Dynamics of complex-forming bimolecular reactions

Péter Szabó, György Lendvay
Institute of Materials and Environmental Chemistry, Research Center for Natural Sciences, Budapest, Hungary
and
University of Pannonia, Institute of Chemistry, Veszprém, Hungary

A tribute to Antonio Laganà

Hungarian Scientific Research Fund (OTKA) # K109866
Hungarian Development Agency KTIA-2012-2-14
COST Actions CM901, CM1401

$O_2(^1\Delta_g) + H(^2S) \rightarrow OH(^2\Pi) + O(^3P)$ vs. $O_2(^3\Sigma_g^+) + H(^2S) \rightarrow OH(^2\Pi) + O(^3P)$

Explore the dynamics of the reaction using classical mechanics validated against quantum mechanical calculations

ANTONIO LAGANÀ
the reaction dynamicist
the computer scientist
the European collaboration builder
the international educator
promoter of virtual reality

Joint papers
M. Alagia, N. Balucani, P. Casavecchia, A. Laganá, G. Ochoa de Aspuru, E. H. Van Kleef, G.G. Volpi, and G. Lendvay
On the dynamics of the O(1D) + CF3Br reaction
Chem. Phys. Letters 258, 323-329 (1996)

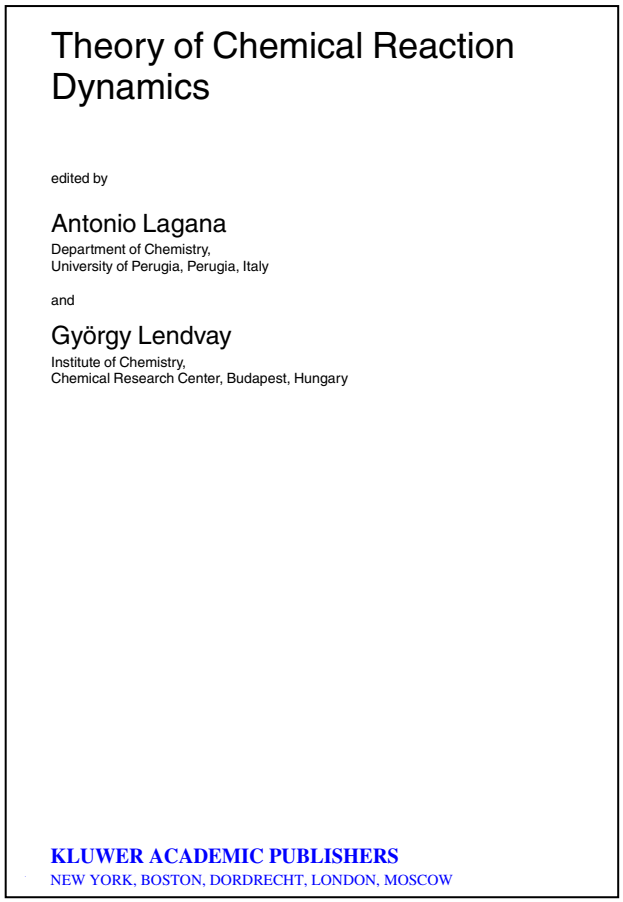
E. Garcia, A. Saracibar, A. Rodriguez, A. Laganà and G. Lendvay
Calculated versus measured product distributions of the OH+D2 reaction
Mol. Phys. 104, 839-846 (2006)

Papers upon inspiration from A.L.
Á. Bencsura and G. Lendvay
Parallelization of reaction dynamics codes using P-GRADE: a case study
Lecture Notes in Computer Science **3044**, 290-299, Springer, 2004.

Á. Bencsura and G. Lendvay
Parallelization of a quantum scattering code using P-GRADE: a case study
in: Distributed and parallel systems: clusters and grid computing, Kluwer International Series in Engineering and Computer Sciece, Vol, 777, Z. Juhász, P. Kacsuk, D. Kranzlmüller, Eds, pp. 121-128, Springer, 2004.

Common projects
COST Actions
D9 (1997-2002), D23 (2001-2005), D26 (2002-2006)
D37 (2006-2010), CM901 (2011-2014)

Conference organized jointly


Theory of Chemical Reaction Dynamics

edited by

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Chemical Research Center, Budapest, Hungary

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Explore the dynamics of the reaction using classical mechanics validated against quantum mechanical calculations

$O_2 + H \rightarrow O + OH$

The "single most important combustion reaction"

J. A. Miller, R. J. Kee, and C. K. Westbrook,
Annu. Rev. Phys. Chem. **41**, 345 (1990).

Combustion models most sensitive to its rate constant

Turányi et al.

Heavily studied both experimentally and theoretically

Lowest potential surface $\tilde{X}\,^2A''$

DMBE IV
XXZLG
PES
Xu, Xie, Zhang, Lin, Guo,
J. Chem. Phys. 2005, **122**, 244305.
dynamics
J. Chem. Phys., 2007, **126**, 074315.
J. Am. Chem. Soc., 2008, **130**, 14962.

Correlates with $O_2(^3\Sigma_g^+)$

$2H_2 + O_2 \rightarrow 2H_2O$

$H + O_2 \rightarrow O + OH$
$H + O_2 + M \rightarrow HO_2 + M$
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$H_2 + M \rightarrow 2H + M$
$H_2O + M \rightarrow H + OH + M$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

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$H + H_2O_2 \rightarrow OH_2 + OH$
$H_2 + M \rightarrow 2H + M$
$H_2O + M \rightarrow H + OH + M$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

O_2 has low-lying excited states

lowest one is $O_2(^1\Delta_g)$ - 0.96 eV (~22 kcal/mol, ~92 kJ/mol)

High-temperature kinetic experiments may involve excited singlet O_2
assuming thermal equilibrium, at high T there may be >0.5% excited O_2
at 1000 K >0.5%
at 2000 K ~1.5% $O_2(^1\Delta_g)$

In addition to

$$O_2(^3\Sigma_g^+) + H(^2S) \rightarrow OH(^2\Pi) + O(^3P),$$

the reaction

$$O_2(^1\Delta_g) + H(^2S) \rightarrow OH(^2\Pi) + O(^3P)$$

can be important in flames.

Previous interest
DOIL- Discharge Induced Iodine Laser
Initiation of combustion by laser or discharge

V. Aquilanti, G. Grossi, A. Lagana'
A computational study of spin flip in collisions of H and Mu with oxygen molecules
Hyperfine Interactions (ISSN:0304-3843) 8, 347-350 (1981).

$$O_2(^1\Delta_g) + H(^2S) \rightarrow OH(^2\Pi) + O(^3P)$$

Rate measurement

Glass et al. (1982) $k=(1.46 \pm 0.49) \times 10^{-11} \exp(-4 \pm 0.2 \text{ kcal/mol}/RT) \text{ cm}^3/\text{s}$

