Ion-polar reactions

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Mechanism

$A^+ + B \rightarrow AB^+$ capture

$AB^+ \rightarrow$ products

if fast: capture controlled

$AB^+ \rightarrow C^+ + D \quad k_f(E,J)$

$AB^+ \rightarrow A^+ + B \quad k_b(E,J)$

complex-forming bimolecular

if complex long-lived:

statistical unimolecular rate theory;

capture and $k_b(E,j)$ are linked

by microscopic reversibility

unimolecular rate theory:

rigid transition states:

RRKM theory

loose transition states:

VTST, SACM, SSACM

potential needs to be known

to some extent

rate ≤ capture rate

Ion-polar capture rate theory

Theory complete for closed-shell polar

(polarizable, quadrupolar, …) neutral

Rates in simple analytical form from

T = 0 (ultralow) to low (0.1 – 100 K)

to high temperatures

for linear, symmetric and asymmetric top molecules

theories often unnecessarily complicated

and inaccurate: use the right one !

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J. Chem. Phys. **105**, 6249 (1996)

A. I. Maergoiz, E. E. Nikitin, J. Troe, V. G. Ushakov

J. Chem. Phys. **105**, 6263, 6270 (1996)

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

J. Chem. Phys. **118**, 7313 (2003)

A. I. Maergoiz, E. E. Nikitin, J. Troe

Int. J. Mass Spectrometry in press (2008)

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SACM/CT $\rightarrow E_{0,i}(l)$

$$k_{cap} = \frac{kT}{h}\left(\frac{h^2}{2\pi\mu kT}\right)^{3/2}\frac{Q^*}{Q_{rot}}$$

$$Q^* = \sum_l (2l+1)\sum_i \exp\left(-E_{0,i}(l)/kT\right)$$

classical limit:

Su-Chesnavich equation

$k/k_{Langevin} \approx 0.4767\ x + 0.62$ for $x > 2$

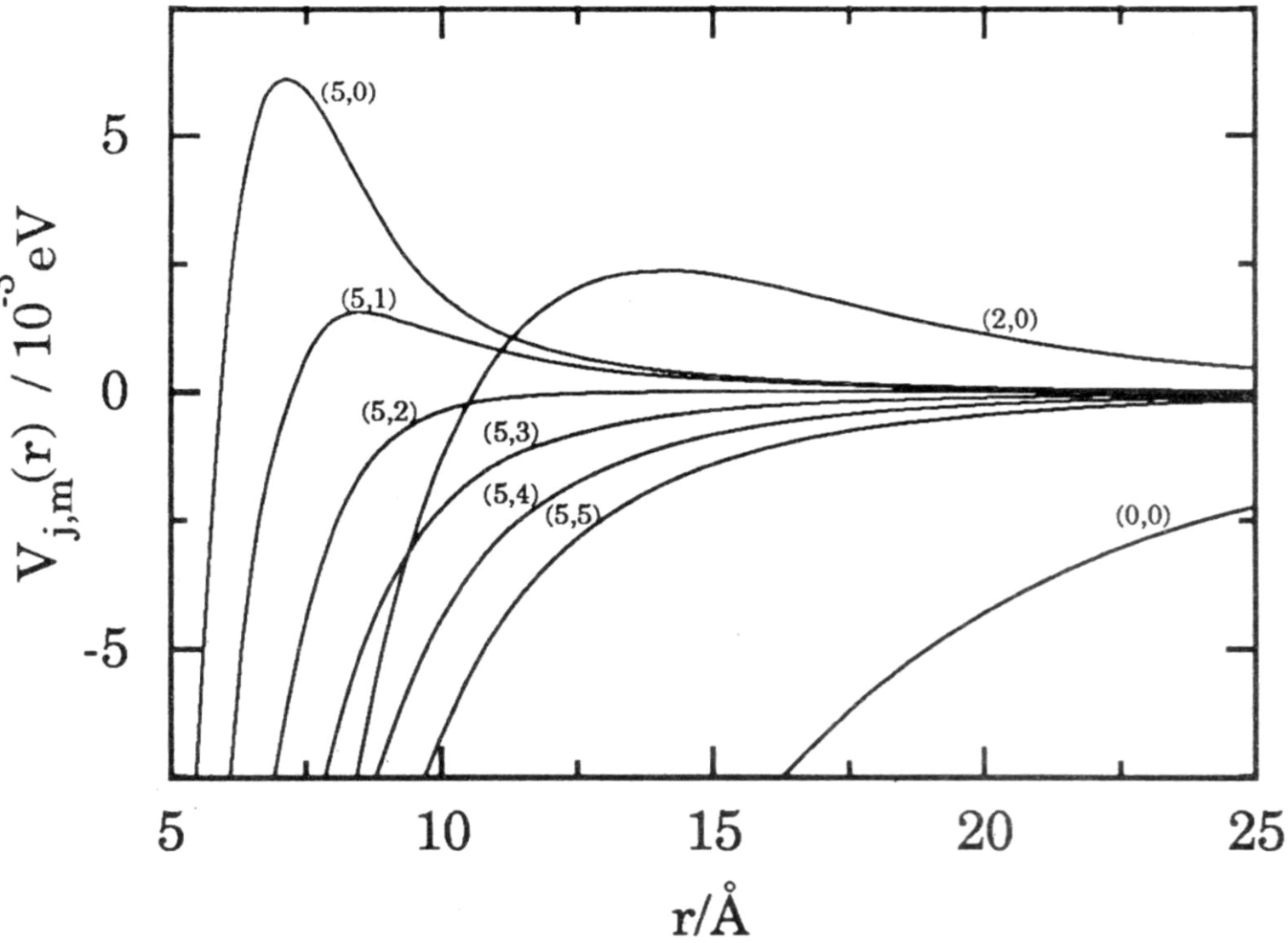
$\approx (x + 0.509)^2/10.526 + 0.9754$ for $x < 2$

