# Neutral-Neutral Reactions

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Panel Meeting
ISSI Bern
2nd December 2008

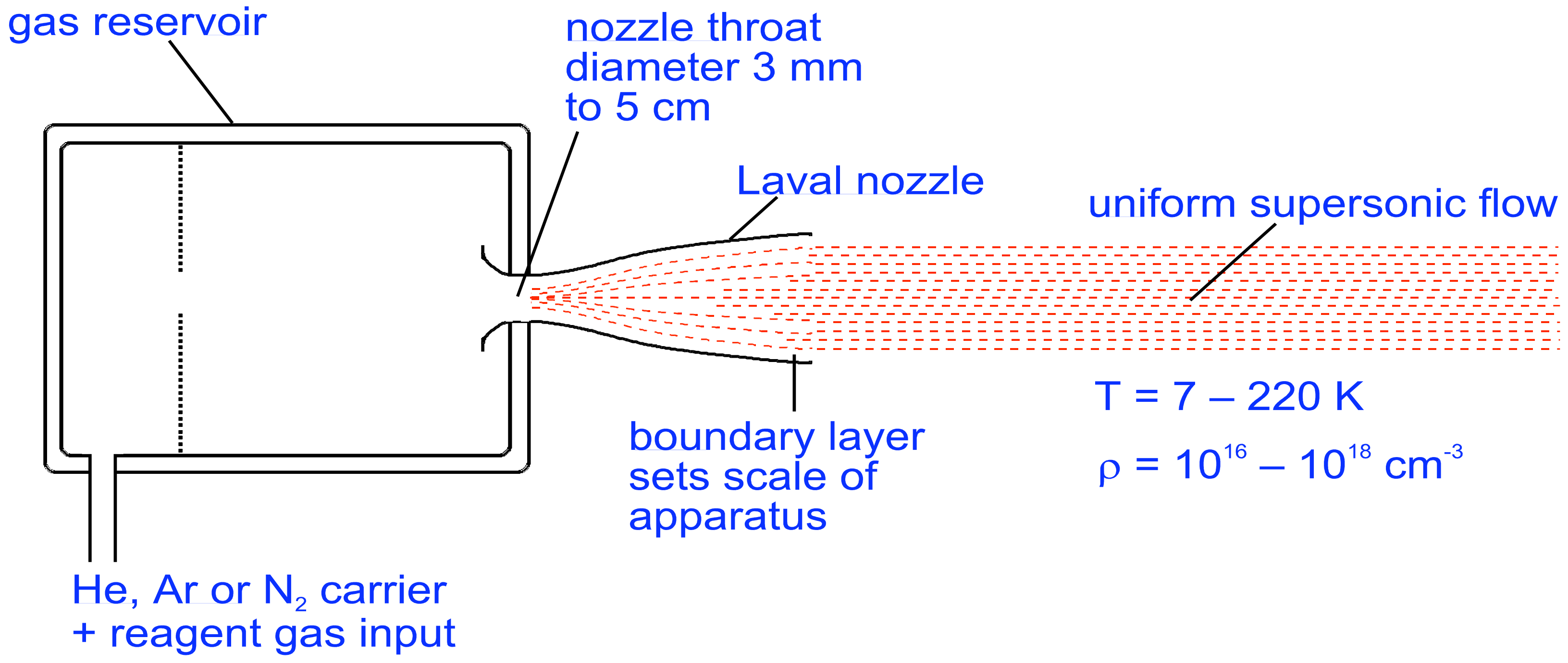
# Interstellar & Circumstellar Molecules

## (E. Herbst(2007) & www.astrochymist.net)

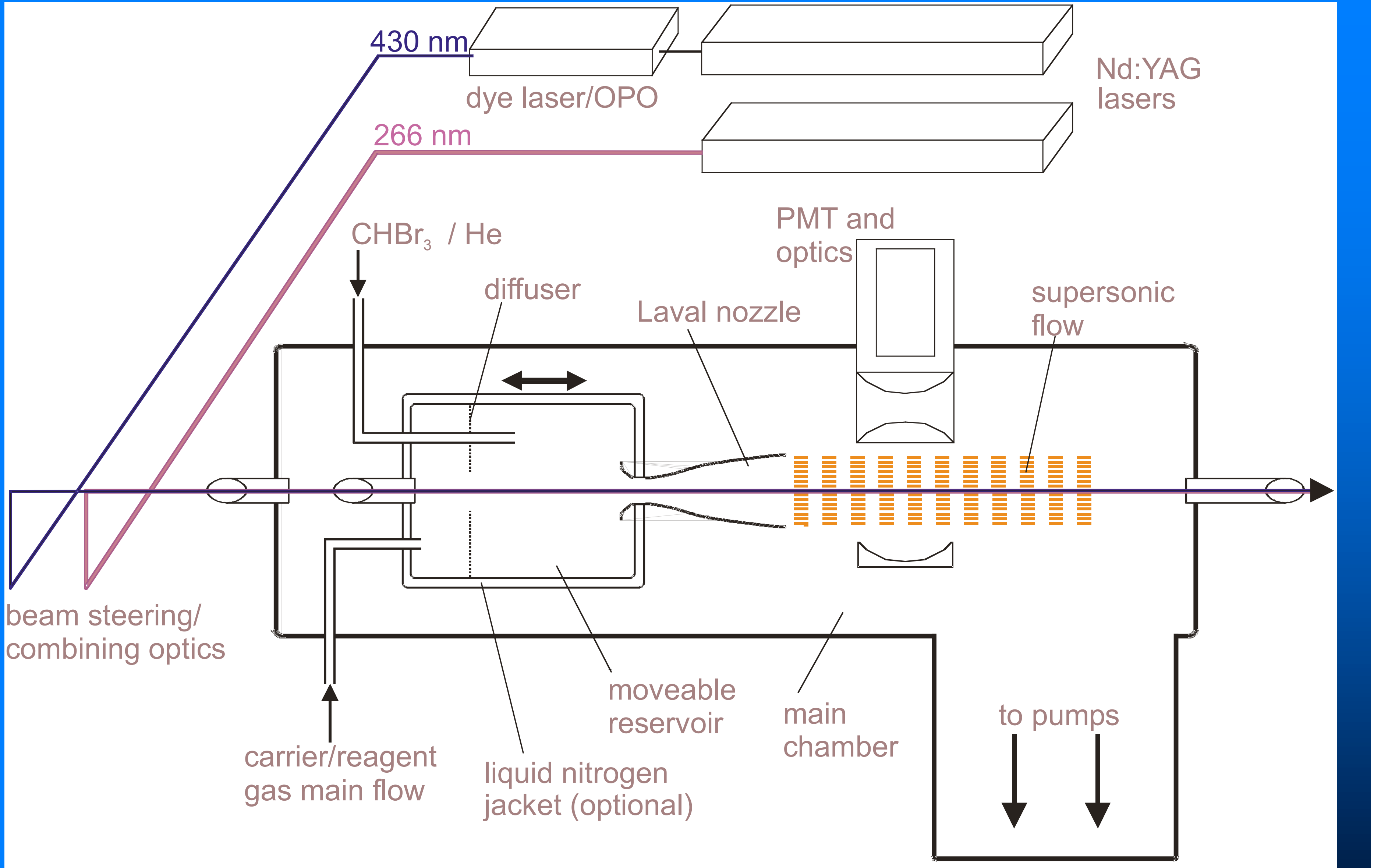
| N=2 | N=2 | N=3 | N=3 | N=4 | N = 5 | N = 6 | N = 7 | N = 8 | N = 9 | N = 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| $H_2$ | AlF | $H_3$+ | $C_3$ | $CH_3$ | $CH_4$ | $CH_3OH$ | $CH_3NH_2$ | $HCOOCH_3$ | $(CH_3)_2O$ | $(CH_3)CO$ |
| CH | AlCl | $CH_2$ | $C_2O$ | $NH_3$ | $SiH_4$ | $CH_3SH$ | $CH_3CCH$ | $CH_3C_2CN$ | $C_2H_5OH$ | $CH_3C_4CN$ |
| $CH^+$ | NaCl | $NH_2$ | $C_2S$ | $H_3O^+$ | $CH_2NH$ | $C_2H_4$ | $CH_3CHO$ | $HC_6H$ | $C_2H_5CN$ | $CH_3CH_2CHO$ |
| NH | KCl | $H_2O$ | $C_2P$ | $H_2CO$ | $H_2C_3$ | $CH_3CN$ | c-$CH_2OCH_2$ | $C_7H$ | $CH_3C_4H$ | $(CH_2OH)_2$ |
| OH | SiC | $H_2S$ | $CO_2$ | $H_2CS$ | *c*-$C_3H_2$ | $CH_3NC$ | $CH_2CHCN$ | $HOCH_2CHO$ | $C_8H$ | |
| SH | SiN | $C_2H$ | $N_2O$ | *l*-$C_3H$ | $H_2COH^+$ | $HC_2CHO$ | $HC_4CN$ | $CH_3COOH$ | $HC_6CN$ | |
| HF | SiO | HCN | OCS | *c*-$C_3H$ | $H_2CCN$ | $NH_2CHO$ | $C_6H$ | $H_2CCCHCN$ | $CH_3CHCH_2$ | |
| $C_2$ | SiS | HNC | $SO_2$ | HCCH | $H_2NCN$ | $HC_3NH^+$ | $H_2CCHOH$ | $H_2C_6$ | $CH_3CONH_2$ | |
| CN | PO | HCO | c-$SiC_2$ | $HCNH^+$ | $H_2CCO$ | $H_2C_4$ | $C_6H^-$ | $CH_2CHCHO$ | $C_8H^-$ | N = 11 |
| CO | SO | $HCO^+$ | SiCN | $H_2CN$ | HCOOH | $HC_4H$ | | $NH_2CH_2CN$ | | $HC_8CN$ |
| $CO^+$ | $SO^+$ | $HOC^+$ | SiNC | HCCN | $C_4H$ | $C_5H$ | | $C_2H_6$ | | $CH_3C_6H$ |
| $CF^+$ | FeO | HCP | AlNC | HNCO | $HC_2CN$ | $C_5N$ | | | | |
| CP | $N_2^+$ | HNO | MgCN | $HOCO^+$ | $HC_2NC$ | $C_5O$ | | | | N = 12 |
| CS | | $HN_2^+$ | MgNC | HNCS | $C_4Si$ | $C_5S$ | | | | $C_6H_6$ |
| NO | | $HCS^+$ | | $C_2CN$ | $C_5$ | | | | | |
| PN | | | N=4 | $C_3O$ | $C_4N$ | | | | | N = 13 |
| NS | | | $C_3N^-$ | $C_3S$ | CNCHO | | | | | $HC_{10}CN$ |
| | | | ? $PH_3$? | c-$SiC_3$ | $C_4H^-$ | | | | | |

# CRESU Technique for Ultra-Low Temperatures (B R Rowe)

- Isentropic expansion of gas through Laval nozzle
- Frequent collisions maintain thermal equilibrium
- Each nozzle provides a supersonic flow uniform in temperature, density and velocity



**Isentropic Expansion and Uniform Supersonic Flow**



**Schematic diagram of combined PLP-LIF / CRESU apparatus**

# The CRESU method – ‘Pros and Cons’

- Rapid expansion and lack of collisions with walls mean super-saturated conditions can be obtained
- Only method for studying thermal rates of molecular processes over a range of very low temperatures (down to ca 13 K)

- New nozzle for each temperature

- Can only reach 13 K
- Solution: development of new pulsed version of the CRESU method

- Reaction products and branching ratios
- Solution: observation of products by IR diode laser spectroscopy ?