ХИМИЧЕСКАЯ ФИЗИКА

1989 Том 8, № 8

УДК 541.126

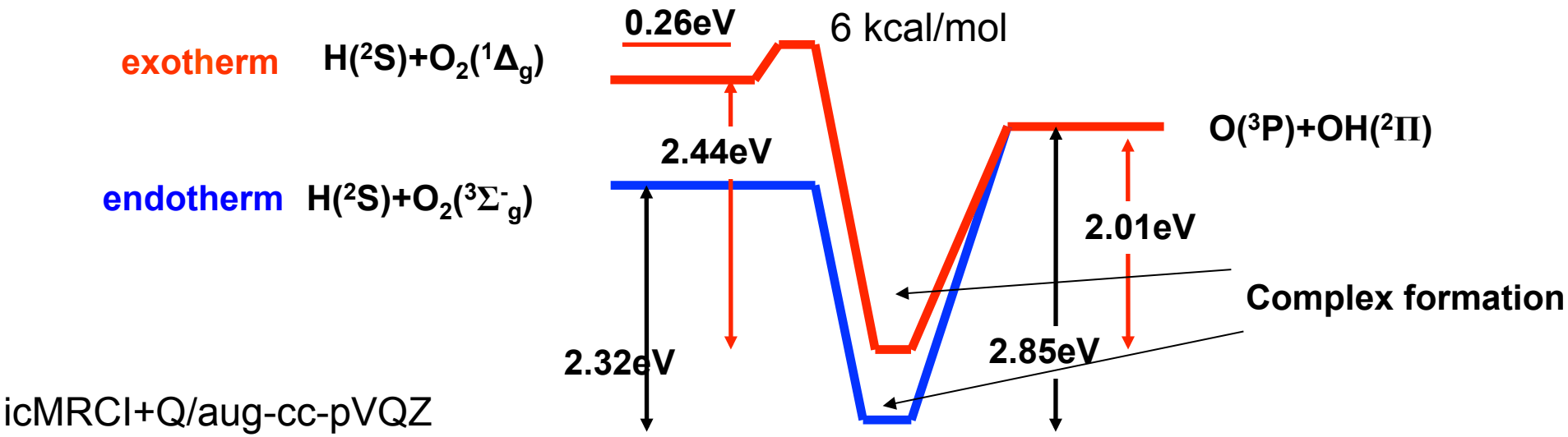
РАСЧЕТ УВЕЛИЧЕНИЯ СКОРОСТИ ВОДОРОДНО-КИСЛОРОДНОГО ПЛАМЕНИ ПРИ ДОБАВКАХ СИНГЛЕТНОГО КИСЛОРОДА

Басевич В. Я., Беляев А. А.

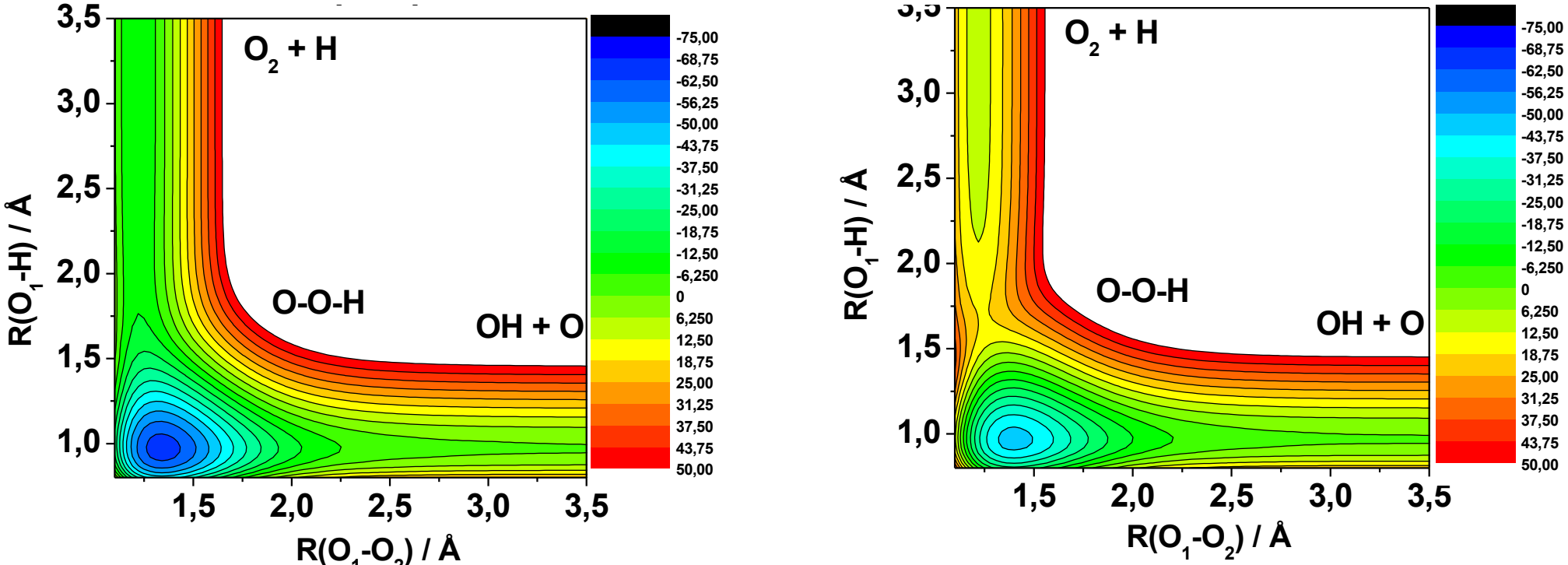
Реакция водорода с кислородом для газофазной кинетики является модельной [1], и поэтому все детали ее протекания имеют принципиальное значение. В опытах [2] было обнаружено ускоряющее влияние предварительной активации кислорода электрическим разрядом на скорость распространения пламени в бедных водородно-кислородных смесях в области низких давлений. Для объяснения наблюдаемого эффекта было сделано предположение о протекании во фронте пламени реакции между образующимся в разряде электронно-возбужденным синглетным кислородом и атомами водорода: $H+O_2(^1\Delta)=OH+O$. Концентрации других химически