with $x = \mu_D/(2\alpha kT)^{1/2}$

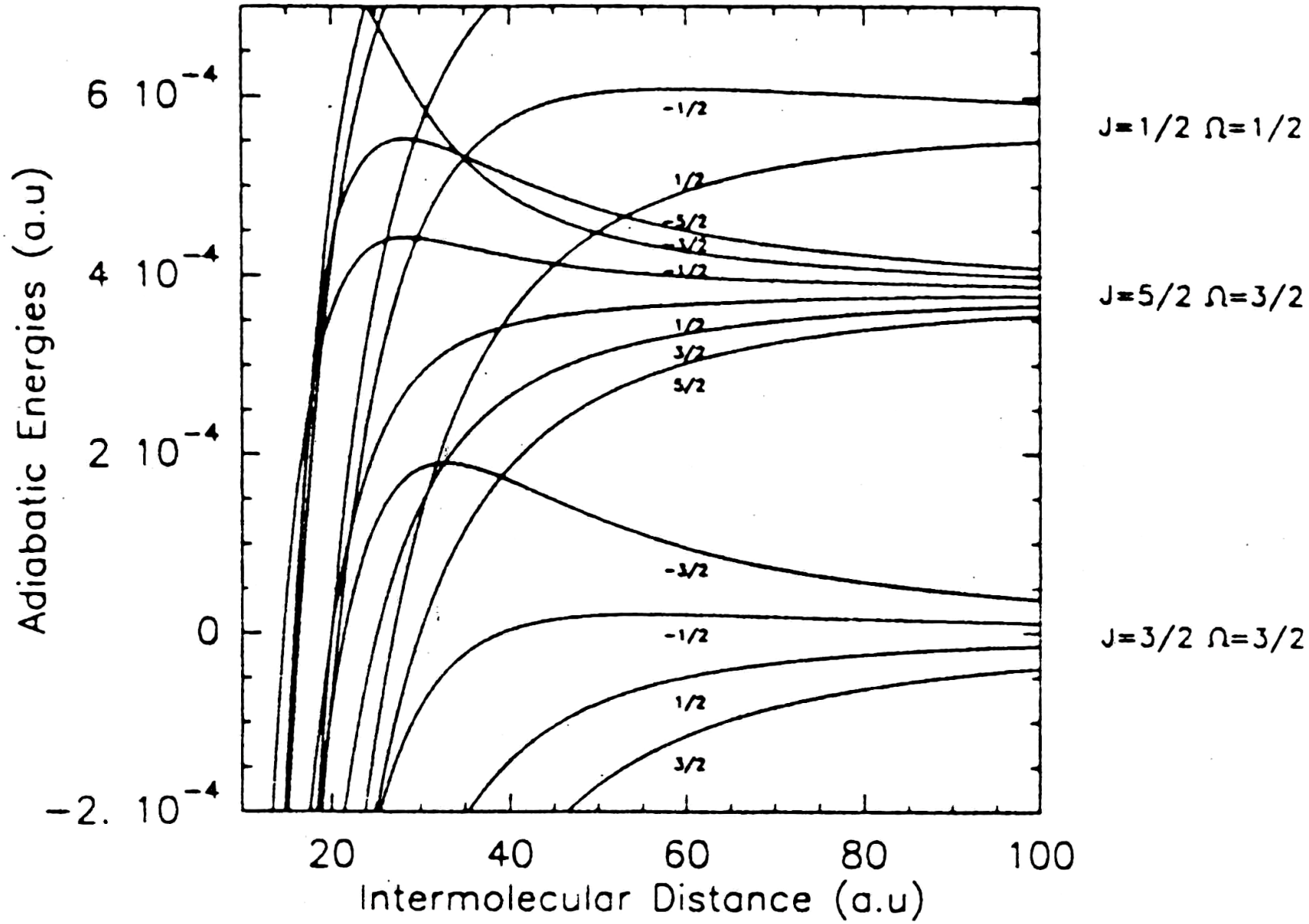
ion-dipole, ion-quadrupole, dipole-dipole, valence-atom + linear, valence-linear + linear

Maergoiz, Nikitin, Troe, Ushakov (1996 – 2002)

Capture **HCl + H_3^+** (L = 0)



Markovic 1989



Dubernet, Gargaud, and McCarroll 1992

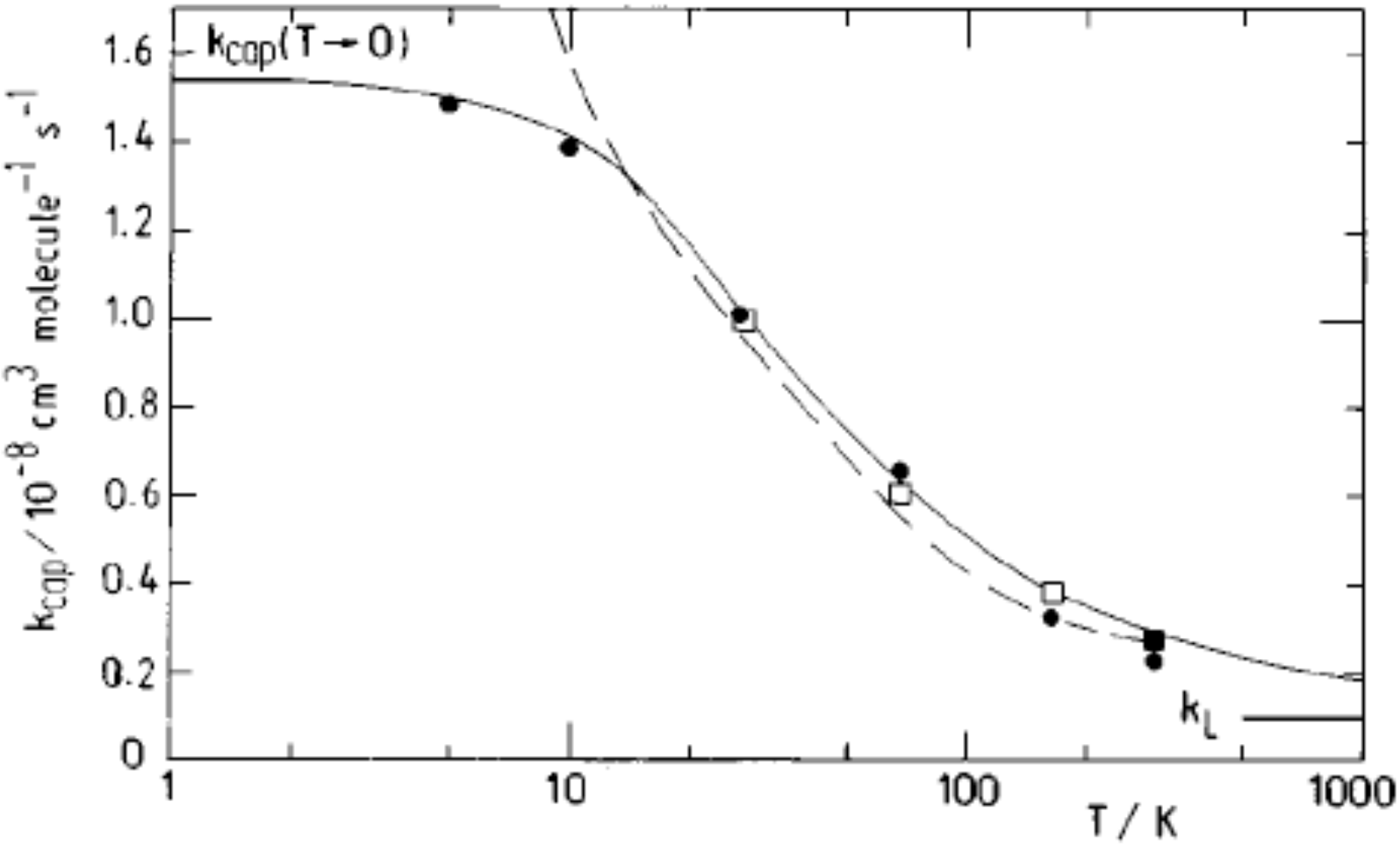


FIG. 13. Thermal rate constants for capture by N^+ of H_2O. (Full line: SACM symmetric top treatment of this work; ●: SACM asymmetric top treatment from Ref. 27; dashed line: ACCSA treatment from Ref. 47; □: experiments from Ref. 44; ■: experiments from Refs. 45 and 46.)