- Very large gas flows make experiments difficult where co-reagents require synthesis
- Solution: pulsed Laval nozzles

- Difficult to study reactions between unstable radicals: e.g. $O(^3P) + OH \rightarrow O_2 + H$
- Solution: produce both radicals by pulsed photolysis

# Neutral-Neutral Reactions: Summary of Experiments

- Canosa *et al*. list 93 reactions: 73 studied in continuous CRESU (Rennes, Birmingham, Bordeaux); 20 in pulsed CRESU (Arizona, Berkeley, Göttingen)

- Continuous CRESU reach as low as 13 K; pulsed CRESU to 53 K

- **Radicals**: B($^2P_J$), C ($^3P_J$) , O ($^3P_J$), Al ($^2P_J$), and Si ($^3P_J$)
  CN, OH, CH, NH, $C_2$(X), $C_2$(a), $C_2H$, $C_4H$

- **Molecules**: alkenes/alkynes (52); saturated molecules (19); radicals (15); aromatics (2); others (5)

| Reactions | Concerned species | Person(s) in charge |
|---|---|---|
| $C + C_3O \rightarrow C_3 + CO$ | $C_3O$ | IWMS & J-CL |
| $C + OCN \rightarrow CO + CN$ | OCS | IWMS & J-CL |
| $H + CH_2 \rightarrow CH + H_2$ | CH | IWMS & J-CL |
| $O + CN \rightarrow CO + N$ | CN | IWMS & J-CL |
| $N + CN \rightarrow C + N_2$ | CN | IWMS & J-CL |
| $O + C_2 \rightarrow CO + C$ | $C_2$ | IWMS & J-CL |
| $O + C_2H \rightarrow CO + CH$ | $C_2H$ | J-CL (& IWMS) |
| $O + C_3H \rightarrow CO + C_2H$ | $C_3H$ | J-CL (& IWMS) |
| $N + NO \rightarrow N_2 + O$ | NO | J-CL (& IWMS) |
| $CN + NH_3 \rightarrow NH_2CN + H$ | $NH_2CN$ | IWMS (& Dahbia Talbi, Paul Seakins) |

| Reactions | Concerned species | Person(s) in charge |
|---|---|---|
| $O + NH \rightarrow NO + H$ | | IWMS |
| $O + NH_2 \rightarrow HNO + H$ | | IWMS |
| $O + HNO \rightarrow NO + OH$ | | IWMS |
| $N + C_2N \rightarrow CN + CN$ | | IWMS |
| $N + C_4N \rightarrow CN + C_3N$ | | IWMS |
| $O + C_3N \rightarrow CO + C_2N$ | | IWMS |
| $N + C_3 \rightarrow CN + C_2$ | | IWMS |
| $N + C_2H \rightarrow CN + CH$ | | IWMS |
| $CN + HCCCN \rightarrow NCCCCN + H$ | | IWMS |

| Reactions | Comments |
|---|---|
| $CN + NH_3 \rightarrow NH_2CN + H$ | Rate constants for overall reaction measured down to 13 K. No info on branching ratio (→ $NH_2CN + H$ to $HCN + NH_2$). Dahbia has carried out calculations. Paul Seakins to do experiments (at room *T*). |
| $N + NO \rightarrow N_2 + O$ | Numerous experiments at room *T* and above. New experiments planned in Bordeaux for lower *T* |
| $H + CH_2 \rightarrow CH + H_2$ | Quite extensive exptl measurements on this reaction (and its reverse) at room *T* and above. |
| $O + CN \rightarrow CO + N$ | Several room *T* measurements. Little on *T*-dependence (unlikely to be strong) |
| $N + CN \rightarrow C + N_2$ | There are two experimental measurements: one at room *T*, one suggests a very bizarre *T*-dependence' |
| $O + C_2H \rightarrow CO + CH$ | 2 measurements from same group giving rather different values – one gives *T*-dependence |
| $C + C_3O \rightarrow C_3 + CO$ | No measurements available. Estimate based on comparison of reactions of $C(^3P)$ with alkenes |
| $C + OCN \rightarrow CO + CN$ | No measurements available. |
| $O + C_2 \rightarrow CO + C$ | No measurements available, apart from one at 8000 K!! |
| $O + C_3H \rightarrow CO + C_2H$ | No measurements; same value adopted as for $O + C_2H$ |

# ‘Rationale’ for estimating rate constants

- If room *T* rate constant is available, is it >> than $10^{-11}$ cm$^3$ s$^{-1}$? If so, *k*(10 K) is probably of the order of $10^{-10}$ cm$^3$ s$^{-1}$
- If reaction is one between two radicals, a factor involving the electronic degeneracies is assumed to lower the rate constant from simple collision value (i.e., reaction does not occur on all PES’s)

# Radiative Association

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| Reactions | Concerned species | Person(s) in charge |
|---|---|---|
| $C + H_2 \rightarrow CH_2 + h\nu$ | 73 ! | J-CL (& IWMS) |
| $CH_3^+ + H_2 \rightarrow C_2H_5^+ + h\nu$ | 18 | DG (& IWMS) |
| $C^+ + H_2 \rightarrow CH_2^+ + h\nu$ | $C_3$ | DG (& IWMS) |
| $C_2H_2^+ + H_2 \rightarrow C_2H_4^+ + h\nu$ | $C_2H_2O$; $C_2H_3$; $C_2H_2^+$;<br>$C_2HO^+$; $C_2H_2N^+$; $H_3C_3$+ | DG (& IWMS) |
| $CH_3^+ + CO \rightarrow C_2H_3O^+ + h\nu$ | $C_2H_2O$; $C_2H_3O^+$ | DG |
| $C_3H^+ + H_2 \rightarrow C_3H_3^+ + h\nu$ | $C_3H_2$; $H_2C_3$; $C_3H^+$;<br>$C_3H_2^+$; $C_3H_3^+$; $H_3C_3$+ | DG |
| $HCO^+ + H_2O \rightarrow CH_3O_2^+ + h\nu$ | $CH_2O_2$ | DG |
| $S + CO \rightarrow OCS + h\nu$ | OCS | J-CL (& IWMS) |
| $Si^+ + H_2 \rightarrow SiH_2^+ + h\nu$ | HNSi | DG (?) |

# Radiative Association: Direct Experiments

- Experiments are possible in case of ion + neutral – down to 10 K with $H_2$ as neutral
- Results obtained using 22-pole ion trap reported by Dieter Gerlich in mid 1990's for $C^+ + H_2$, $CH_3^+ + H_2$, $C_2H_2^+ + H_2$. These are the basis of the recommendations on the data sheets.
- Experiments employed both *p*-$H_2$ and *n*-$H_2$. Form of $H_2$ in dense clouds?
- No experiments possible on neutral-neutral reactions: e.g. $C + H_2$

| Reactions | Concerned species | Person(s) in charge |
|---|---|---|
| $C + H_2 \rightarrow CH_2 + h\nu$ | 73 ! | J-CL (& IWMS) |
| $CH_3^+ + H_2 \rightarrow C_2H_5^+ + h\nu$ | 18 | DG (& IWMS) |
| $C^+ + H_2 \rightarrow CH_2^+ + h\nu$ | $C_3$ | DG (& IWMS) |
| $C_2H_2^+ + H_2 \rightarrow C_2H_4^+ + h\nu$ | $C_2H_2O$; $C_2H_3$; $C_2H_2^+$; $C_2HO^+$; $C_2H_2N^+$; $H_3C_3$+ | DG (& IWMS) |
| $CH_3^+ + CO \rightarrow C_2H_3O^+ + h\nu$ | $C_2H_2O$; $C_2H_3O^+$ | DG |
| $C_3H^+ + H_2 \rightarrow C_3H_3^+ + h\nu$ | $C_3H_2$; $H_2C_3$; $C_3H^+$; $C_3H_2^+$; $C_3H_3^+$; $H_3C_3$+ | DG |
| $HCO^+ + H_2O \rightarrow CH_3O_2^+ + h\nu$ | $CH_2O_2$ | DG |
| $S + CO \rightarrow OCS + h\nu$ | OCS | J-CL (& IWMS) |
| $Si^+ + H_2 \rightarrow SiH_2^+ + h\nu$ | HNSi | DG (?) |

# Collisional and Radiative Association

‘low pressure conditions’:

$$\begin{array}{ccc} & k_d & \\ A\ +\ B & \leftrightarrows & (AB)^{\dagger} \\ & k_a & \downarrow + M \\ & & \downarrow\ k_M[M] \\ & & \downarrow \\ & & AB \end{array}$$

‘*very* low pressure conditions’:

$$\begin{array}{ccc} & k_d & \\ A\ +\ B & \leftrightarrows & (AB)^{\dagger} \\ & k_a & \downarrow \\ & & \downarrow\ k_{rad} \\ & & \downarrow \\ & & AB \end{array}$$

$$k_M{}^{o} \;=\; k_M[M]\,(k_a / k_d)$$

$$k_{RA}{}^{o} \;=\; k_{rad}\,(k_a / k_d)$$

$$k_{RA}{}^{o} \;=\; (k_M{}^{o} / [M])\,(k_{rad} / k_M)$$

*T*-dependence: of $(k_{rad} / k_M)$ slight; of $k_{RA}{}^{o}$ and $(k_M{}^{o} / [M])$ similar

# $C + H_2 \rightarrow CH_2 + h\nu$ – an important test case

- Husain and co-workers have measured the third-order rate constant for association at 300 K: $k_{He}°$ = 6.9 × $10^{-32}$ [He] $cm^3\ s^{-1}$. Given a reasonable estimate for $k_{He}$ of 1.0 × $10^{-11}$ $cm^3\ s^{-1}$, we find ($k_a$ / $k_d$) = 6.9 × $10^{-22}$ $cm^3$, and therefore:

  $$k_{RA} = k_{rad}\,(k_{ass} / k_{diss}) = k_{rad} \times 6.9 \times 10^{-22}\ cm^3$$

- The vibrational modes of $CH_2$ have low transition probabilities: estimates yield $k_{rad}$ = 140 $s^{-1}$ – so

  $$k_{RA} \approx 10^{-19}\ cm^3\ s^{-1} \text{ at 300 K}$$

  (J-CL suggests a value 5 times less)

# $C + H_2 \rightarrow CH_2 + h\nu$ – some more ‘thoughts’

- Harding et al have calculated *ab initio* PES’s for $CH_2$. They consider that $CH_2(X^3B_1)$ is formed via a transition from a weakly bound $^3A_2$ state that correlates with $C(^3P) + H_2$. This may mean that internal states close to the dissociation limit have mixed $X^3B_1$ and $^3A_2$ character and that *electronic transitions* from these levels to low-lying levels in $X^3B_1$ may cause stabilisation

- A possible approach is to vary the radiative association rate coefficient between wide limits to find the ‘best’ values by comparing predicted and observed abundances

- Another possibility is that theory explores the possibility that I suggest.

# ISSI Meeting: Questions to be addressed

- Assumption: emphasis mainly on chemistry in ‘cold cores’ of dense ISC’s
- Errors in rate coefficients measured at low temperatures
- Estimates of rate coefficients at low temperatures from data at higher temperatures
- Estimates where there are no measurements of rate coefficients
- Products of reactions?