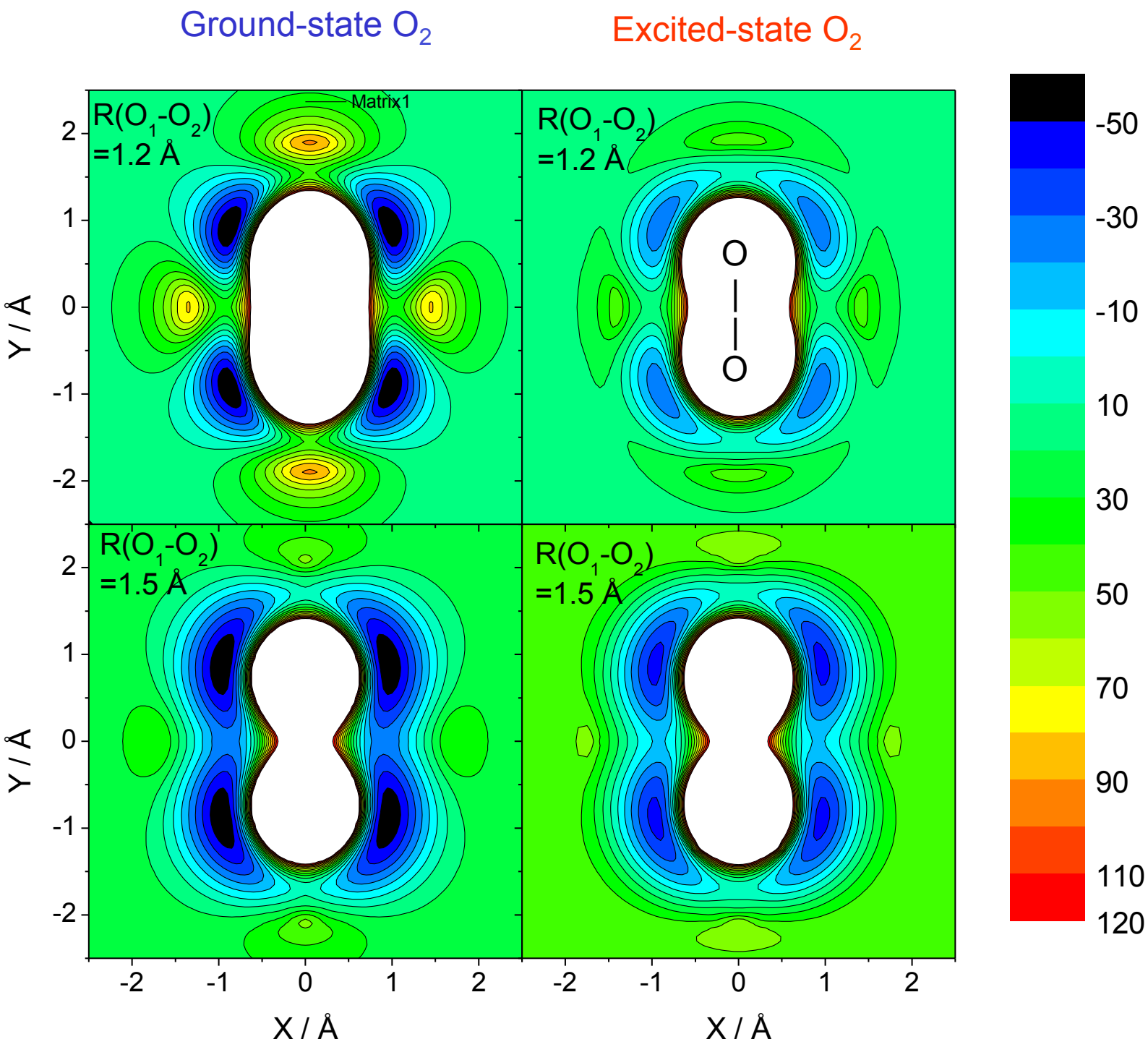
$H + O_2 \rightarrow O + OH$

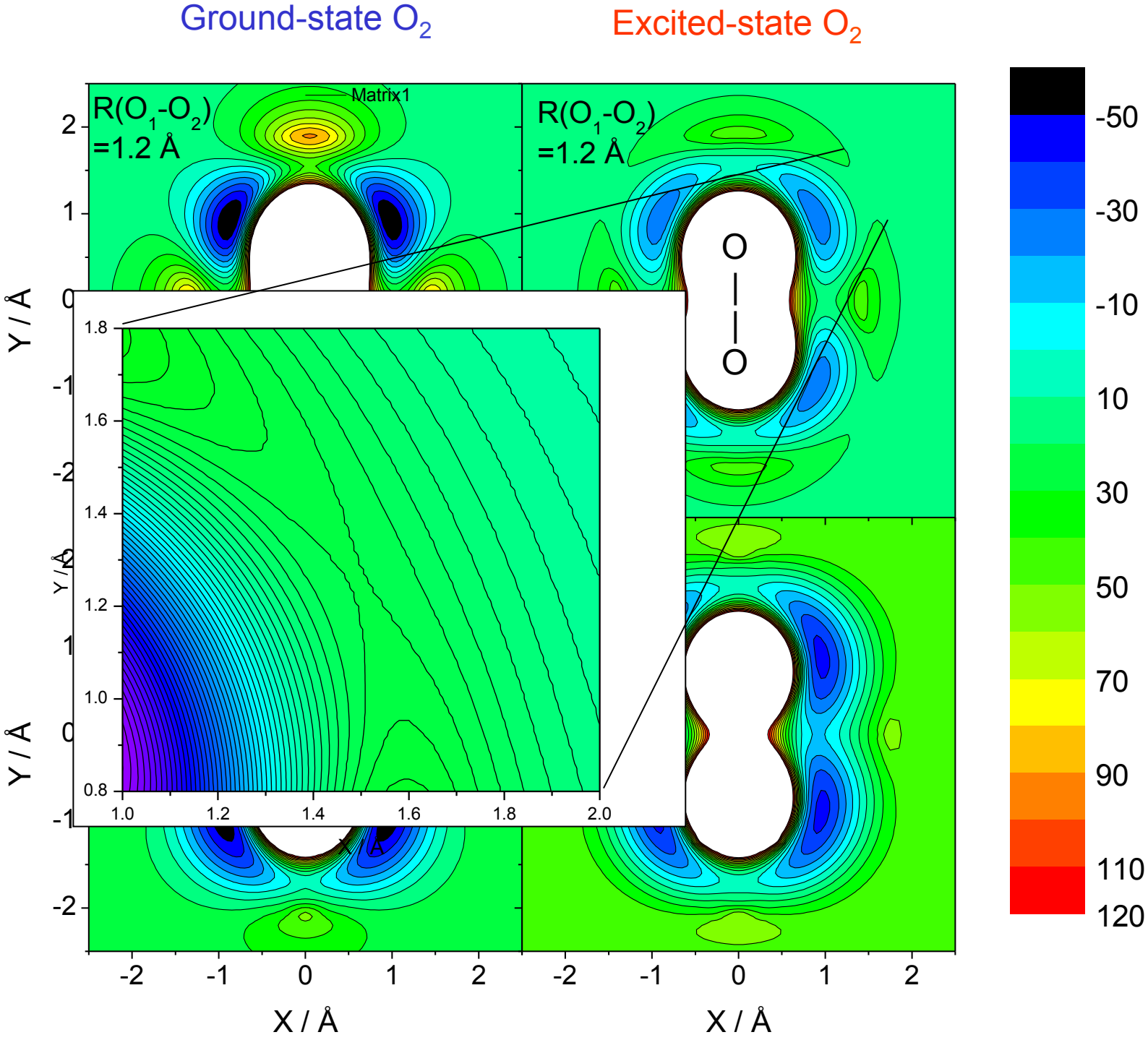
Comparison of the A″ and A′ potential energy surfaces



XXZLG Li, Xie, Dawes, Jasper, Ma, Guo JCP **133**, 144306 (2010)