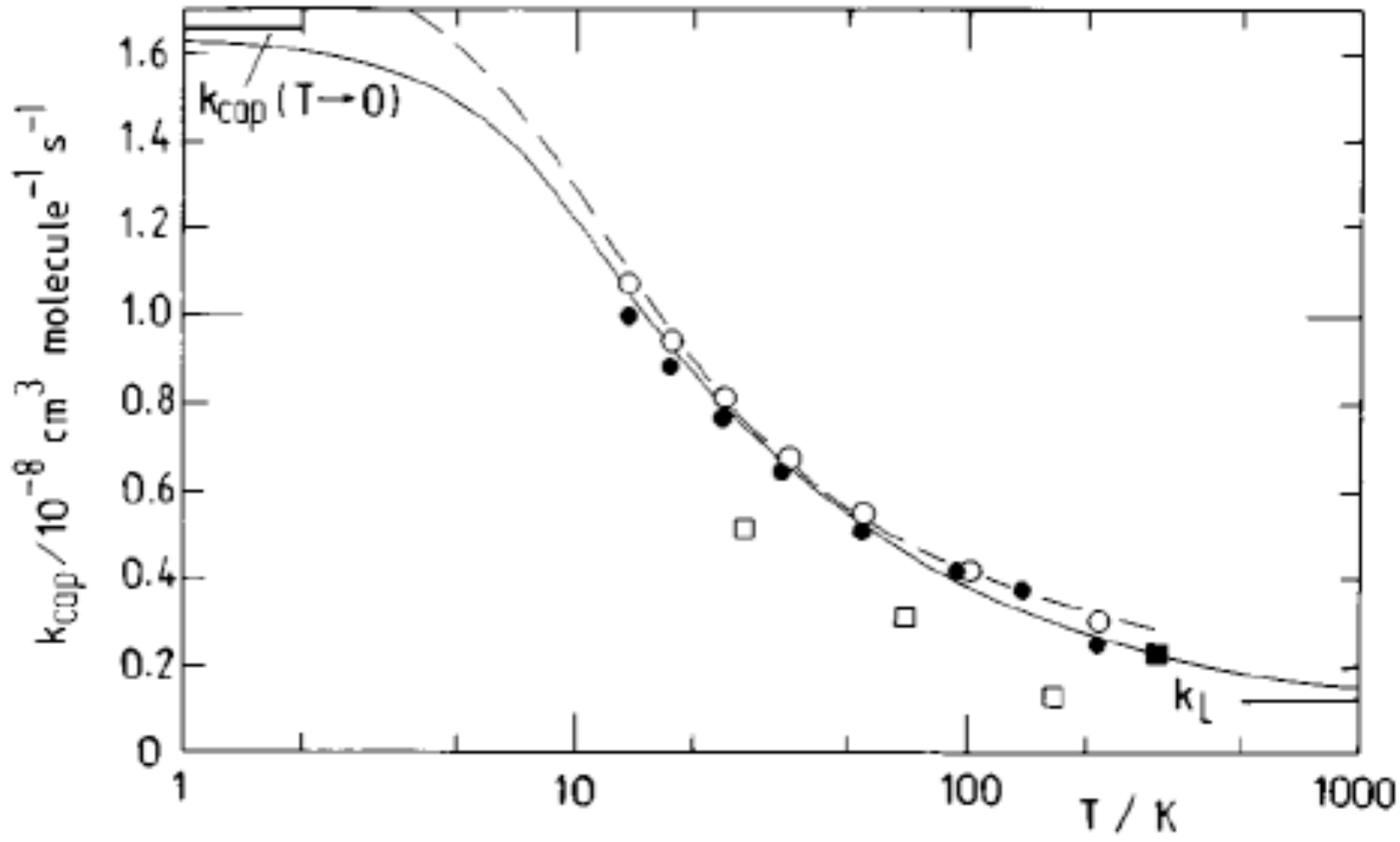
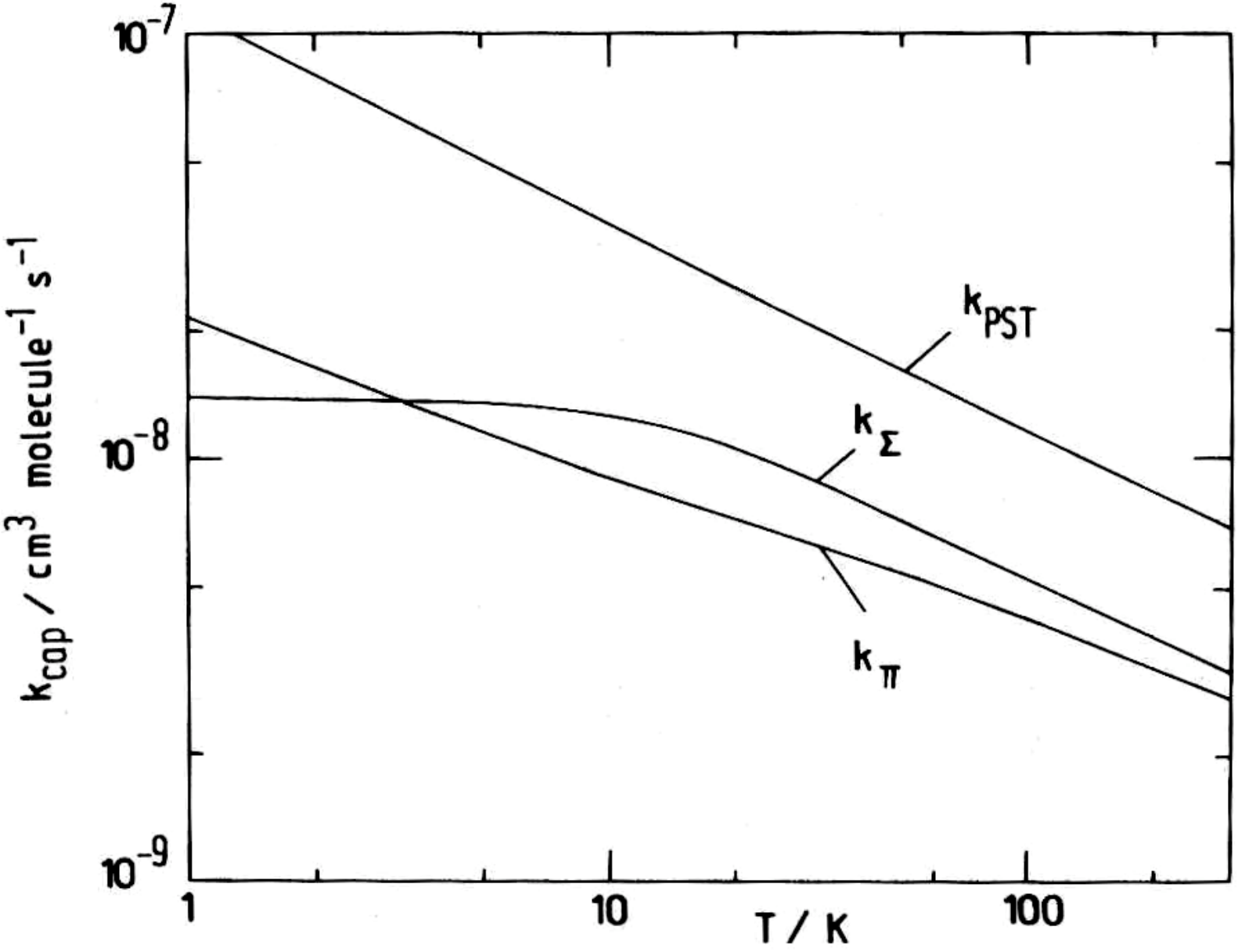