# Categories of Reaction

- **Ion-Molecule Reactions**
  - (a) ions + non-polar molecules
  - (b) ions + polar molecules

- **Neutral-Neutral Reactions**
  - (a) radicals + molecules
  - (b) radicals + radicals

- **Radiative Association**

**{electron-molecule processes}** X

# Caveats and Acknowledgements

- **Kinetic experiments measure rate coefficients but rarely products or branching ratios – which are equally important in models**

- **Reactants for reactions in ISM may not be in LTE – local thermodynamic equilibrium**

- **This presentation leans heavily on articles by Canosa *et al* and by Gerlich in**

  ***Low Temperatures and Cold Molecules***

  **ed. IWMS to be published by World Scientific in 2008**

# Reactions of Ions with Non-Polar Molecules

- ‘Langevin model’ assumes central potential (in cgs):

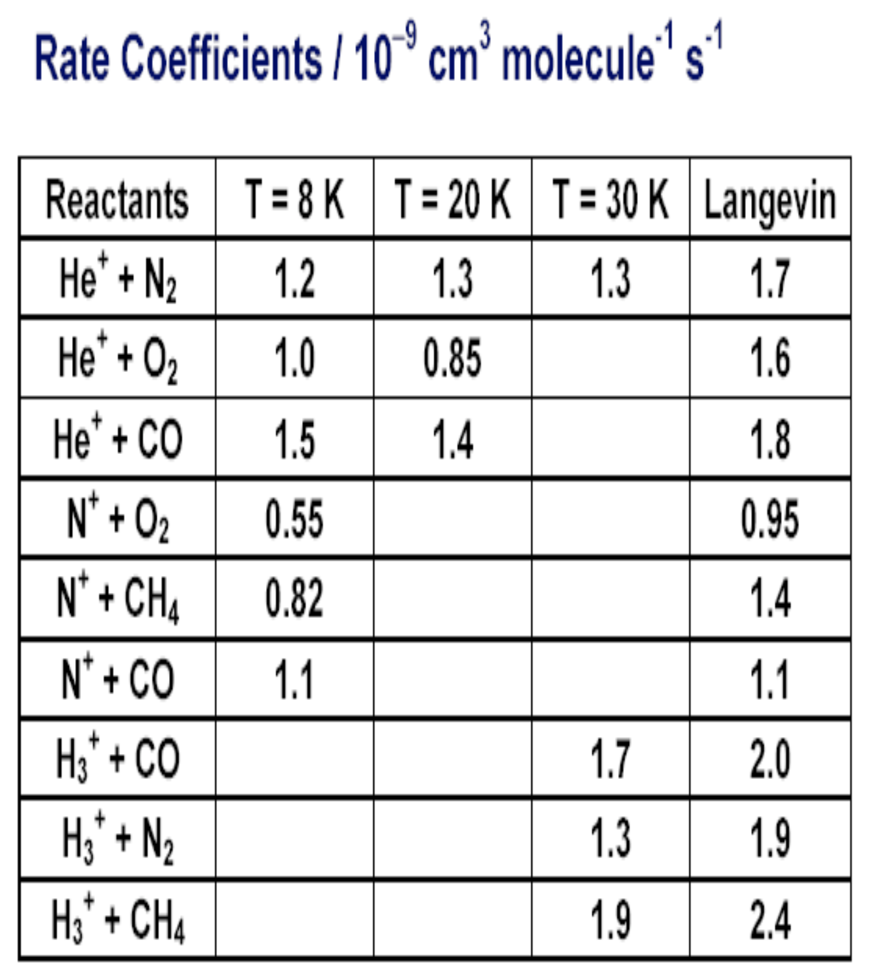
$$V(R_{AB}) = -\alpha\, q^2 / 2\, R_{AB}{}^4$$

- Leads to

$$k(T) = 2\pi q\, (\alpha/\mu)^{1/2}$$

- Model predictions borne out by experiment

- No apparent influence of quadrupole or non-spherical polarisability
- Possible effects of fine-structure (spin-orbit) states



Rate Coefficients / $10^{-9}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

| Reactants | T = 8 K | T = 20 K | T = 30 K | Langevin |
|---|---|---|---|---|
| $He^+ + N_2$ | 1.2 | 1.3 | 1.3 | 1.7 |
| $He^+ + O_2$ | 1.0 | 0.85 | | 1.6 |
| $He^+ + CO$ | 1.5 | 1.4 | | 1.8 |
| $N^+ + O_2$ | 0.55 | | | 0.95 |
| $N^+ + CH_4$ | 0.82 | | | 1.4 |
| $N^+ + CO$ | 1.1 | | | 1.1 |
| $H_3^+ + CO$ | | | 1.7 | 2.0 |
| $H_3^+ + N_2$ | | | 1.3 | 1.9 |
| $H_3^+ + CH_4$ | | | 1.9 | 2.4 |

# Comparison of *T*-dependence: non-polar *versus* polar molecules

△,▲: $N^+ + O_2$

○,●: $He^+ + N_2$

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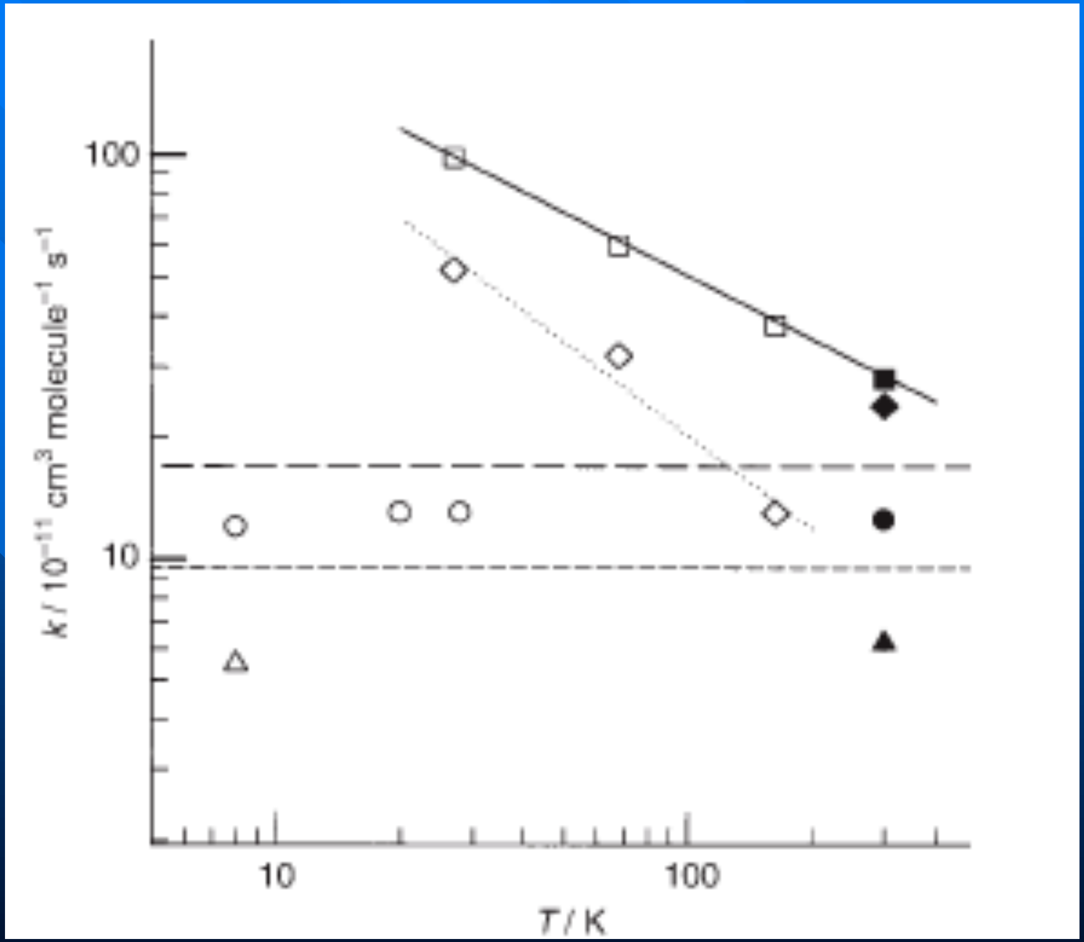
□,■: $N^+ + H_2O$

◇◆: $N^+ + NH_3$

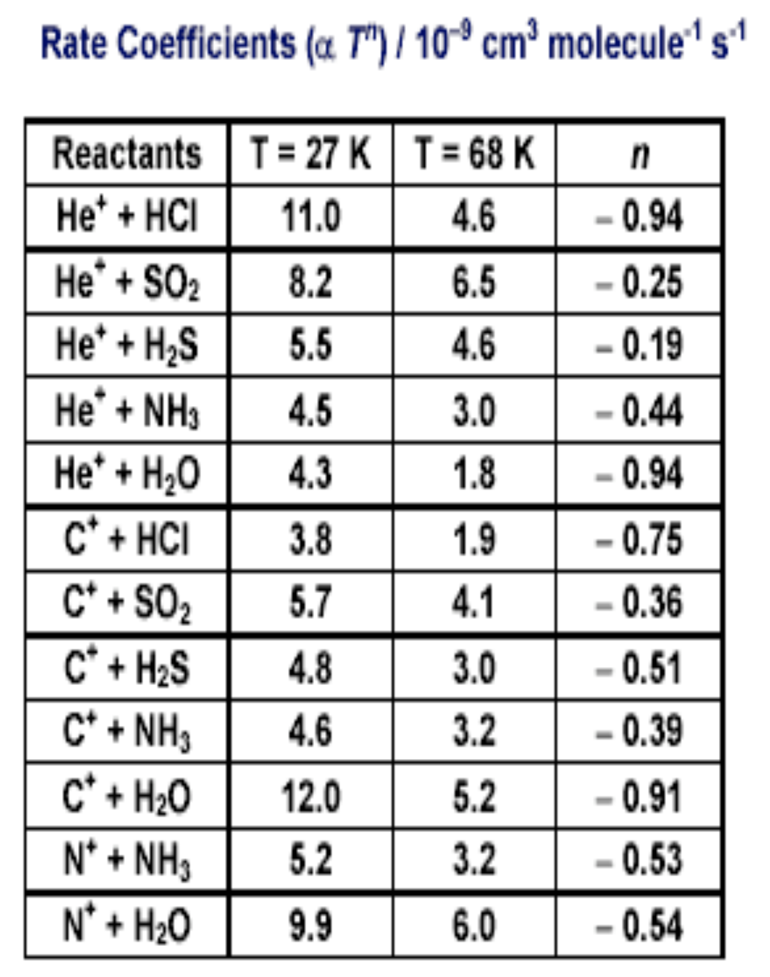


# Reactions of Ions with Polar Molecules

- Potential now depends on orientation:

$$V(\mathrm{R_{AB}}) = -\,\alpha\, q^2 / 2\,\mathrm{R_{AB}}^4 \\ -\,q\,\mu_D \cos\theta / 2\,\mathrm{R_{AB}}^2$$

- Theory (Bowers, Troe, Clary, etc) based on ‘capture’ – suggests *k*(*T*) depends on rotational state of reactants