Ground-state O_2
Excited-state O_2
Matrix1
$R(O_1-O_2)$ =1.2 Å
$R(O_1-O_2)$ =1.2 Å
O
O
$R(O_1-O_2)$ =1.5 Å
$R(O_1-O_2)$ =1.5 Å
Y / Å
X / Å
-50
-30
-10
10
30
50
70
90
110
120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-30
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10
30
50
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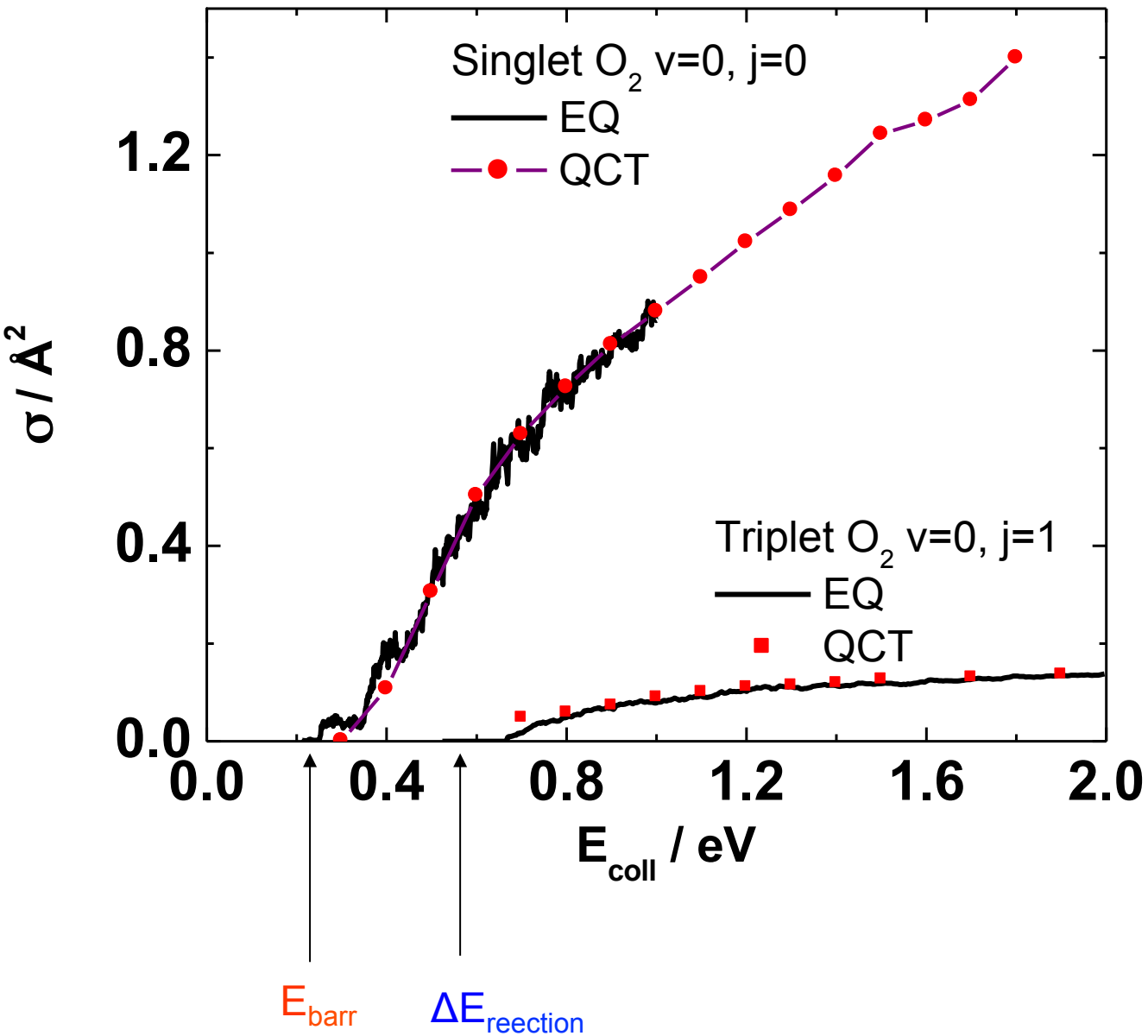
110
120

Reaction cross sections



Method:

GW-QCT
Standard QCT + Gauss-weighted product state analysis

Validation:

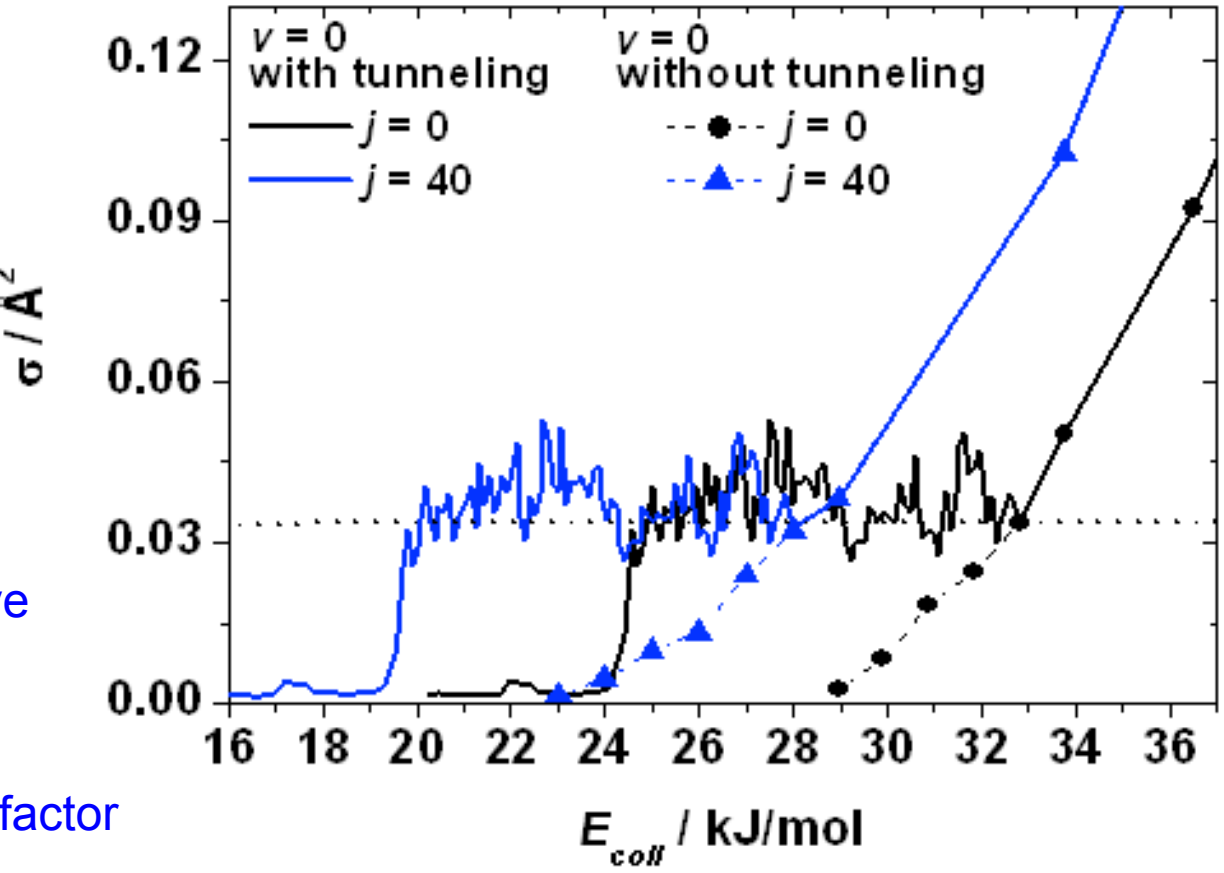
vs. EQ calculations of Hua Guo + coworkers $j(O_2)=0$ only

QCT works embarrassingly well

Thermal rate coefficients

QCT for
impact parameters up to 12 Å
$j(O_2)$ up to 65

Tunneling correction
1. Take the initial segment of the excitation function for $j(O_2)$=0 obtained in accurate quantum scatttering calculation (from Guo et al.)
2. replace the initial segment of the classical excitation function for $j(O_2)$>0 by the quantum mechanical segment derived above