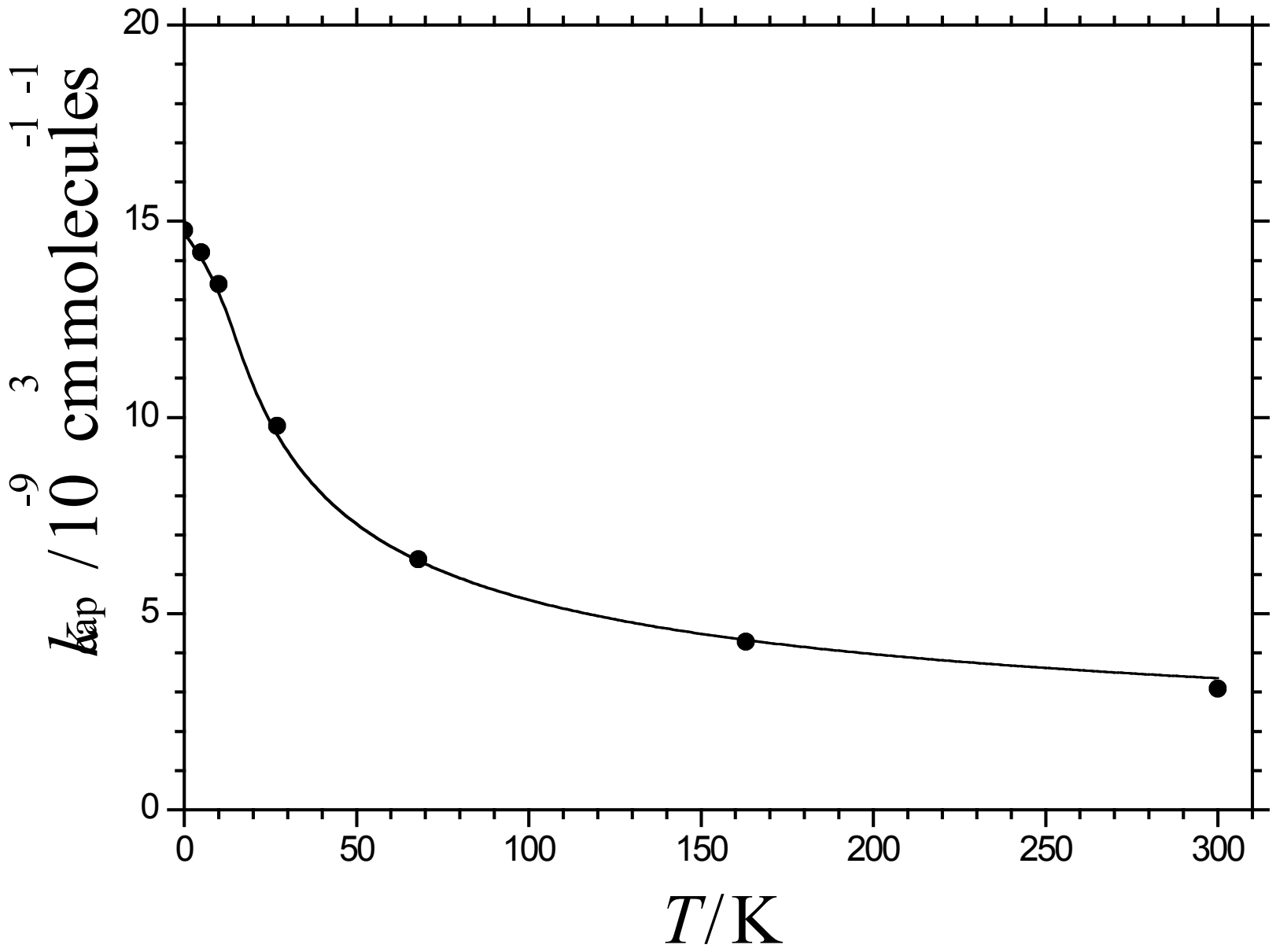