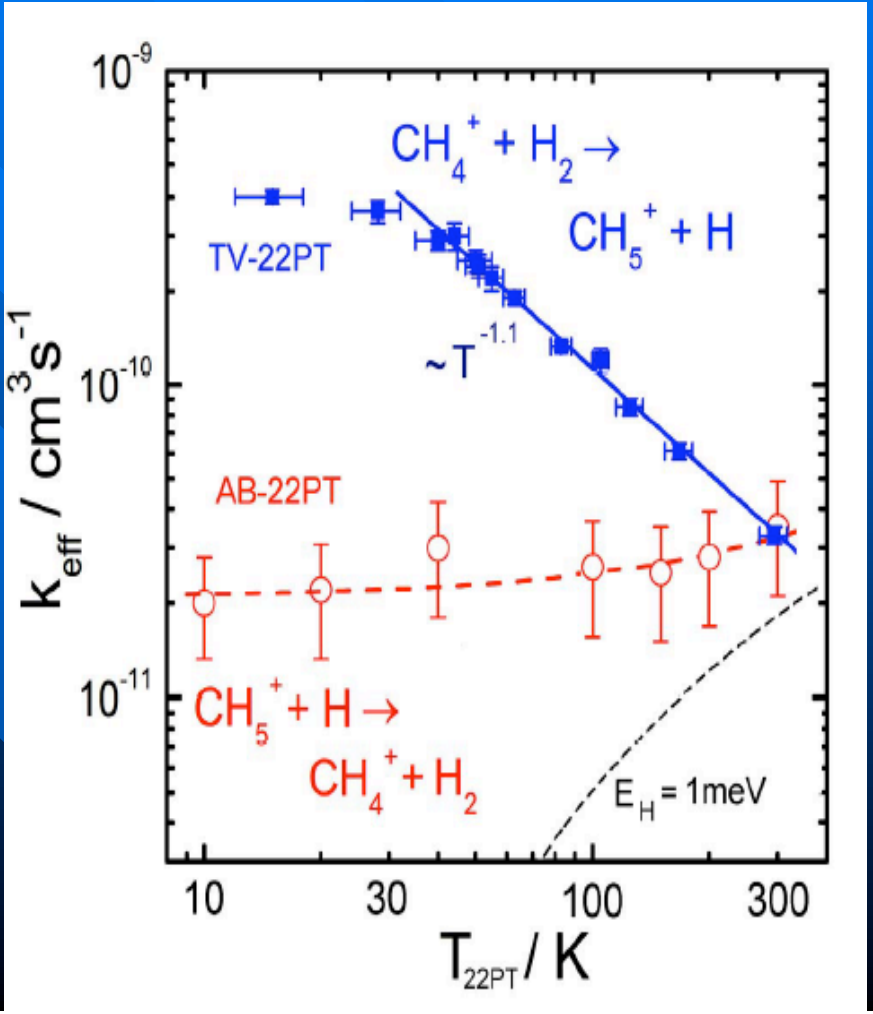
Rate Coefficients ($\alpha\ T^n$) / $10^{-9}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

| Reactants | T = 27 K | T = 68 K | *n* |
|---|---|---|---|
| $He^+ + HCl$ | 11.0 | 4.6 | – 0.94 |
| $He^+ + SO_2$ | 8.2 | 6.5 | – 0.25 |
| $He^+ + H_2S$ | 5.5 | 4.6 | – 0.19 |
| $He^+ + NH_3$ | 4.5 | 3.0 | – 0.44 |
| $He^+ + H_2O$ | 4.3 | 1.8 | – 0.94 |
| $C^+ + HCl$ | 3.8 | 1.9 | – 0.75 |
| $C^+ + SO_2$ | 5.7 | 4.1 | – 0.36 |
| $C^+ + H_2S$ | 4.8 | 3.0 | – 0.51 |
| $C^+ + NH_3$ | 4.6 | 3.2 | – 0.39 |
| $C^+ + H_2O$ | 12.0 | 5.2 | – 0.91 |
| $N^+ + NH_3$ | 5.2 | 3.2 | – 0.53 |
| $N^+ + H_2O$ | 9.9 | 6.0 | – 0.54 |

# Ion-Molecule Reactions: Summary and Exceptions

- Where for $A^+ + B$:
  $k(298\ K) > 10^{-9}\ cm^3\ s^{-1}$
  if B is *non-polar*,
  assume $k(T) = k(298\ K)$
  if B is *polar*,
  assume $k(T)\ \alpha\ T^{-0.5}$

- If $k(298\ K) < 10^{-10}\ cm^3\ s^{-1}$,
  ?? e.g. $CH_4^+ + O_2$,
  examples in figure
  (Gerlich)

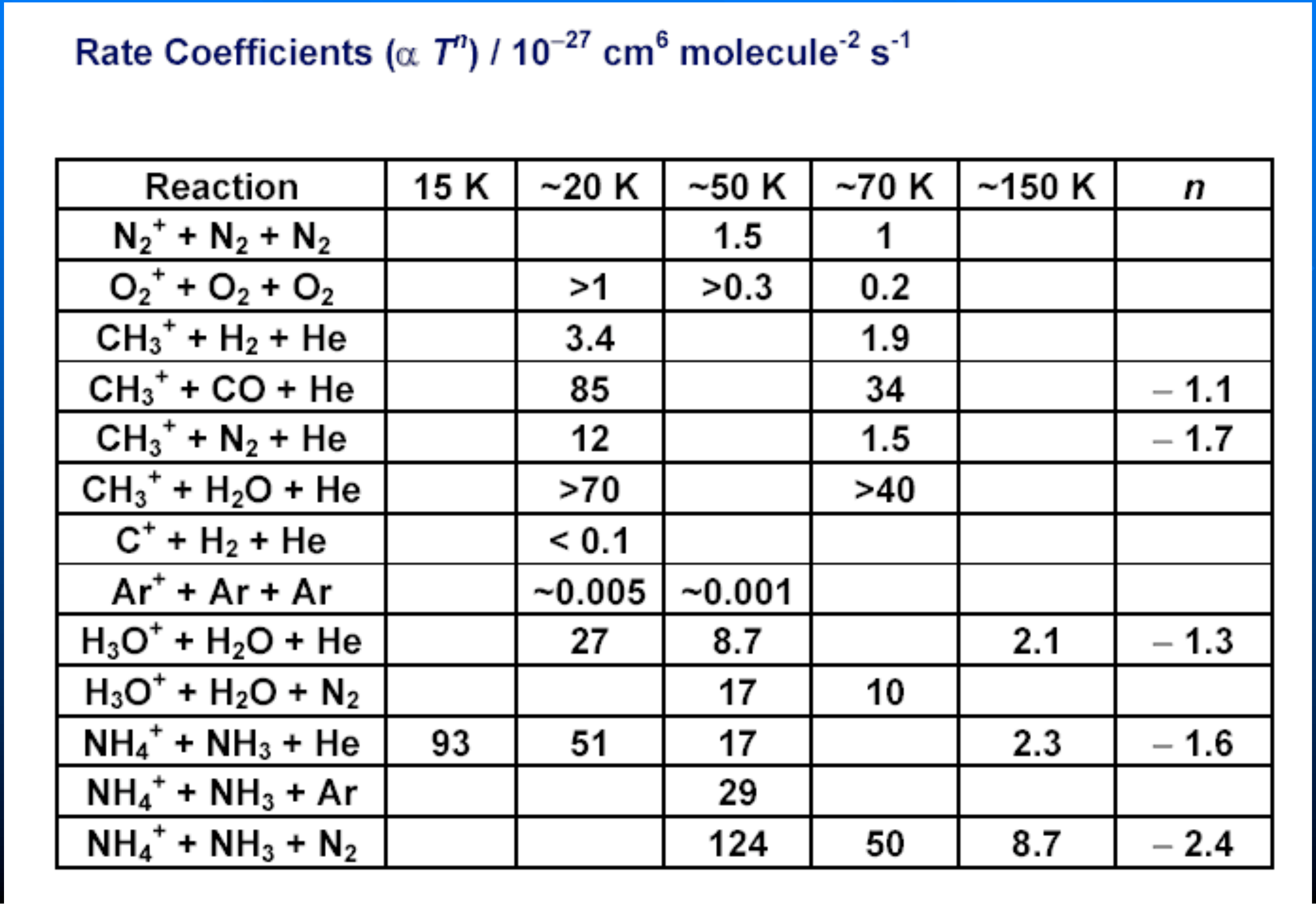


# Categories of Reaction

- Ion-Molecule Reactions
  - (a) ions + non-polar molecules
  - (b) ions + polar molecules
- Neutral-Neutral Reactions
  - (a) radicals + molecules
  - (b) radicals + radicals
- Radiative Association

{electron-molecule processes} X

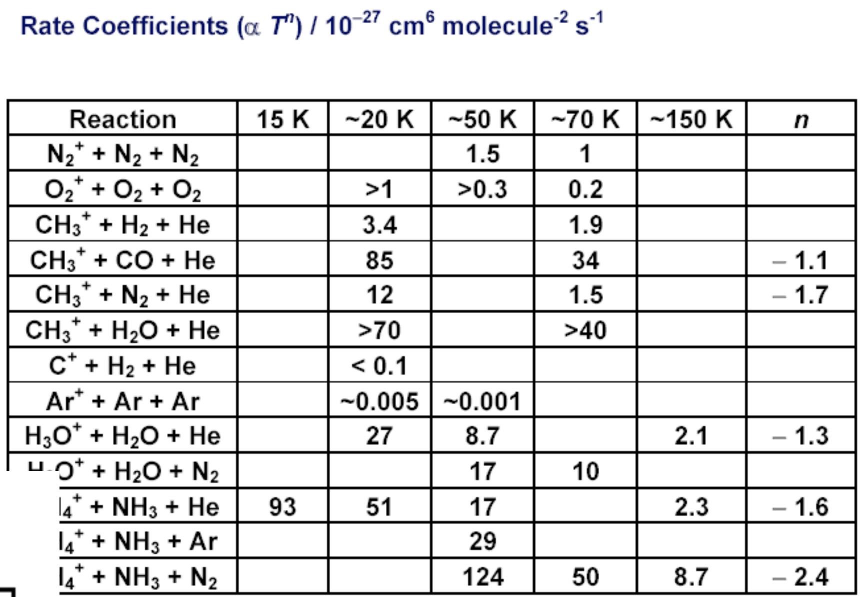
# Rate Coefficients and *T*-dependence for Collisional Association



Rate Coefficients ($\propto T^n$) / $10^{-27}$ $cm^6$ $molecule^{-2}$ $s^{-1}$

| Reaction | 15 K | ~20 K | ~50 K | ~70 K | ~150 K | *n* |
|---|---|---|---|---|---|---|
| $N_2^+ + N_2 + N_2$ | | | 1.5 | 1 | | |
| $O_2^+ + O_2 + O_2$ | | >1 | >0.3 | 0.2 | | |
| $CH_3^+ + H_2 + He$ | | 3.4 | | 1.9 | | |
| $CH_3^+ + CO + He$ | | 85 | | 34 | | – 1.1 |
| $CH_3^+ + N_2 + He$ | | 12 | | 1.5 | | – 1.7 |
| $CH_3^+ + H_2O + He$ | | >70 | | >40 | | |
| $C^+ + H_2 + He$ | | < 0.1 | | | | |
| $Ar^+ + Ar + Ar$ | | ~0.005 | ~0.001 | | | |
| $H_3O^+ + H_2O + He$ | | 27 | 8.7 | | 2.1 | – 1.3 |
| $H_3O^+ + H_2O + N_2$ | | | 17 | 10 | | |
| $NH_4^+ + NH_3 + He$ | 93 | 51 | 17 | | 2.3 | – 1.6 |
| $NH_4^+ + NH_3 + Ar$ | | | 29 | | | |
| $NH_4^+ + NH_3 + N_2$ | | | 124 | 50 | 8.7 | – 2.4 |