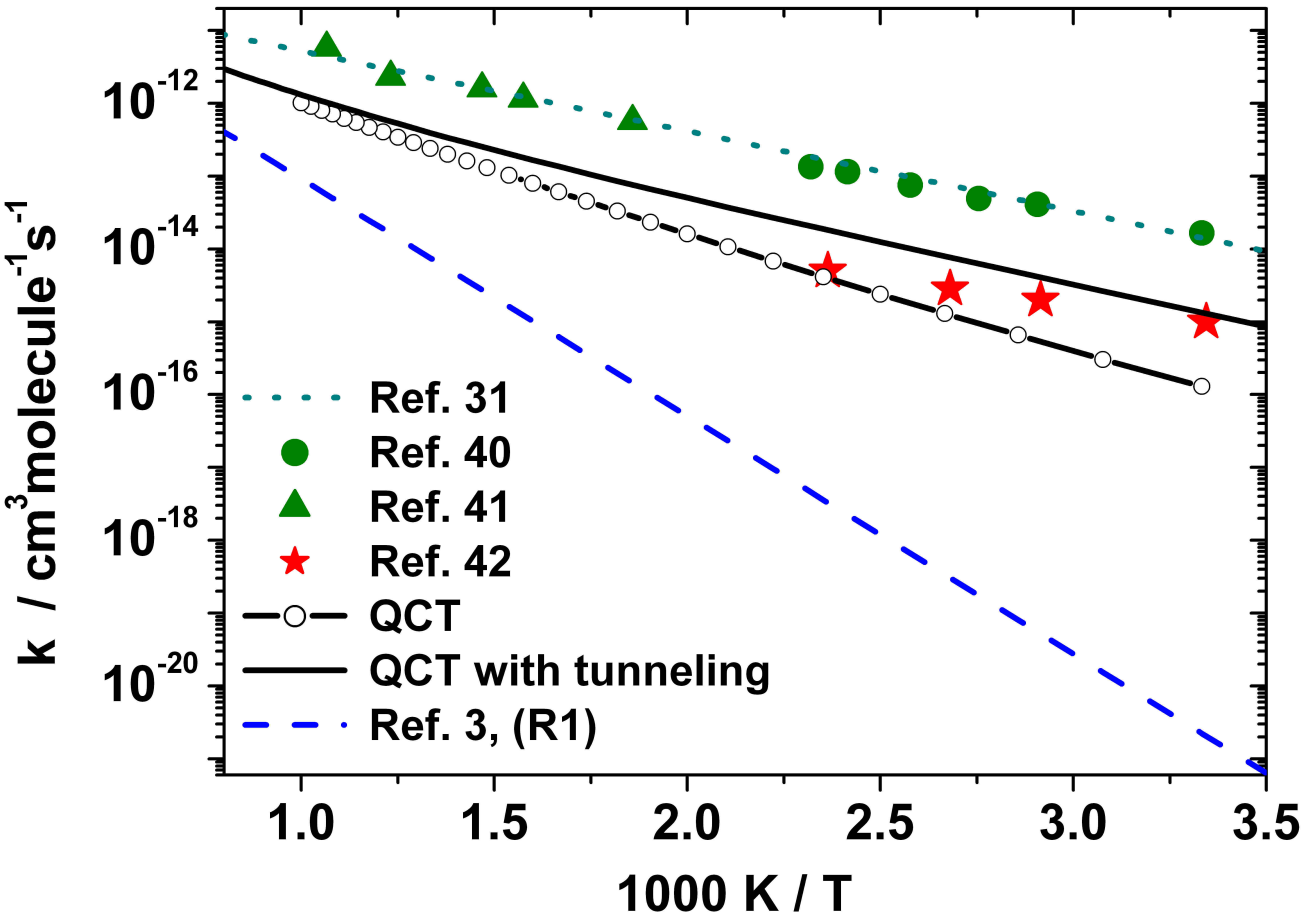
Tunneling enhances the rate by a factor of 10 at 300K and 5 at 500K

Thermal rate coefficients - comparison with experiments

Two kinds of experiment have been done for this reaction

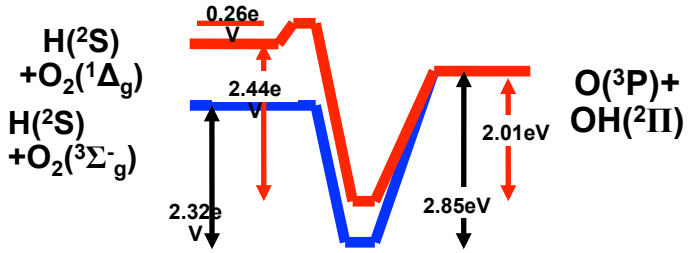
Basevich et al, Endo et al. ▲
rate probably includes reactive and nonreactive quenching of $O_2(^1\Delta_g)$
„old"

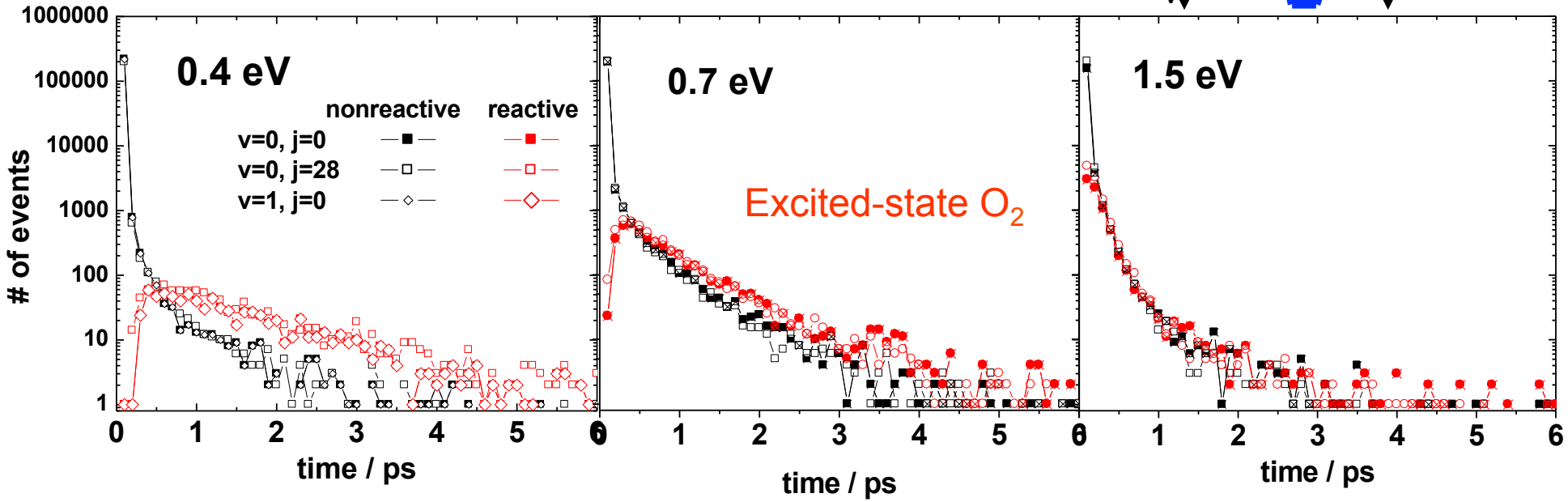
Hack et al. ★
pure reactive quenching
„more recent"