FIG. 14. Thermal rate constants for capture by N^+ of NH_3. (Full line: SACM treatment of this work; dashed line: ACCSA treatment of Ref. 47; ●: perturbed rotational state method of Ref. 18; ○: adiabatic invariance method of Ref. 21; □ and ■: experiments of Refs. 44–46.)

$C^+ + OH$ capture



Troe 1987


20
15
10
5
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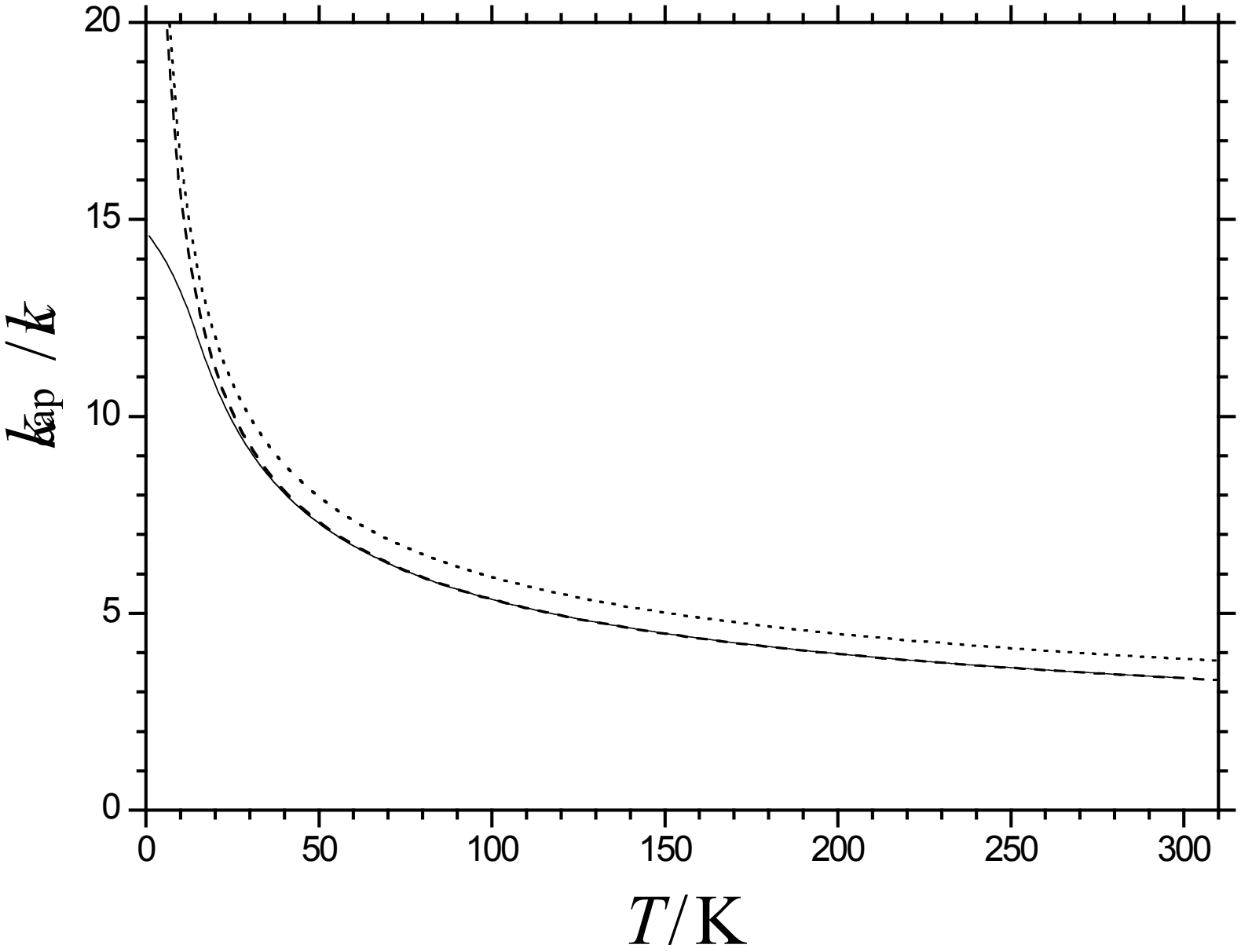
200
250
300
k_{ap} /10^{-9} cm^{3} molecules^{-1} s^{-1}
T/K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250
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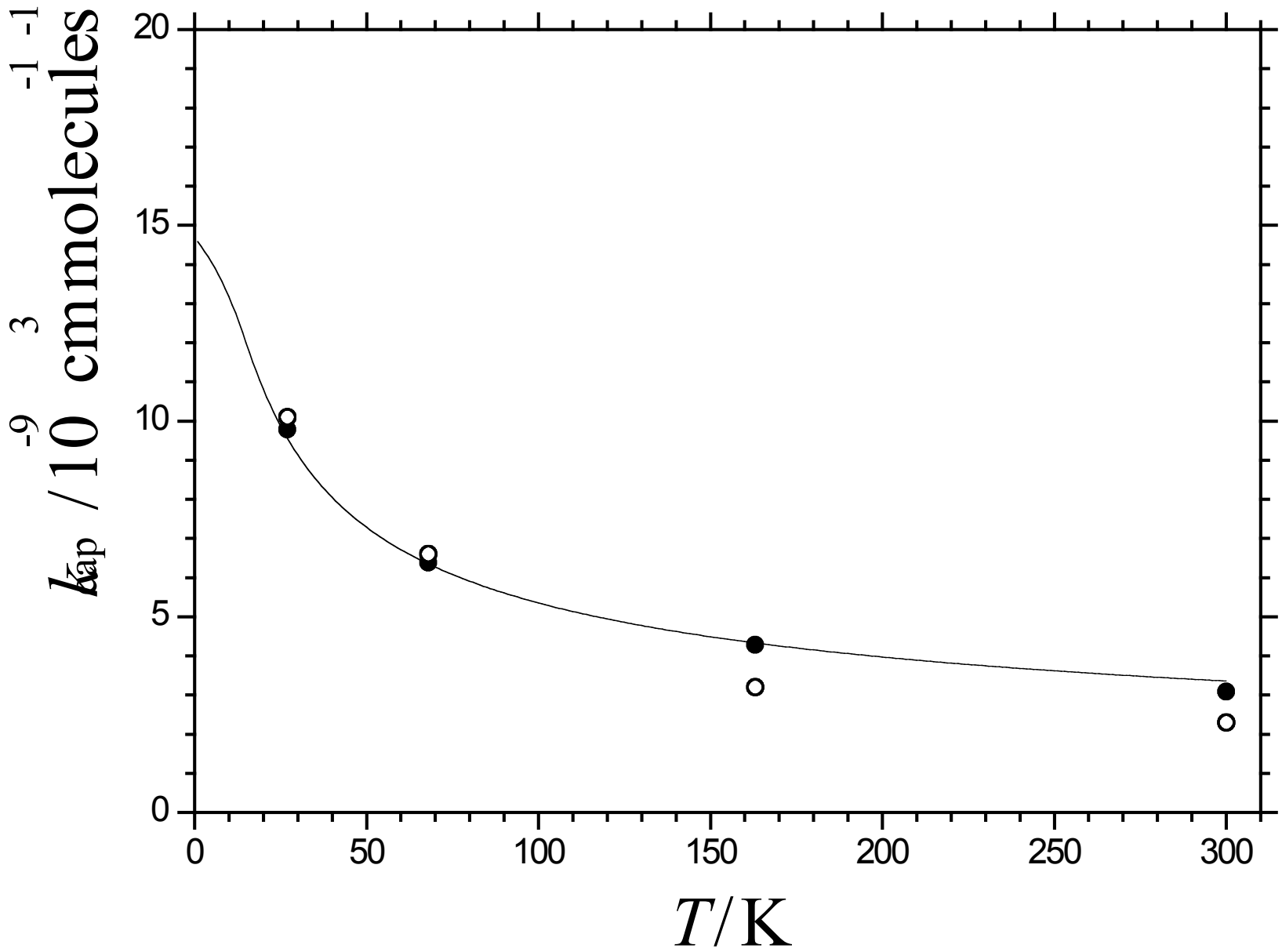
k_{ap}/k
T/K