# Rate Coefficients and *T*-dependence for Collisional Association



Rate Coefficients ($\alpha\ T^n$) / $10^{-27}$ cm$^6$ molecule$^{-2}$ s$^{-1}$

| Reaction | 15 K | ~20 K | ~50 K | ~70 K | ~150 K | *n* |
|---|---|---|---|---|---|---|
| $N_2^+ + N_2 + N_2$ | | | 1.5 | 1 | | |
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| $H\ O^+ + H_2O + N_2$ | | | 17 | 10 | | |
| $_4^+ + NH_3 + He$ | 93 | 51 | 17 | | 2.3 | – 1.6 |
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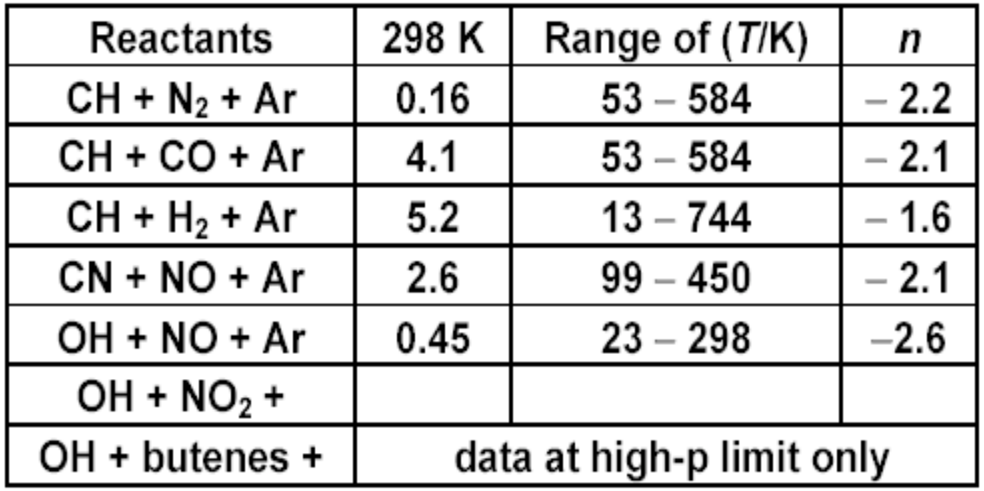


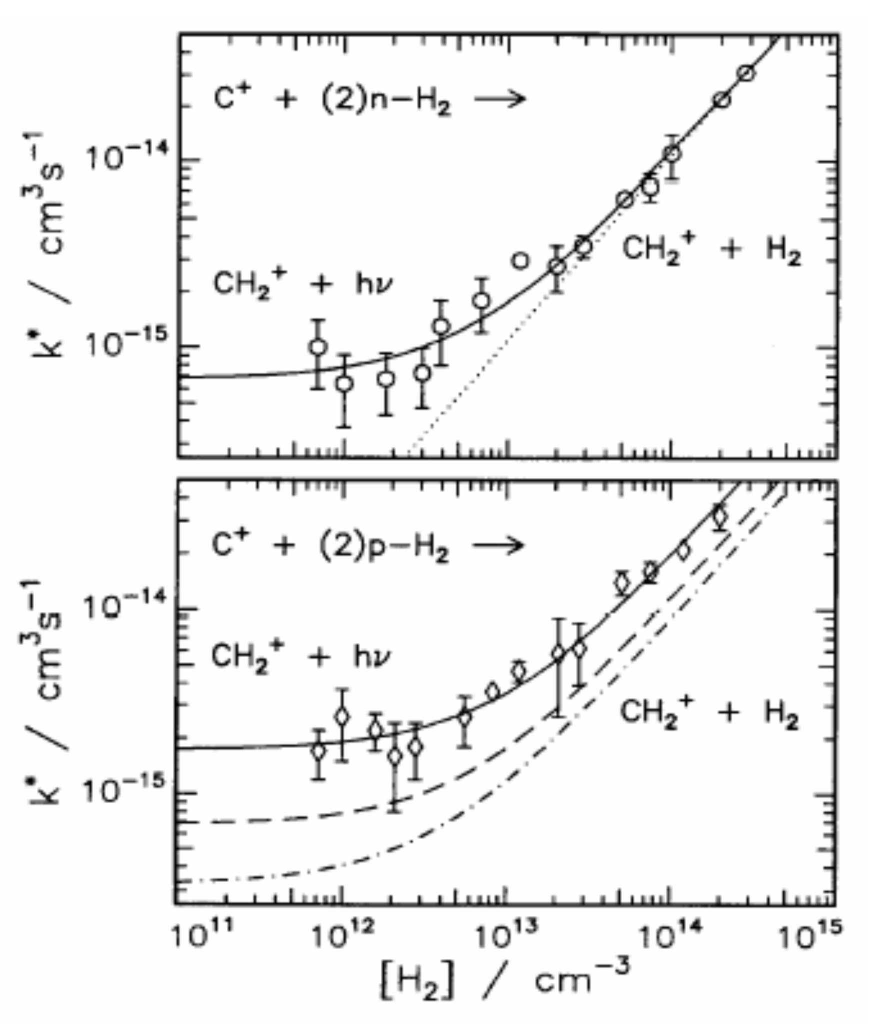
Rate Coefficients ($\alpha\ T^n$) / $10^{-30}$ cm$^6$ molecule$^{-2}$ s$^{-1}$

| Reactants | 298 K | Range of (*T*/K) | *n* |
|---|---|---|---|
| $CH + N_2 + Ar$ | 0.16 | 53 – 584 | – 2.2 |
| $CH + CO + Ar$ | 4.1 | 53 – 584 | – 2.1 |
| $CH + H_2 + Ar$ | 5.2 | 13 – 744 | – 1.6 |
| $CN + NO + Ar$ | 2.6 | 99 – 450 | – 2.1 |
| $OH + NO + Ar$ | 0.45 | 23 – 298 | –2.6 |
| $OH + NO_2 +$ | | | |
| OH + butenes + | data at high-p limit only | | |

# Radiative Association and the ISM

- Important processes either (a) involve $H_2$ or (b) large species
- e.g. $C^+ + H_2$ and $CH_2^+ + H_2$ – rate coefficients measured in ion traps
- problems if excited electronic states might be involved: *e.g.* $C + C_n$

*ca*. 10 K (Gerlich)



# Categories of Reaction

- Ion-Molecule Reactions
  - (a) ions + non-polar molecules
  - (b) ions + polar molecules

- Neutral-Neutral Reactions
  - (a) radicals + molecules
  - (b) radicals + radicals

- Radiative Association

{electron-molecule processes} X

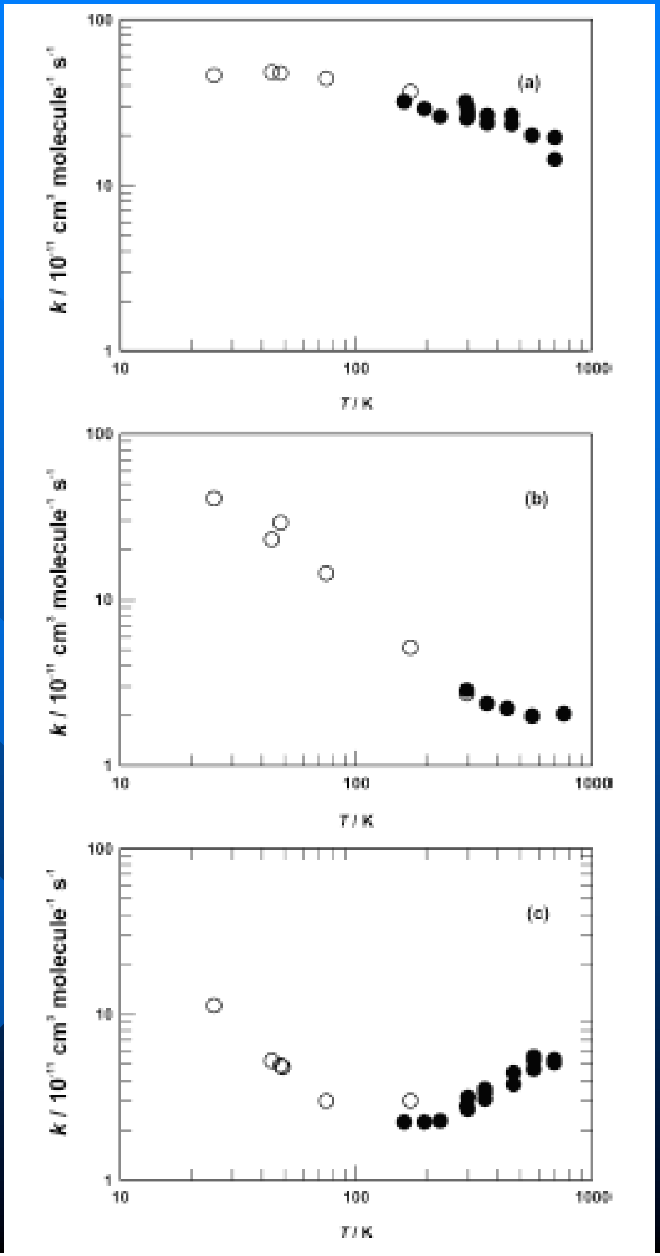
# *T*-dependence of rate coefficients

- ‘all’ fast low temperature reactions have $k$(298 K) > $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
- the rate coefficients increase at lower temperatures – but form of $k(T)$ *versus* $T$ varies
- **For nearly all reactions $k$(10-20 K) are 1 – 4 × $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$**

**CN + $C_2H_2$**

**CN + $NH_3$**

**CN + $C_2H_6$**



# Neutral-Neutral Reactions: Capture Theories

- Capture theories have been applied by Troe, Clary, Stoecklin, Klippenstein and others

- In contrast to ion-molecule reactions, the long-range attraction is much weaker so that maxima in effective potentials are at smaller separations

- Georgievskii and Klippenstein examined 26 neutral-neutral reactions by long-range TST (including all terms in long-range potential)

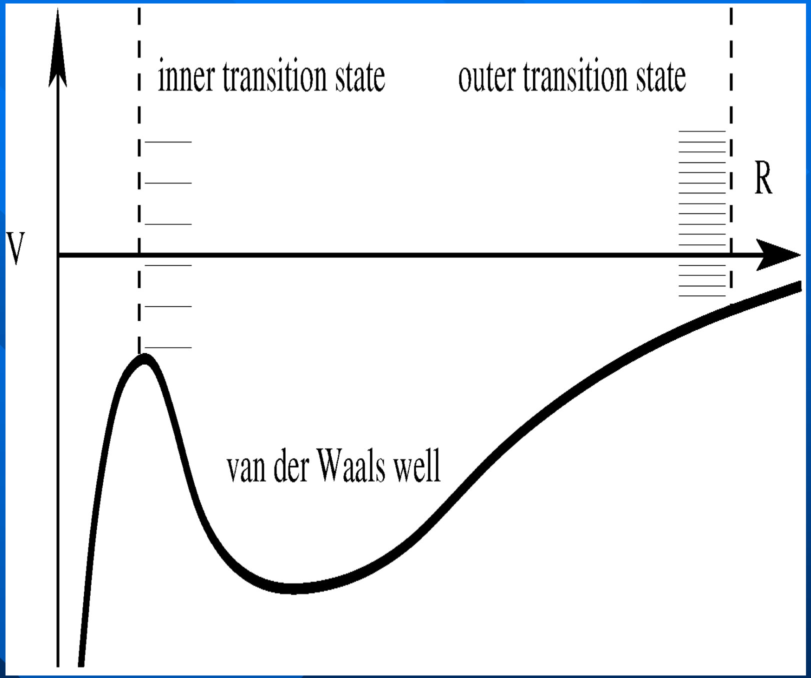
- They found that for 18 reactions $k_{calc} > 1.5 \times k_{expt}$