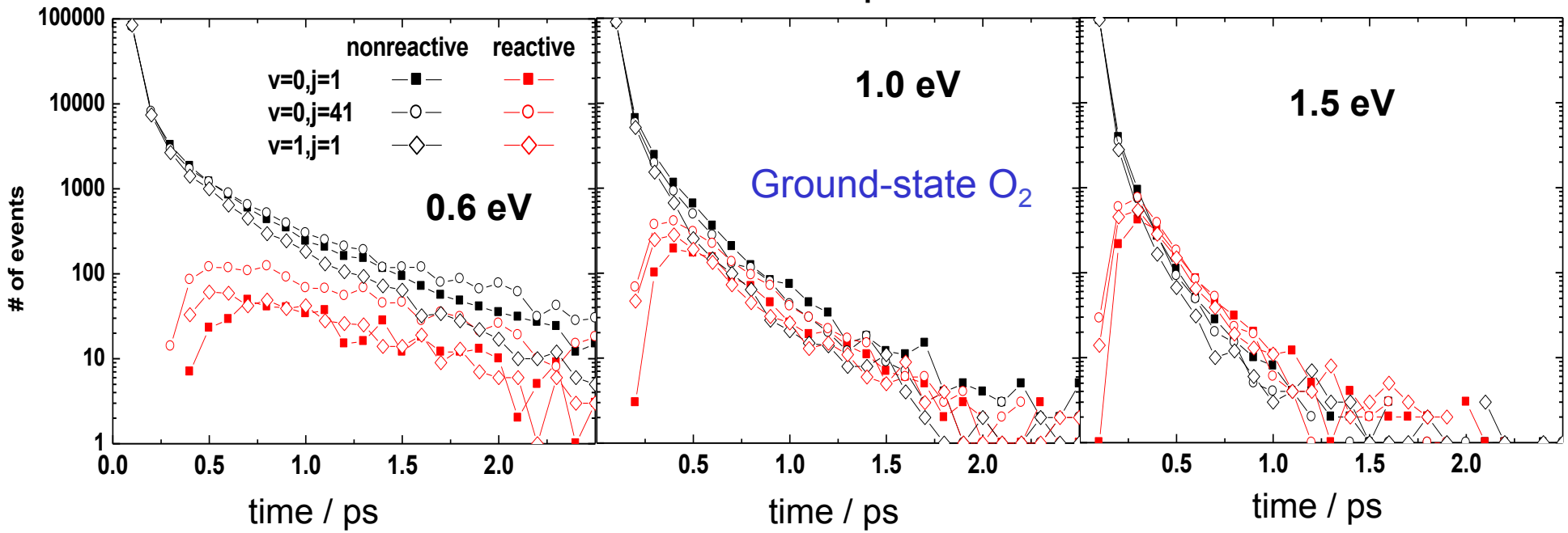


According to QCT calculations
-- Electronic excitation makes the reaction 6 orders of magnitude faster at room T, 10x faster at flame temperature
-- Old experiments very probably include reaction and electronic quenching
3. based on this assumption, electronic quenching is about 10x faster than reactive between 300K and 1000K

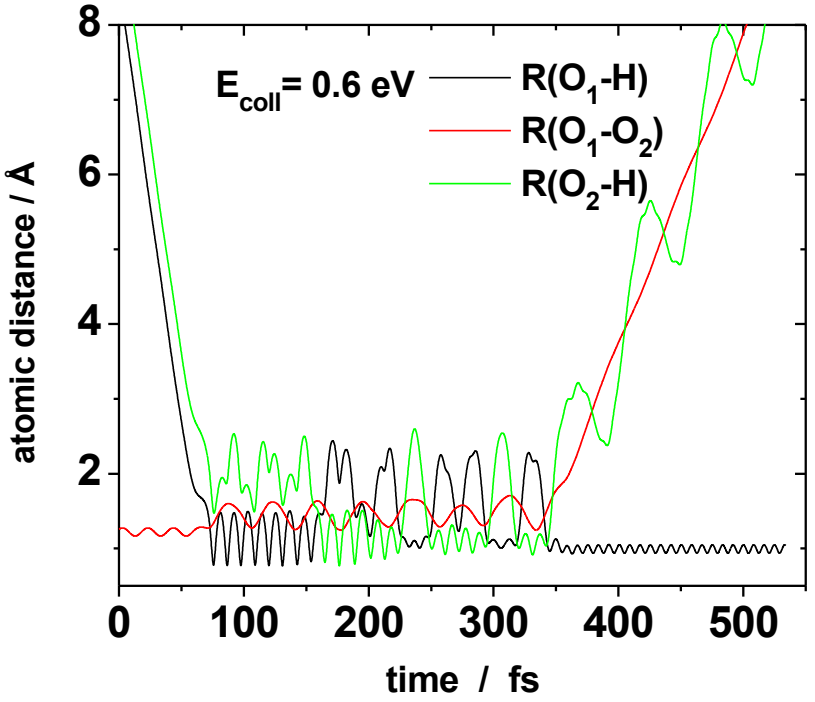
Lifetime distributions as a function of collision energy