k_{ap} / 10^{-9} cm^3 $molecules^{-1}$ s^{-1}
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15
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5
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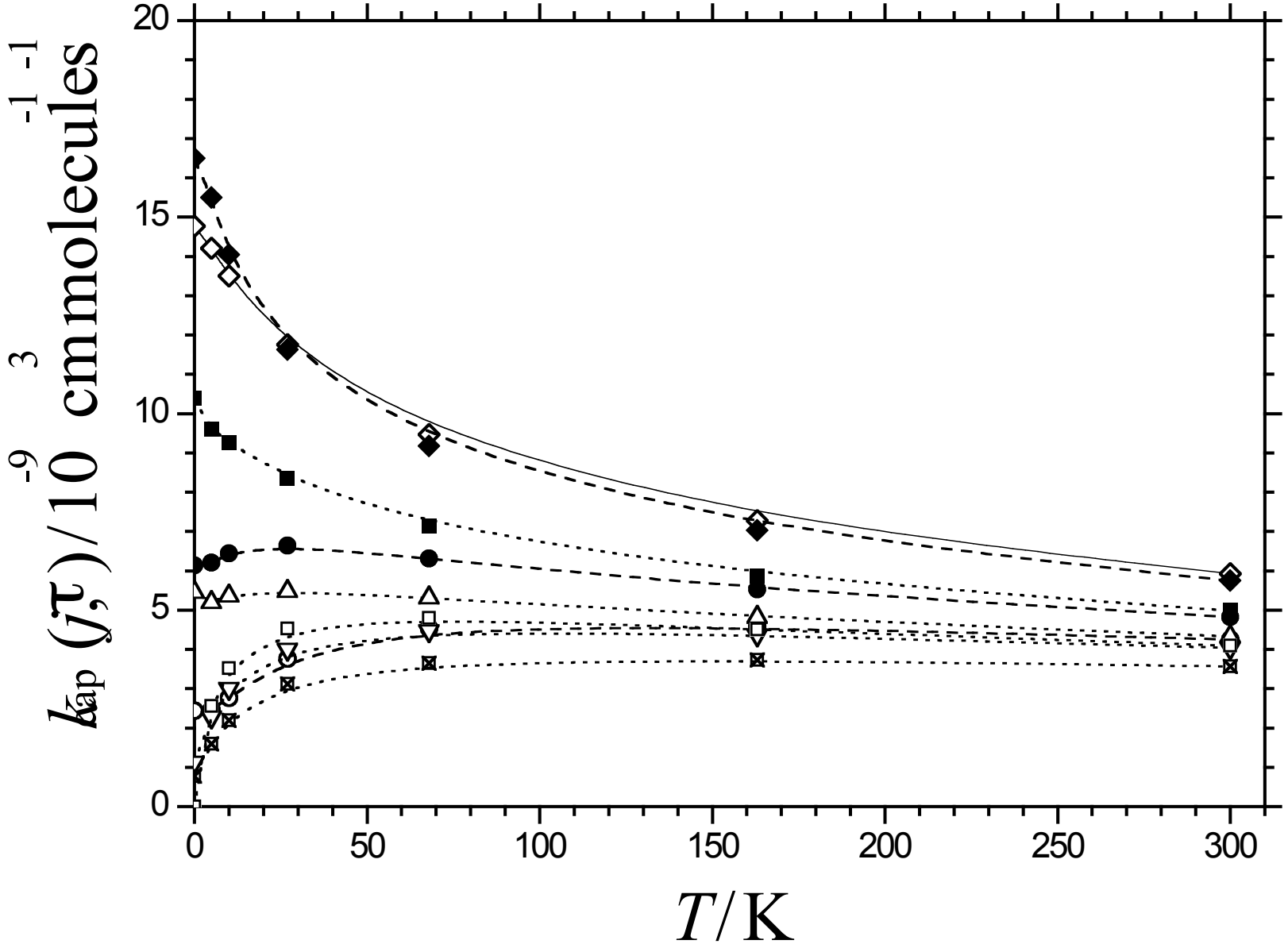
250
300
T/K


$k_{ap}(j,\tau)/10^{-9}$ cm^3 molecules^{-1} s^{-1}
20
15
10
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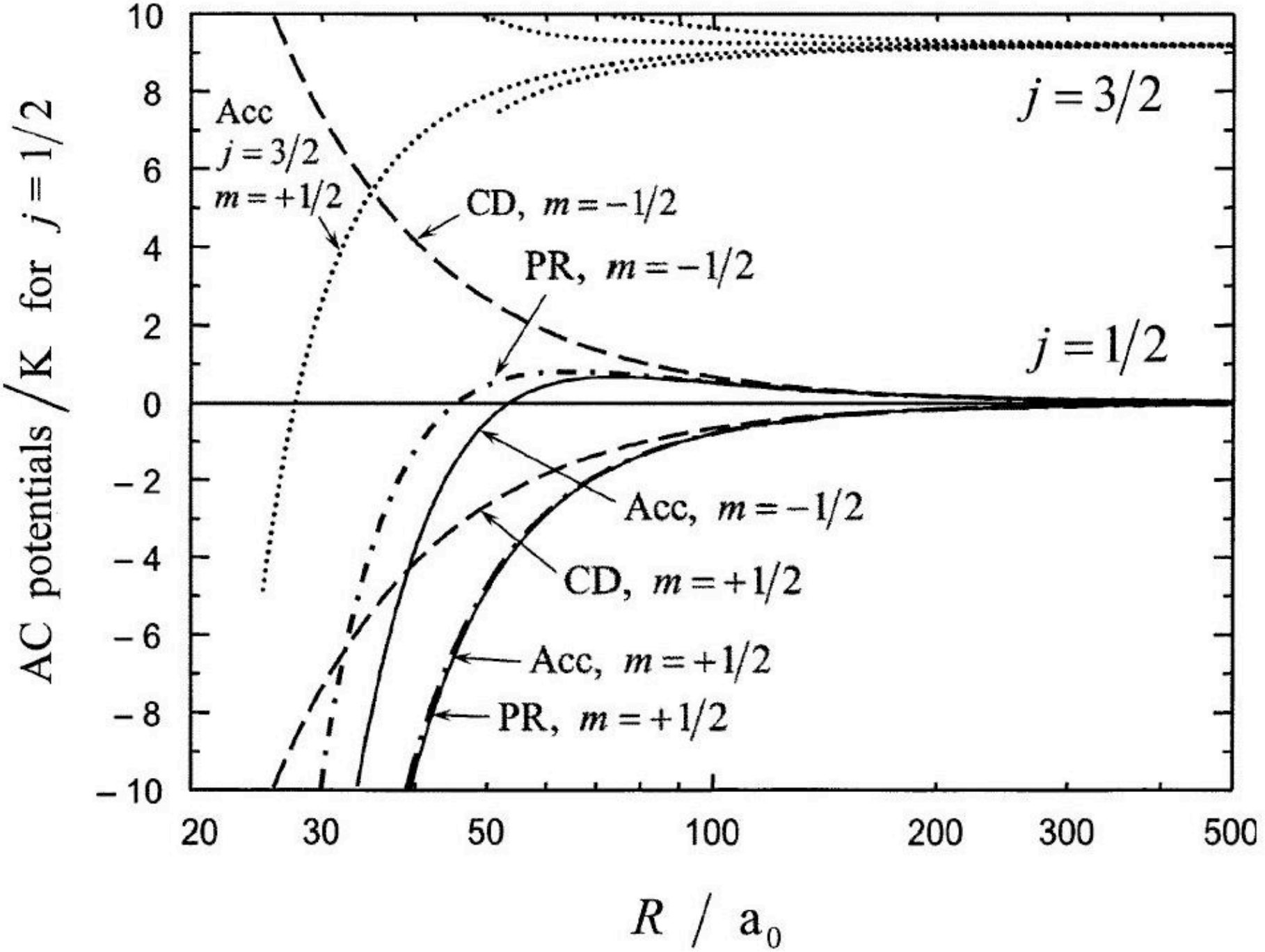
0
0
50
100
150
200
250
300
T/K