# Two transition state model (Klippenstein)

- Rate coefficient may be limited by 'inner' transition state – which may have higher or lower value of $V(R_{AB})$ but will have lower entropy
- Quantitative application requires:

  (a) accurate long/ medium range potential

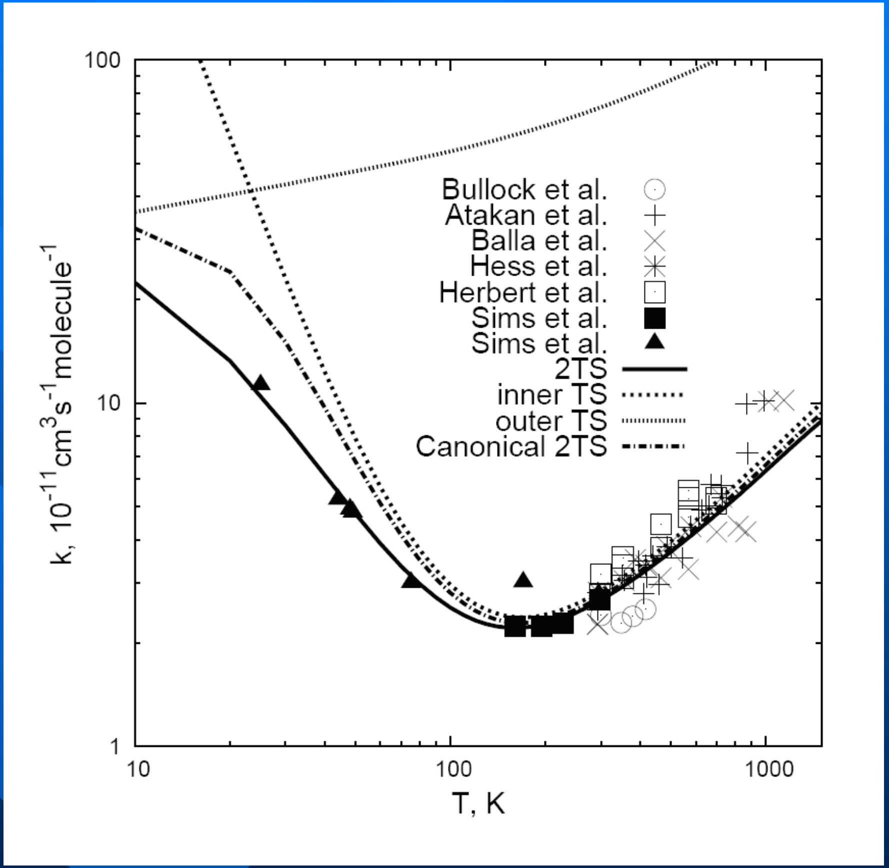
  (b) $\mu J$ application of TST



# Two transition state model: CN + $C_2H_6$

Comparison between experimental and $\mu J$-TST calculations for

**CN + $C_2H_6$**



?? Can results be generalised ??

# Neutral-Neutral Reactions

**Ian Smith**

*Universities of Cambridge and Birmingham, UK*

**Panel Meeting**
**ISSI Bern**
**9th January 2008**

# Reported Interstellar and Circumstellar Molecules

| N=2 | N=2 | N=3 | N=3 | N=4 | N = 5 | N = 6 | N = 7 | N = 8 | N = 9 | N = 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| $H_2$ | AlCl | $H_3$+ | HCP | $NH_3$ | $CH_4$ | $CH_3OH$ | $CH_3NH_2$ | $HCOOCH_3$ | $(CH_3)_2O$ | $(CH_3)CO$ |
| CH | PN | $CH_2$ | OCS | $H_3O^+$ | $SiH_4$ | $CH_3SH$ | $CH_3CCH$ | $CH_3C_2CN$ | $C_2H_5OH$ | $CH_3C_4CN$ |
| $CH^+$ | SiN | $NH_2$ | MgCN | $H_2CO$ | $CH_2NH$ | $C_2H_4$ | $CH_3CHO$ | $C_6H_2$ | $C_2H_5CN$ | $CH_3CH_2CHO$ |
| NH | SiO | $H_2O$ | MgNC | $H_2CS$ | $H_2C_3$ | $CH_3CN$ | c-$CH_2OCH_2$ | $C_7H$ | $CH_3C_4H$ | $(CH_2OH)_2$ |
| OH | SiS | $H_2S$ | NaCN | *l*-$C_3H$ | *l*-$C_3H_2$ | $CH_3NC$ | $CH_2CHCN$ | $HOCH_2CHO$ | $C_8H$ | |
| HF | $CO^+$ | $C_2H$ | $SO_2$ | *c*-$C_3H$ | *c*-$C_3H_2$ | $H_2CCHO$ | $HC_4CN$ | $CH_3COOH$ | $HC_6CN$ | |
| $C_2$ | $SO^+$ | HCN | $N_2O$ | HCCH | $H_2CCN$ | $NH_2CHO$ | $C_6H$ | $H_2CCCHCN$ | $CH_3CHCH_2$ | |
| CN | PO | HNC | SiCN | $HCNH^+$ | $H_2NCN$ | $HC_3NH^+$ | $H_2CCHOH$ | $H_2C_6$ | $CH_3CONH_2$ | |
| CO | SH | HCO | $CO_2$ | $H_2CN$ | $CH_2CO$ | $H_2C_4$ | $C_6H^-$ | $CH_2CHCHO$ | $C_6H^-$ | **N = 11** |
| CS | AlF | $HCO^+$ | c-$SiC_2$ | *c*-$C_3H$ | HCOOH | $C_5H$ | | | | $HC_8CN$ |
| CP | FeO | $HOC^+$ | SiNC | HCCN | $C_4H$ | $C_5N$ | | | | $CH_3C_6H$ |
| NO | SiC | $HN_2^+$ | AlNC | HNCO | $HC_2CN$ | $C_5O$ | | | | |
| NS | $CF^+$ | HNO | | $HOCO^+$ | $HC_2NC$ | $C_5S$ | | | | **N = 12** |
| SO | ? $N_2$ ? | $HCS^+$ | | HNCS | $C_4Si$ | | | | | $C_6H_6$ |
| HCl | | $C_3$ | | $C_2CN$ | $C_5$ | | | | | |
| NaCl | | $C_2O$ | | $C_3O$ | $C_4N$ | | | | | **N = 13** |
| KCl | | $C_2S$ | | $C_3S$ | $H_2COH^+$ | | | | | $HC_{10}CN$ |
| | | | | $SiC_3$ | $C_4H^-$ | | | | | |

# Neutral-Neutral Reactions: Summary of Experiments

- Canosa *et al*. list 93 reactions: 73 studied in continuous CRESU (Rennes, Birmingham, Bordeaux); 20 in pulsed CRESU (Arizona, Berkeley, Göttingen)

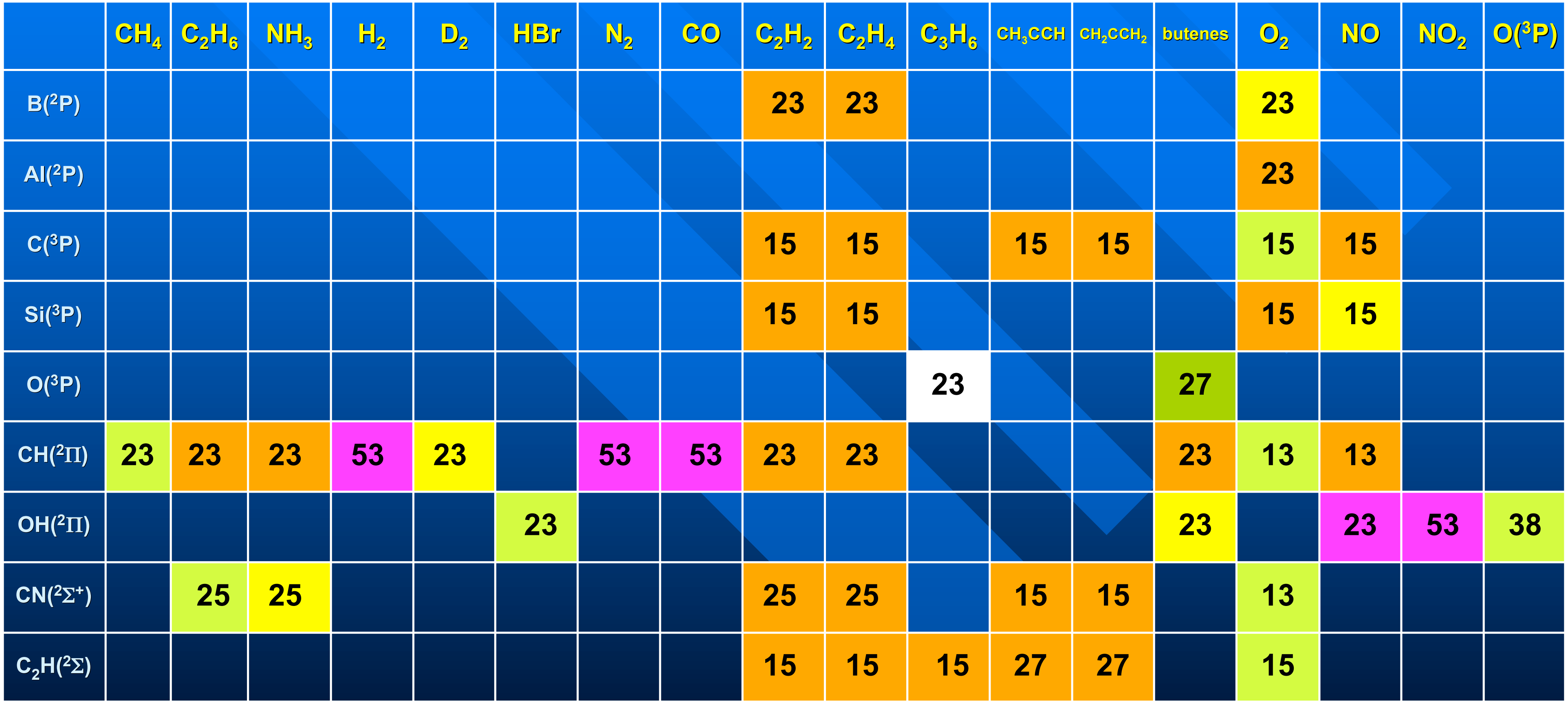
- Continuous CRESU reach as low as 13 K, more generally *ca*. 25 K; pulsed CRESU to 53 K

- **Radicals**: B($^2P_J$), C ($^3P_J$) , O ($^3P_J$), Al ($^2P_J$), and Si ($^3P_J$)
  CN, OH, CH, NH, $C_2(X)$, $C_2(a)$, $C_2H$, $C_4H$

- **Molecules**: alkenes/alkynes (52); saturated molecules (19); radicals (15); aromatics (2); others (5)