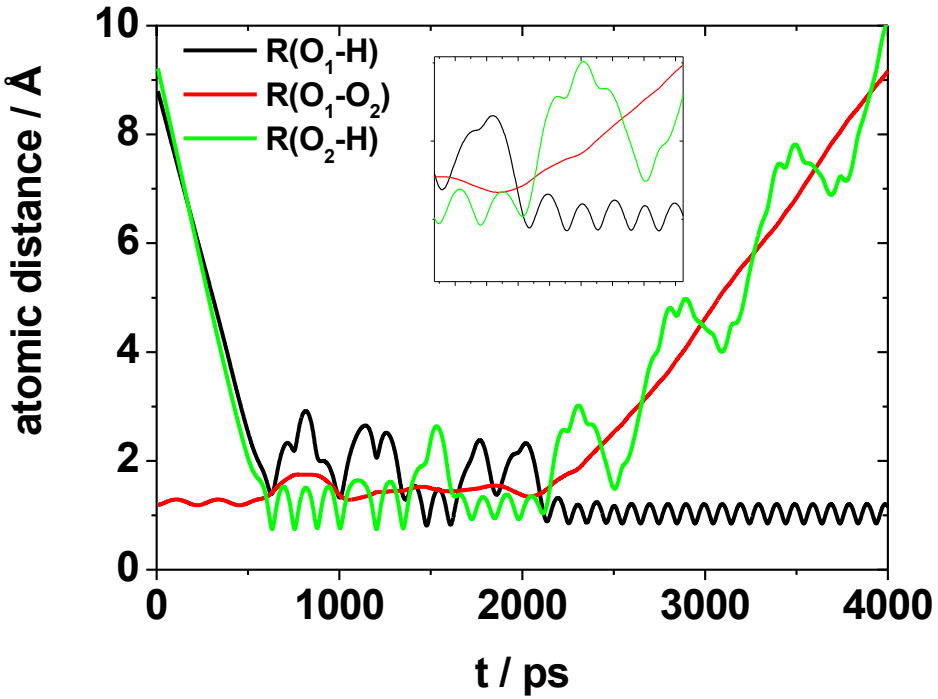






Isomerization within the complex

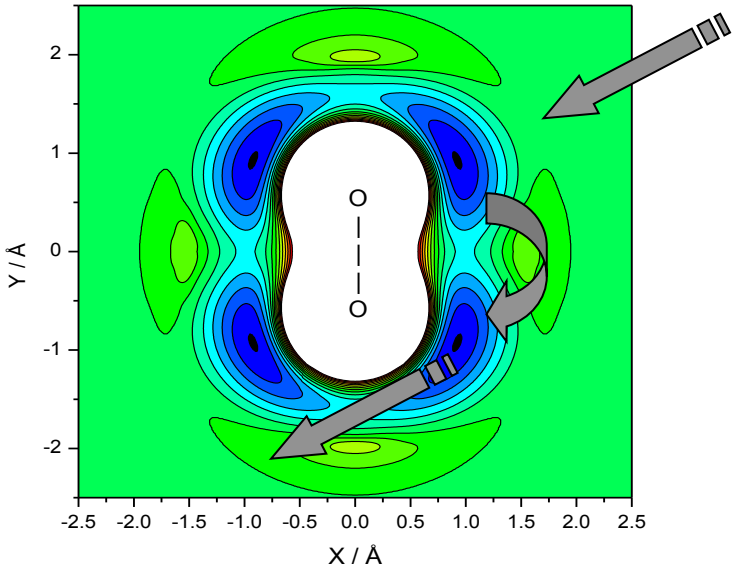




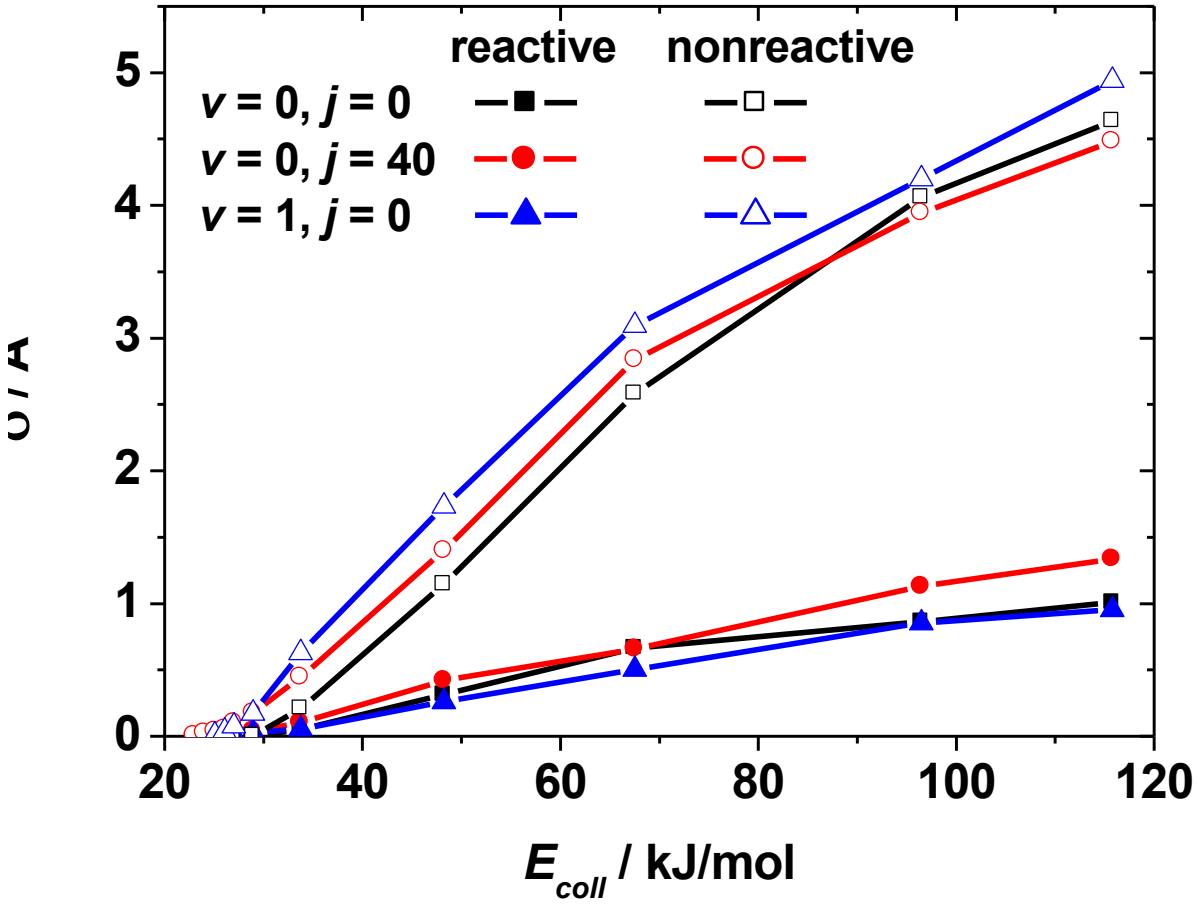
Excited O_2: 85%

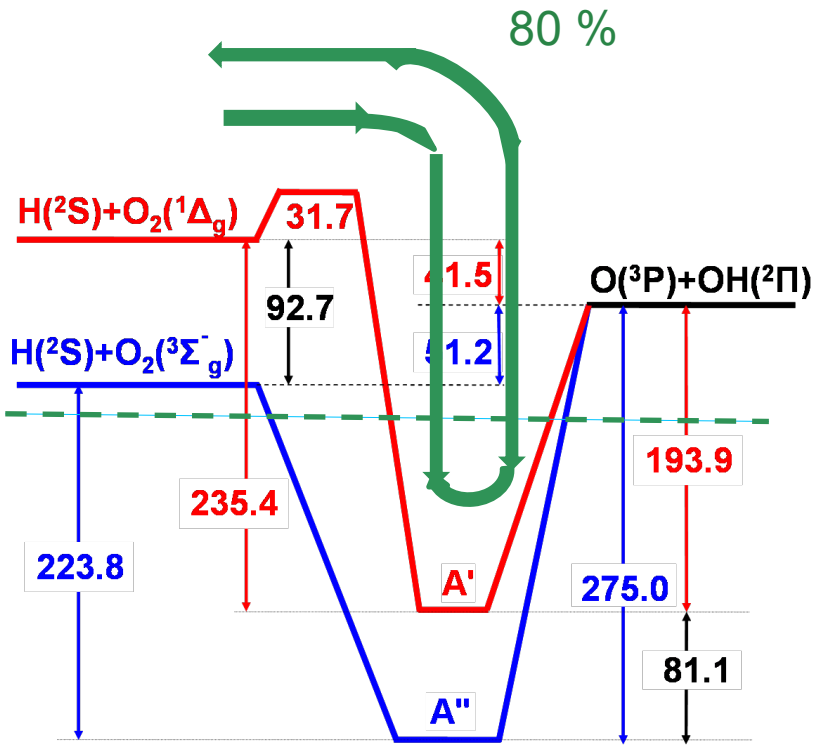
Ground-sate O_2: 80%

of reactive trajectories involve isomerization



Cross sections characterizing complex formation by H and $O_2(^1\Delta_g)$





Conditions for applicability of TST

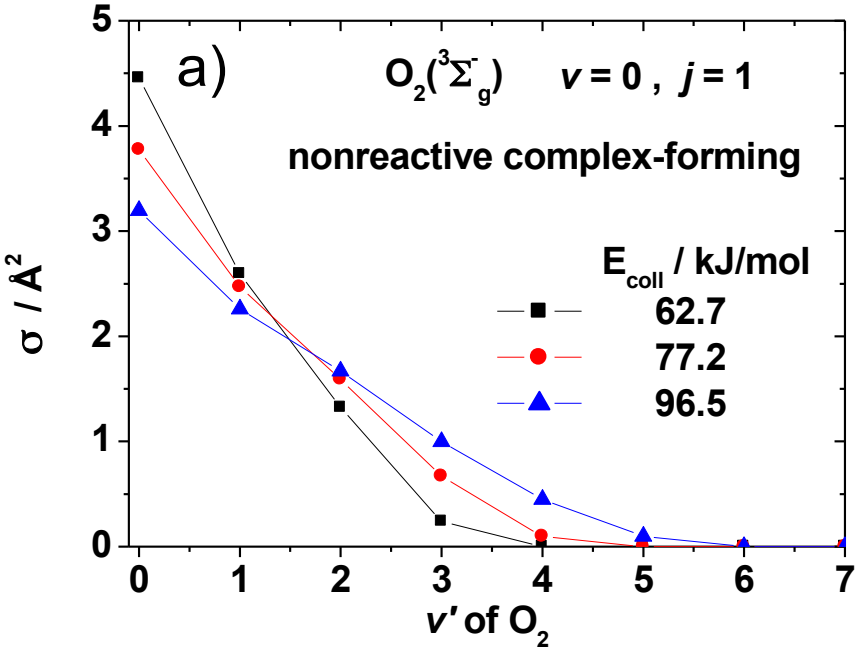
1 Statistical mechanics holds: energy is flowing freely among its degrees of freedom - long complex lifetime