Ion	k	k_L	k/k_L	cap	c_1	c_2
C^+	2.70	1.050	2.57	+	0.65	2.87
C^-	0.50	1.050	0.48	–	0.65	2.87
CH^+	4.06	1.026	3.96	+	0.64	2.80
CH_2^+	1.20	1.004	1.20	–	0.62	2.74
CH_3^+	0.002	0.985	0.00	–	0.61	2.69
CH_4^+	2.60	0.968	2.69	+	0.60	2.65
CH_5^+	3.70	0.953	3.88	+	0.59	2.60
H^+	6.90	2.887	2.39	+	1.79	7.89
H^-	3.8	2.887	1.32	–	1.79	7.89
H_2^+	7.3	2.094	3.49	+	1.30	5.72
C_2^+	0.88	0.879	1.00	–	0.54	2.40
C_2H^+	0.87	0.871	1.00	–	0.54	2.38
$C_2H_2^+$	0.22	0.864	0.25	–	0.54	2.36
$C_2H_3^+$	1.11	0.858	1.29	–	0.53	2.34
$C_2H_5^+$	1.40	0.846	0.92	–	0.52	2.31
C_2N^+	0.315	0.807	0.39	–	0.50	2.21
$C_2N_2^+$	2.4	0.771	3.11	+	0.48	2.11
C_3H^+	0.45	0.810	0.56	–	0.50	2.21
C_3O^+	0.5	0.771	0.65	–	0.48	2.11
C_4N^+	1.5	0.755	1.99	–	0.47	2.06
$C_2H_6^+$	2.95	0.840	3.51	+	0.52	2.30
CN^+	2.88	0.864	3.33	+	0.54	2.36
CNC^+	1.63	0.807	2.02	+	0.50	2.21
CO^+	2.604	0.852	3.06	+	0.53	2.33
CO_2^+	2.796	0.789	3.54	+	0.49	2.16
H_2Cl^+	2.00	0.809	2.47	+	0.50	2.21
H_2CO^+	2.60	0.840	3.09	+	0.52	2.30
H_2S^+	0.81	0.821	0.99	–	0.57	2.24
H_3CO^+	0.23	0.835	0.28	–	0.52	2.28
HCN^+	3.60	0.858	4.20	+	0.53	2.34
HCO^+	2.50	0.846	2.96	+	0.52	2.31
HCO_2^+	2.30	0.786	2.93	+	0.49	2.15
$HCOOH_2^+$	0.021	0.781	0.03	–	0.48	2.13
HN_2^+	2.60	0.846	3.07	+	0.52	2.31
HNO^+	2.30	0.835	2.75	+	0.52	2.28
$HNSi^+$	2.00	0.791	2.53	+	0.49	2.16
$HOCS^+$	3.40	0.756	4.50	+	0.47	2.07
HPO^+	0.34	0.779	0.44	–	0.48	2.13
HS^+	0.78	0.826	0.94	–	0.51	2.26
$HSiS^+$	1.10	0.756	1.46	–	0.47	2.07
HSO_2^+	2.13	0.751	2.84	+	0.47	2.05
N_2^+	2.80	0.852	3.29	+	0.53	2.33
N_2O^+	2.289	0.789	2.90	+	0.49	2.15
$NCCNH^+$	0.51	0.769	0.66	–	0.48	2.10
O_2H^+	0.82	0.826	0.99	–	0.51	2.26
P^+	0.55	0.836	0.66	–	0.52	2.28
PH^+	1.20	0.831	1.44	–	0.52	2.27
PH_2^+	0.49	0.826	0.59	–	0.51	2.26
Si^+	0.23	0.851	0.27	–	0.53	2.33
$SiCH_3^+$	2.00	0.791	2.53	+	0.49	2.16
SiH^+	0.80	0.845	0.95	–	0.52	2.31
SiH_4^+	2.00	0.830	2.41	+	0.51	2.27
SiH_5^+	2.00	0.826	2.42	+	0.51	2.26
H_3^+	5.90	1.753	3.37	+	1.09	4.79
He^+	0.5505	1.558	0.35	–	0.97	4.26
N^+	2.80	1.005	2.79	+	0.62	2.75
NH^+	3.325	0.985	3.38	+	0.61	2.69
NH_2^+	3.005	0.968	3.10	+	0.60	2.65
NH_3^+	0.110	0.927	0.12	–	0.57	2.53
OH^+	2.89	0.953	3.03	+	0.59	2.60