# CRESU measurements of rate constants at low temperatures

- 🟪 Signifies a pressure-dependent association reaction
- 🟧 Metathesis reactions with k(298 K) > 1 × $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
- 🟨 Metathesis reactions with k(298 K) > 10 – 5 × $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
- 🟩 Metathesis reactions with k(298 K) > 5 – 1 × $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$



| | $CH_4$ | $C_2H_6$ | $NH_3$ | $H_2$ | $D_2$ | HBr | $N_2$ | CO | $C_2H_2$ | $C_2H_4$ | $C_3H_6$ | $CH_3CCH$ | $CH_2CCH_2$ | butenes | $O_2$ | NO | $NO_2$ | $O(^3P)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $B(^2P)$ | | | | | | | | | 🟧 23 | 🟧 23 | | | | | 🟨 23 | | | |
| $Al(^2P)$ | | | | | | | | | | | | | | | 🟧 23 | | | |
| $C(^3P)$ | | | | | | | | | 🟧 15 | 🟧 15 | | 🟧 15 | 🟧 15 | | 🟩 15 | 🟧 15 | | |
| $Si(^3P)$ | | | | | | | | | 🟧 15 | 🟧 15 | | | | | 🟧 15 | 🟨 15 | | |
| $O(^3P)$ | | | | | | | | | | | ⬜ 23 | | | 🟩 27 | | | | |
| $CH(^2\Pi)$ | 🟩 23 | 🟧 23 | 🟧 23 | 🟪 53 | 🟨 23 | | 🟪 53 | 🟪 53 | 🟧 23 | 🟧 23 | | | | 🟧 23 | 🟩 13 | 🟧 13 | | |
| $OH(^2\Pi)$ | | | | | | 🟩 23 | | | | | | | | 🟨 23 | | 🟪 23 | 🟪 53 | 🟩 38 |
| $CN(^2\Sigma^+)$ | | 🟩 25 | 🟨 25 | | | | | | 🟧 25 | 🟧 25 | | 🟧 15 | 🟧 15 | | 🟩 13 | | | |
| $C_2H(^2\Sigma)$ | | | | | | | | | 🟧 15 | 🟧 15 | 🟧 15 | 🟧 27 | 🟧 27 | | 🟩 15 | | | |

also data for reactions of $^1C_2(^1\Sigma_g^+)$, $^3C_2(^3\Pi_u)$ and $C_4H$

# CRESU measurements of rate constants at low temperatures

🟦 - radical + saturated molecule
🟥 - radical + unsaturated molecule
🟨 - radical + radical

| | $CH_4$ | $C_2H_6$ | $NH_3$ | $H_2$ | $D_2$ | HBr | $N_2$ | CO | $C_2H_2$ | $C_2H_4$ | $C_3H_6$ | $CH_3CCH$ | $CH_2CCH_2$ | butenes | $O_2$ | NO | $NO_2$ | $O(^3P)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $B(^2P)$ | | | | | | | | | 23 | 23 | | | | | 23 | | | |
| $Al(^2P)$ | | | | | | | | | | | | | | | 23 | | | |
| $C(^3P)$ | | | | | | | | | 15 | 15 | | 15 | 15 | | 15 | 15 | | |
| $Si(^3P)$ | | | | | | | | | 15 | 15 | | | | | 15 | 15 | | |
| $O(^3P)$ | | | | | | | | | | | 23 | | | 27 | | | | |
| $CH(^2\Pi)$ | 23 | 23 | 23 | 53 | 23 | | 53 | 53 | 23 | 23 | | | | 23 | 13 | 13 | | |
| $OH(^2\Pi)$ | | | | | | 23 | | | | | | | | 23 | | 23 | 53 | 38 |
| $CN(^2\Sigma^+)$ | | 25 | 25 | | | | | | 25 | 25 | | 15 | 15 | | 13 | | | |
| $C_2H(^2\Sigma)$ | | | | | | | | | 15 | 15 | 15 | 27 | 27 | | 15 | | | |

**also data for reactions of $^1C_2(^1\Sigma_g^+)$, $^3C_2(^3\Pi_u)$ and $C_4H$**

# Reactions of Radicals with Alkenes/Alkynes

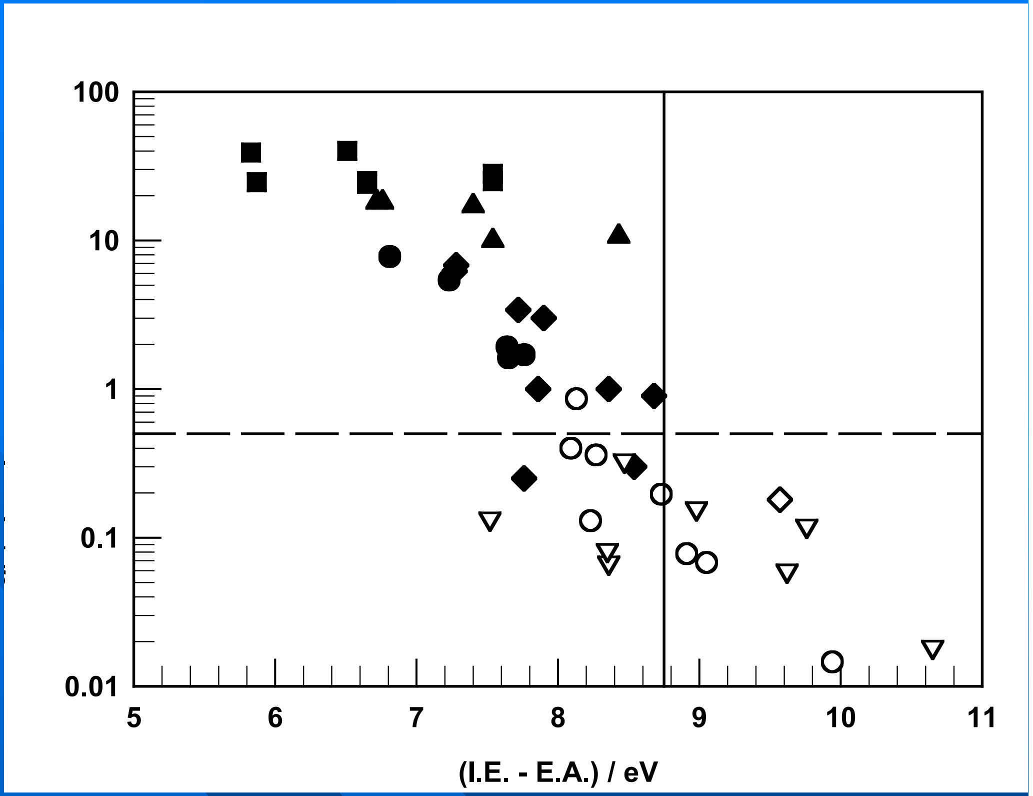
■ - CN radicals

▲ - $C_2H$ radicals

◆, ◇ - OH radicals

●, ○ - O atoms

▽ - H atoms



Reaction will be fast at low temperatures (10 – 20 K) if:

- $k$(298 K) > 5 × $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ and/or
- (I.E. – E.A.) > *ca.* 8.75 eV

Reactions of alkenes/alkynes with $O(^3P)$ atoms should provide crucial test

# Why low temperature kinetics of O + alkenes?

- Extensive kinetics measurements at and above room temperature
- Some reactions show positive *T* dependence (e.g. *propene & 1-butene*) – some negative *T* dependence (e.g. *iso-butene & cis-2-butene*)
- Rate constants and activation energies correlate with I.E. of the alkene (*Cvetanovic et al.*)

?? Will some *k*(*T*)'s decrease to low temperatures, some increase??

# Kinetic Data for Reactions of $O(^3P)$ with Alkenes

| | (I.E. – E.A.)/eV | k(298 K)<br>$10^{-11}$ cm$^3$ s$^{-1}$ | *T*-dependence |
|---|---|---|---|
| *trans*-2-butene | 7.64 | 2.2 | – ve |
| *cis*-2-butene | 7.65 | 1.8 | – ve |
| *iso*-butene | 7.76 | 1.7 | – ve |
| 1-butene | 8.09 | 0.42 | + ve |
| propene | 8.27 | 0.40 | + ve |
| ethene | 9.05 | 0.073 | + ve |

# CRESU Experiments on Reactions of $O(^3P)$ with Alkenes

(*Ludovic Bennier, Hassan Sabbah, Ian Sims & IWMS*)

- $O(^3P)$ atoms are generated by pulsed laser photolysis of $NO_2$ at 355 nm (tripled Nd:YAG laser)
- a small-ish concentration of NO is included in the reaction mixture, and variation in the $O(^3P)$ atom concentration is followed by observing the intensity of the chemiluminescence from $NO_2^*$

