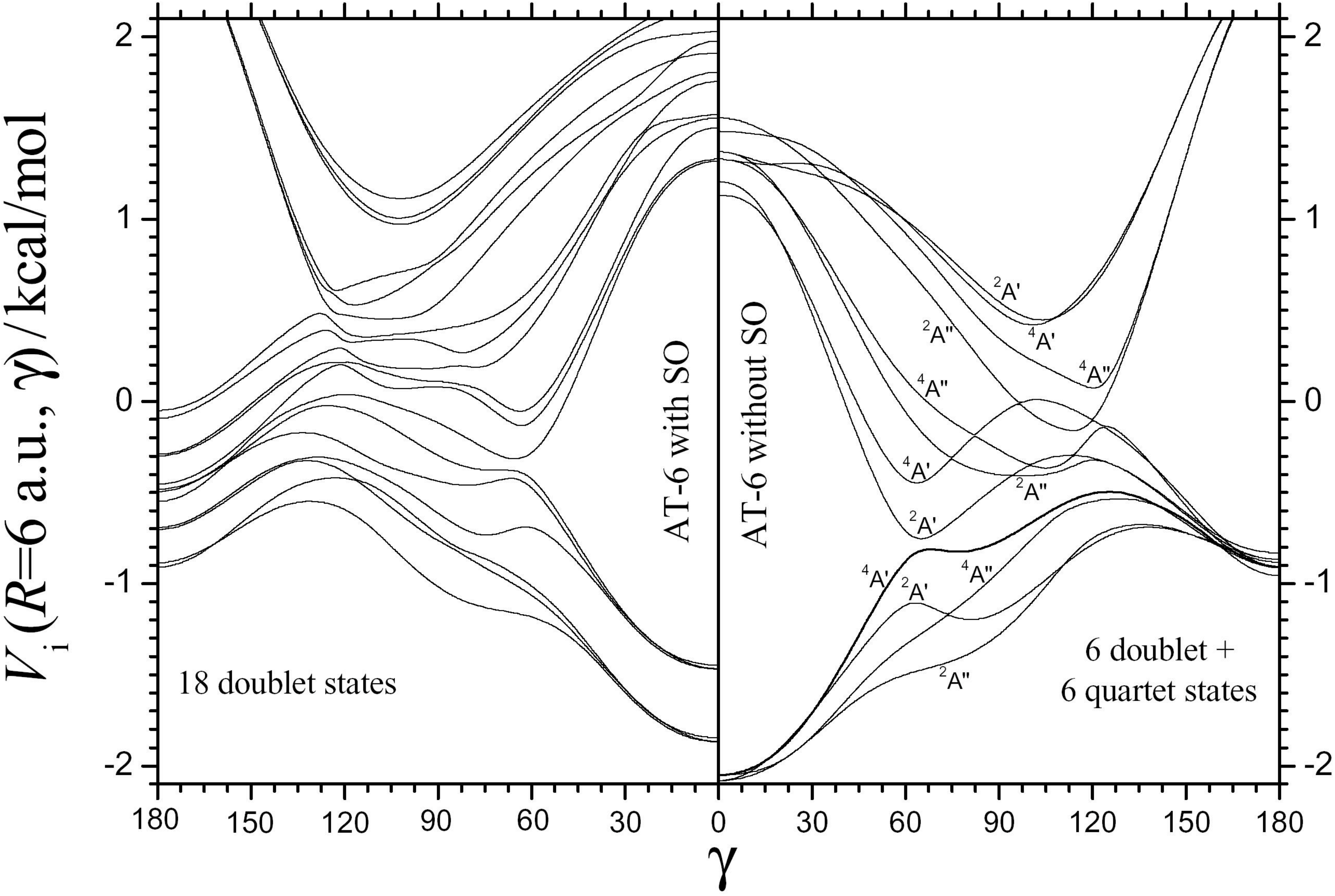
The method: SACM/CT

Maergoiz, Nikitin, Troe, Ushakov 1995 – 2006
various electrostatic potentials + model valence potentials
for capture processes

However, more is needed !
Intrinsic potential surfaces
Only one example: $O + OH \rightarrow O_2 + H$



Comparison of measured and calculated values of k_2 [lower set of three curves=classical calculations from this work and Ref. 8, see Fig. 10, full line up to 70 K=quantum SACM from Ref. 8 with the lowest four channels, ▼=measured k_1 from Eq. (1.6) (Ref. 11) converted to k_2 with K_{eq} from Eq. (1.5), ■=measured k_2 from Ref. 16, ○=measured k_2 from Ref. 15, large circle at 300 K=average k_2 from Refs. 15, 16, 37–39].



V_i(R=6 a.u., γ)/kcal/mol
2
1
0
-1
-2
180
150
120
90
60
30
0
30
60
90
120
150
180
γ
AT-6 with SO
AT-6 without SO
18 doublet states
6 doublet +
6 quartet states
²A'
²A"
⁴A'
⁴A"
⁴A"
⁴A'
²A"
²A'
⁴A'
²A'
⁴A"
²A"