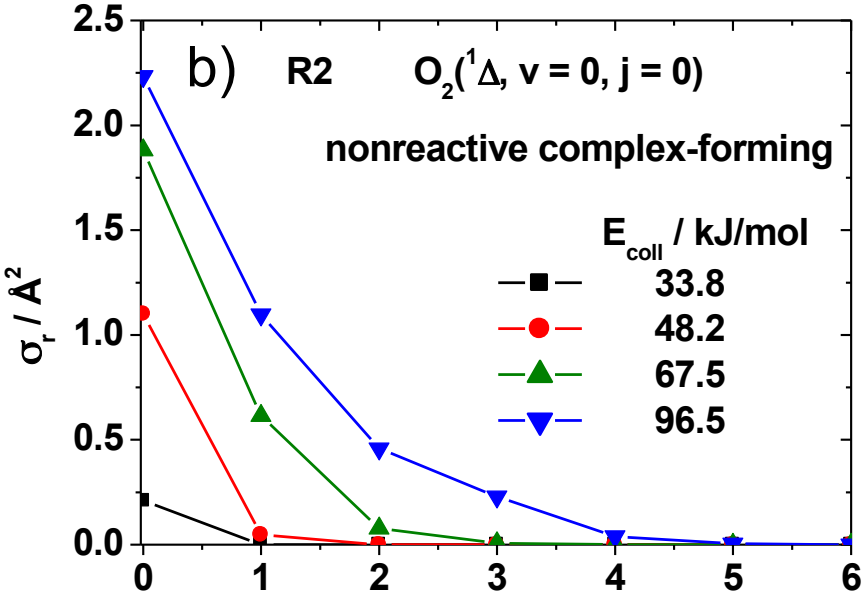
2 There is a dividing surface (near the barrier) that is crossed only once

The majority of trajectories return across the barrier after they passed from the reactant side

No dividing surface that is crossed only once can be designed

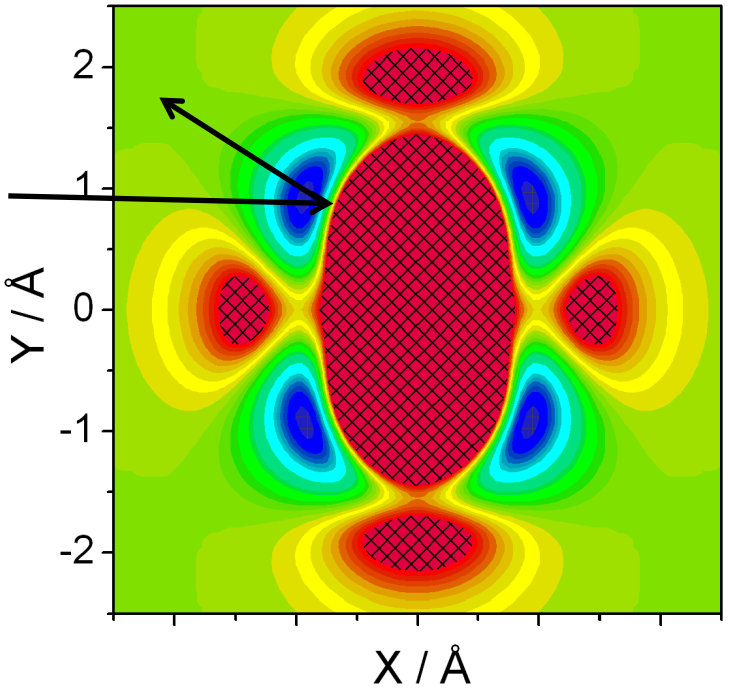
Inelastic complex-forming H - $O_2(^1\Delta_g)$ collisions





Trajectories reflected from the outer repulsive wall
– negligible energy transfer

Trajectories entering the potential well
– very efficient energy transfer
reflection from the inner repulsive wall



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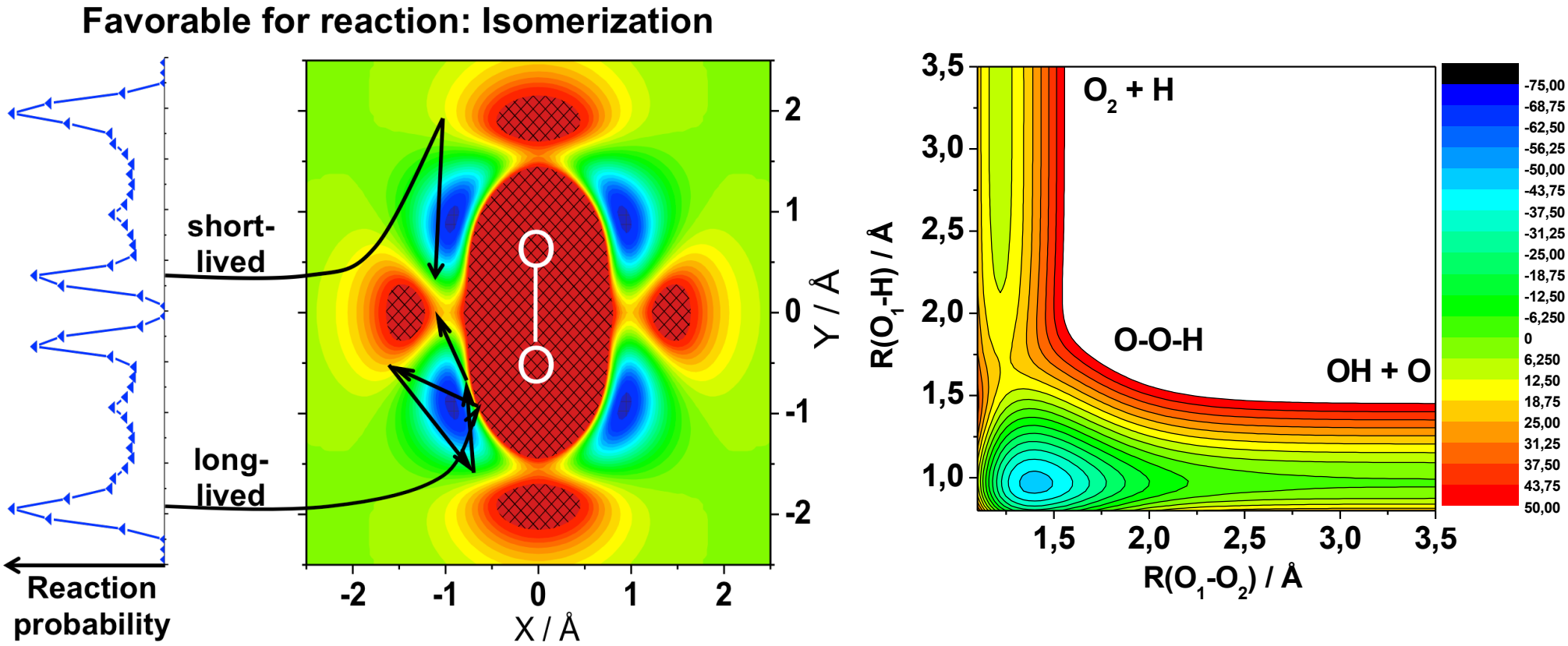

JPCA special issues

Argonne Trio Festschrift

P. Szabó, G. Lendvay, A Quasiclassical Trajectory Study of the Reaction of H Atoms with $O_2(^1\Delta_g)$, J. Phys. Chem. A, **119**, 7180−7189 (2015) **DOI:** 10.1021/jp510202r

Fifty Years of Chemical Reaction Dynamics

P. Szabó, G. Lendvay, Dynamics of Complex-Forming Bimolecular Reactions: A Comparative Theoretical Study of the Reactions of H Atoms with $O_2(^3\Sigma_g^-)$ and $O_2(^1\Delta g)$, J. Phys. Chem. A **119**, 12485–12497 (2015) **DOI:** 10.1021/acs.jpca.5b07938

The reaction of electronically excited O_2 with H atoms

- is much faster than that of triplet O_2
- can accelerate combustion
- QCT works very well for the reaction of both the triplet and singlet O_2
- reaction of the singlet is close to statistical at low,

  nonstatistical at high collision energy

- that of the triplet is not fully statistical
- failure of TST can be expected especially at high T
- singlet O_2 produces vibrationally excited OH, triplet O_2 does not