AC potentials / K for $j = 1/2$
R / a_0
$j = 3/2$
$j = 1/2$
Acc
$j = 3/2$
$m = +1/2$
CD, $m = -1/2$
PR, $m = -1/2$
Acc, $m = -1/2$
CD, $m = +1/2$
Acc, $m = +1/2$
PR, $m = +1/2$
10
8
6
4
2
0
−2
−4
−6
−8
−10
20
30
50
100
200
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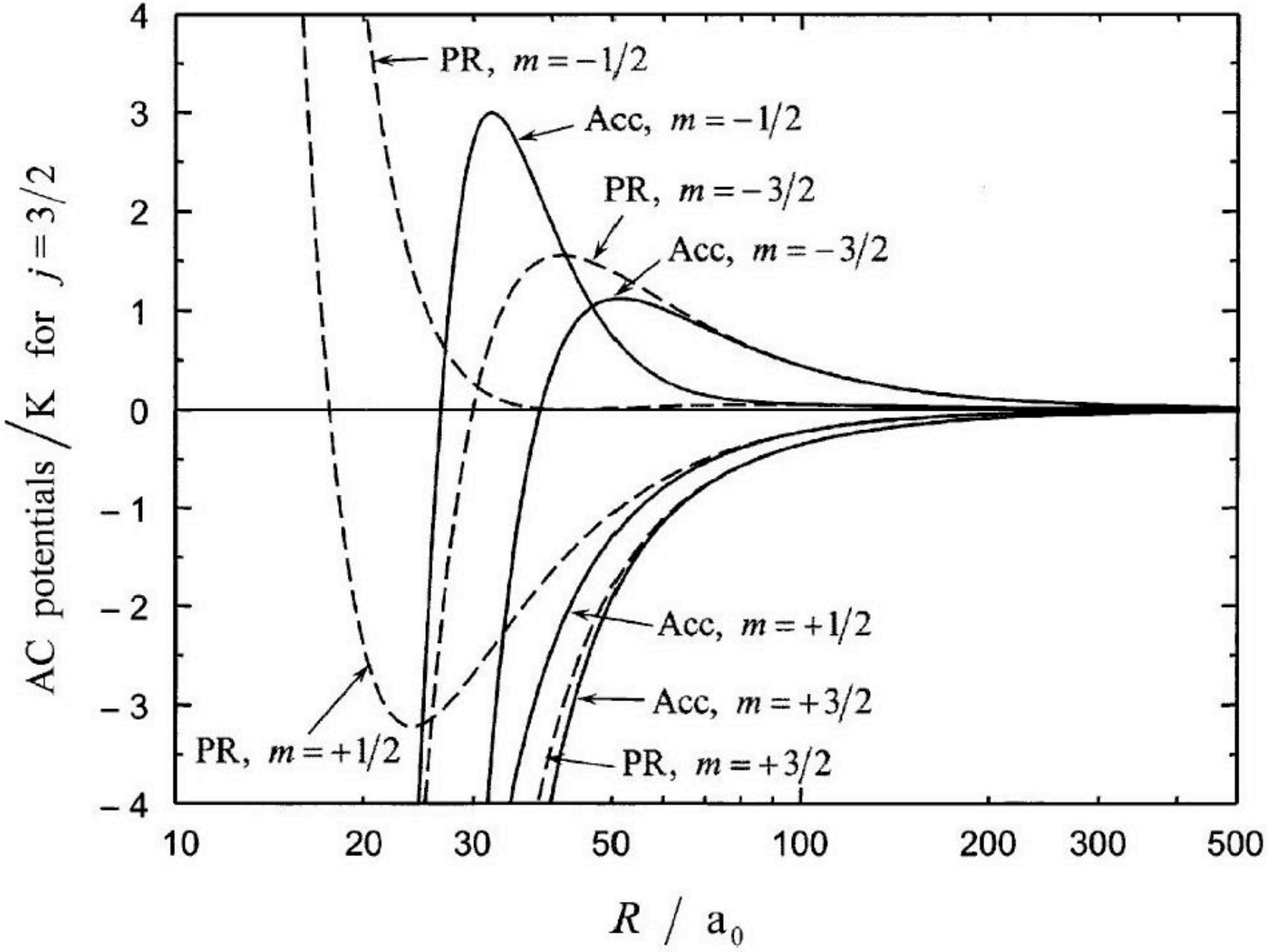
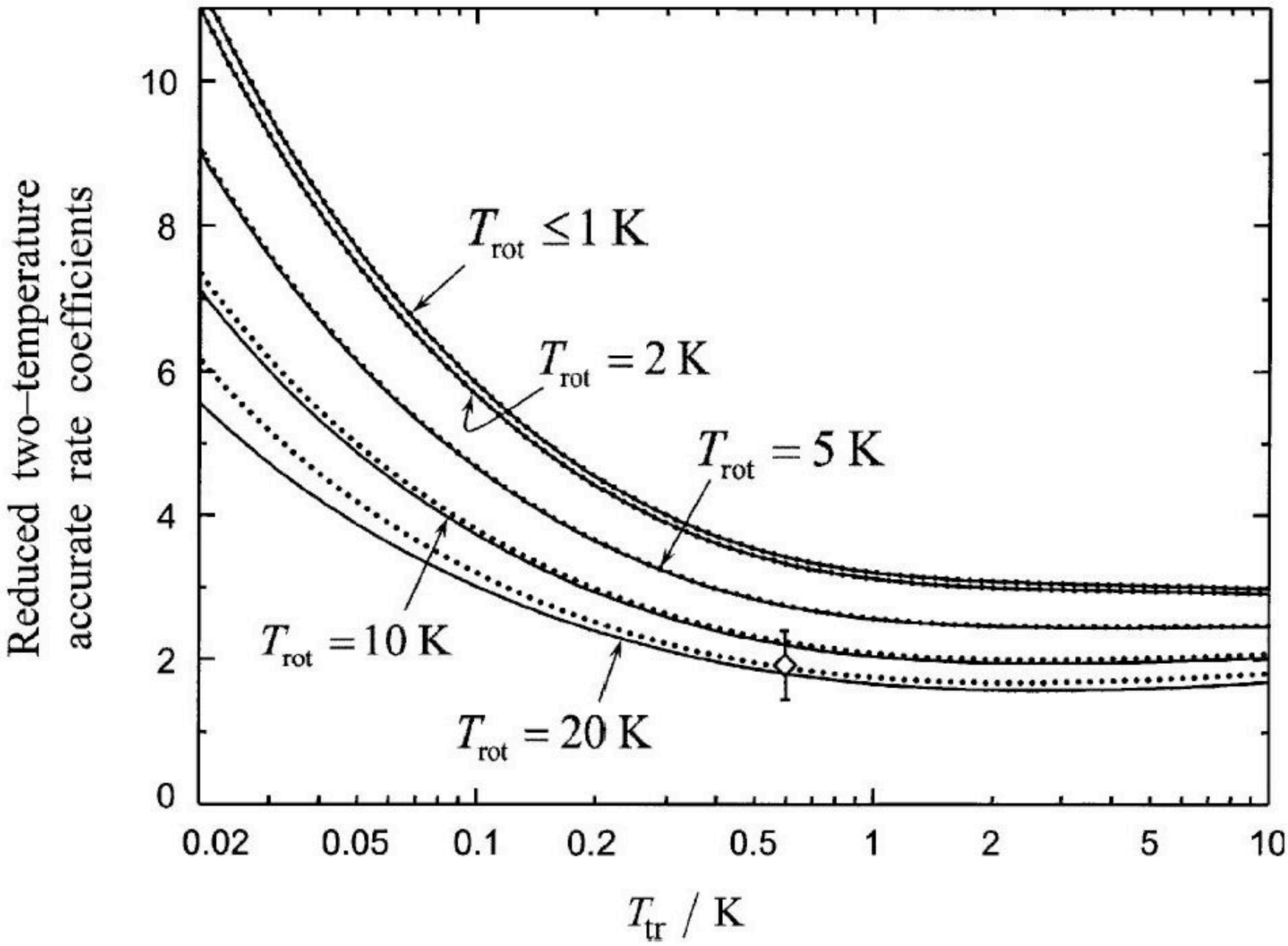
500


AC potentials / K for $j = 3/2$
R / a_0
PR, $m = -1/2$
Acc, $m = -1/2$
PR, $m = -3/2$
Acc, $m = -3/2$
Acc, $m = +1/2$
Acc, $m = +3/2$
PR, $m = +3/2$
PR, $m = +1/2$
4
3
2
1
0
– 1
– 2
– 3
– 4
10
20
30
50
100
200
300
500


Reduced two–temperature accurate rate coefficients
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8
6
4
2
0
$T_{rot} \leq 1$ K
$T_{rot} = 2$ K
$T_{rot} = 5$ K
$T_{rot} = 10$ K
$T_{rot} = 20$ K
0.02
0.05
0.1
0.2
0.5
1
2
5
10
T_{tr} / K