# Rate constants for reaction of O($^3$P) with alkenes

▲ *cis*-butene

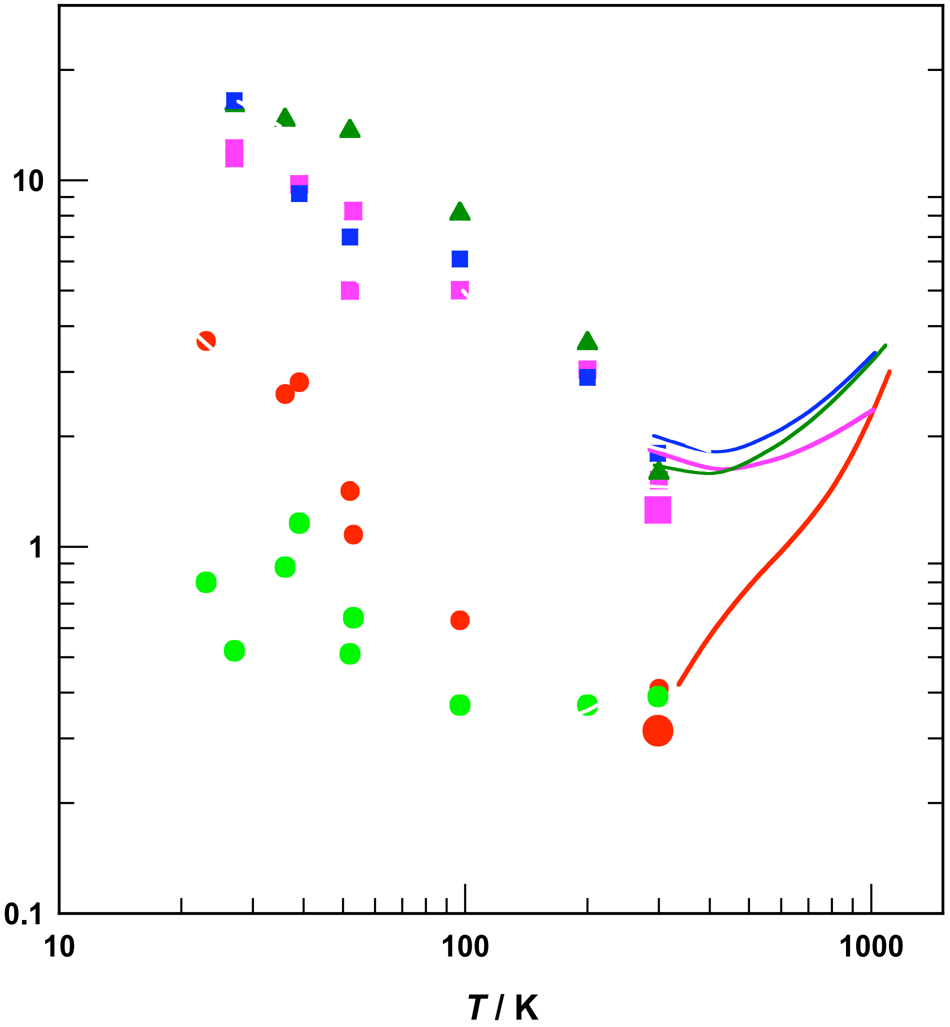
■ *trans*-butene

■ *iso*-butene

● *1*-butene

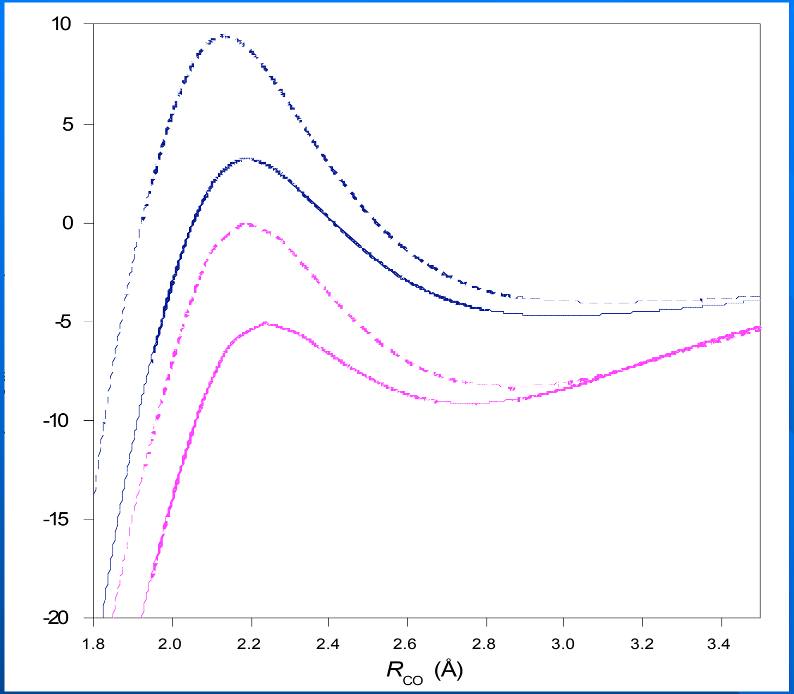
● propene

● and ■ from IWMS 1967!!



# Theoretical calculations on O($^3$P) + alkene reactions

(Yuri Georgievskii and Stephen Klippenstein)



*Ab initio* calculations characterise the long-range potentials

––– *trans*-butene ––– ethene

Generally two maxima – two transition states – 'outer' and 'inner'

- Dynamics treated by $\mu J$ version of TST
- For O($^3$P) + ethene, inner TS is dominant ('real' barrier)
- For O($^3$P) + alkenes with low values of (I.E. – E.A.), outer TS is dominant, barrier is well-submerged
- For intermediate cases, influence of both barriers is important with their relative importance depending on temperature

# Rate constants for reaction of O($^3$P) with alkenes

▲ *cis*-butene

■ *trans*-butene

■ *iso*-butene

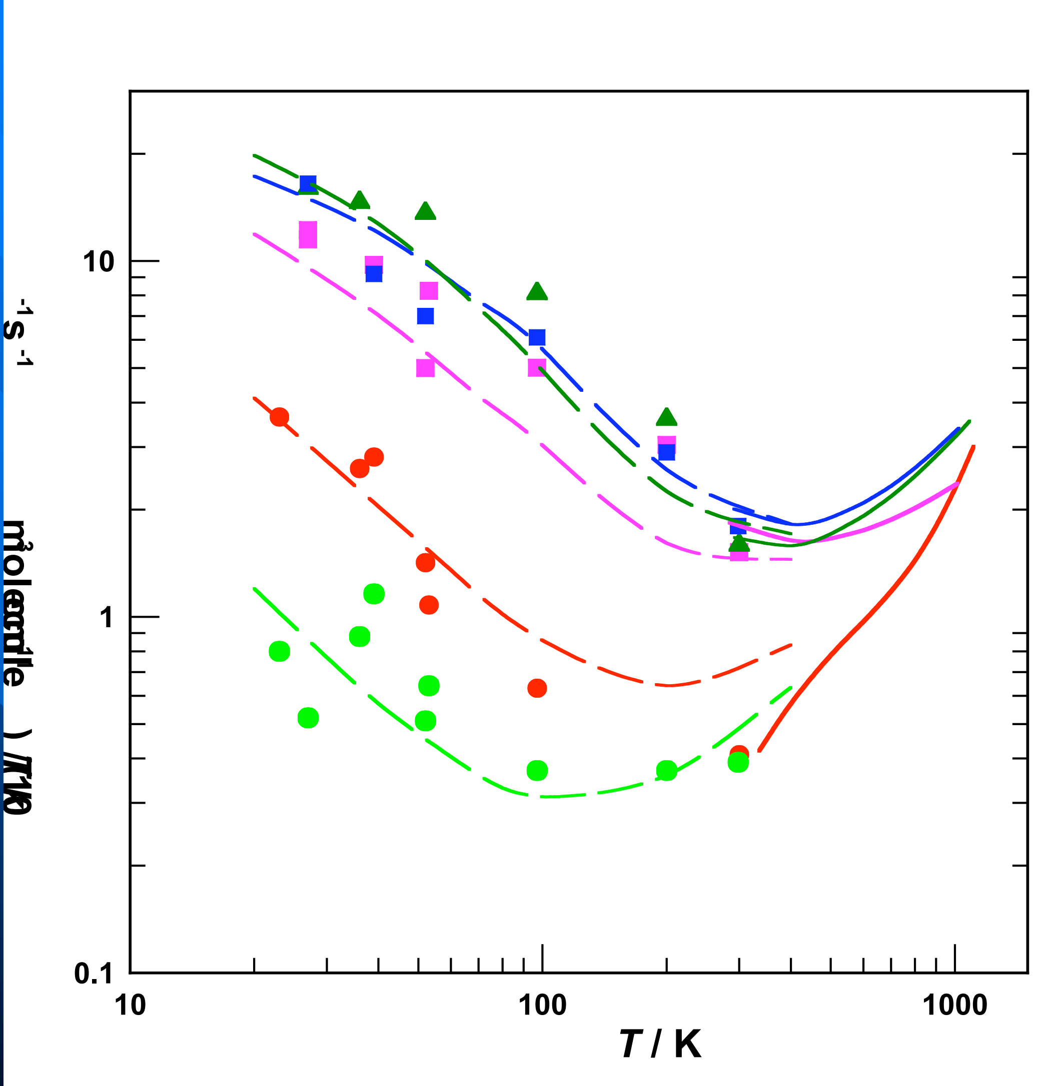
● *1*-butene

● propene

Solid lines from expts of Fontijn

Dashed lines from *μJ*-TST calculations

O($^3$P) + ethene – too slow to measure



# Conclusions

- Rate constants for reaction of O($^3$P) atoms with alkenes show a complex dependence on temperature
- The semi-empirical arguments introduced in the Faraday Discussion paper of Smith et al. that reactants with (I.E. – E.A.) < ca. 8.75 eV will occur rapidly at low temperature hold up rather well
- The values of $k(T)$ and their dependence on $T$ are well-matched by a two transition state model using $\mu J$ version of TST

# Radical-Radical Reactions

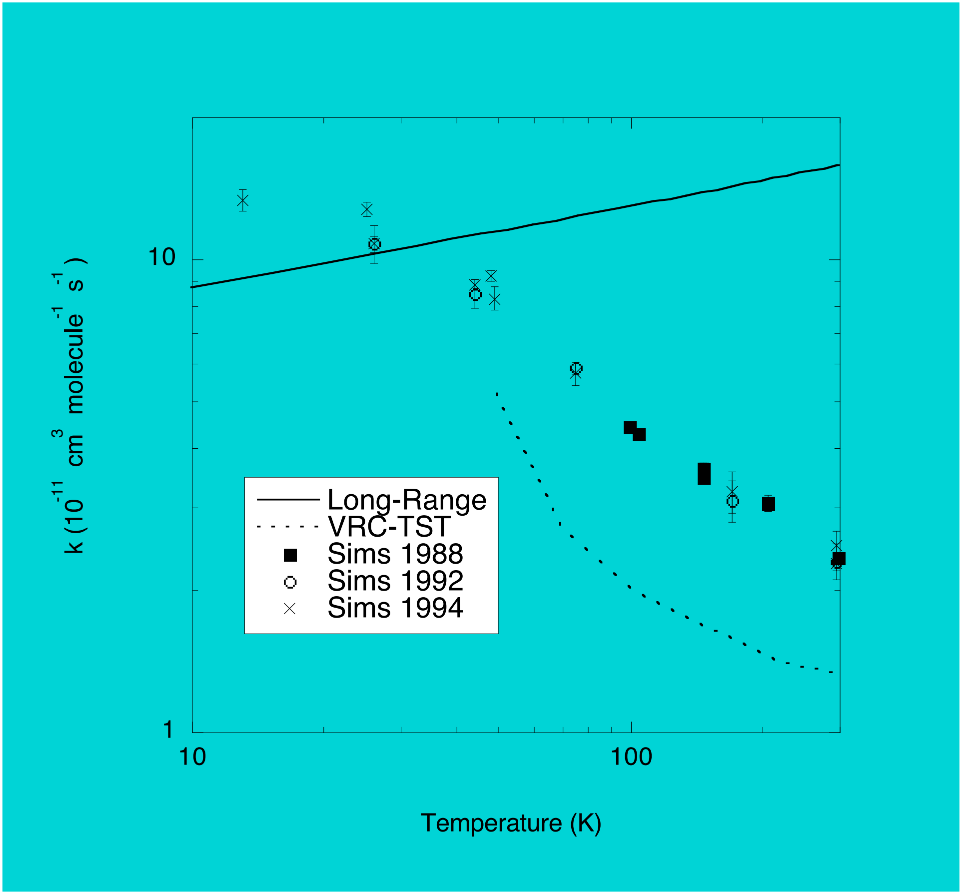
- At least one PES should have no maximum and probably a ‘deep’ minimum
- Several PES’s probably correlate with reactants not all leading (without a barrier) to products
- *k*(*T*) may be lowered by degeneracies and near-degeneracies
- Can an inner transition state lower rate below that for capture?

| | $O_2$ | NO | $NO_2$ | $O(^3P)$ |
|---|---|---|---|---|
| $B(^2P)$ | 23 | | | |
| $Al(^2P)$ | 23 | | | |
| $C(^3P)$ | 15 | 15 | | |
| $Si(^3P)$ | 15 | 15 | | |
| $O(^3P)$ | | | | |
| $CH(^2\Pi)$ | 13 | 13 | | |
| $OH(^2\Pi)$ | | 23 | 53 | 38 |
| $CN(^2\Sigma^+)$ | 13 | | | |
| $C_2H(^2\Sigma)$ | 15 | | | |

# Radical-Radical Reactions: CN + O2

- experimental *k*(*T*) show strong negative *T*-dependence – in contrast to ‘capture’ calculations

- main features of experimental k(*T*) are reproduced by 2-TS model (Klippenstein)



# Reactions of Radical with Saturated Molecules

- Data set from CRESU experiments is limited

| | $CH_4$ | $C_2H_6$ | $NH_3$ | $H_2$ | $D_2$ | HBr |
|---|---|---|---|---|---|---|
| $B(^2P)$ | | | | | | |
| $Al(^2P)$ | | | | | | |
| $C(^3P)$ | | | | | | |
| $Si(^3P)$ | | | | | | |
| $O(^3P)$ | | | | | | |
| $CH(^2\Pi)$ | 23 | 23 | 23 | 53 | 23 | |
| $OH(^2\Pi)$ | | | | | | 23 |
| $CN(^2\Sigma^+)$ | | 25 | 25 | | | |
| $C_2H(^2\Sigma)$ | | | | | | |

# Reactions of Radicals with Saturated Molecules

## Values of $k(298\ \mathrm{K})$ / $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

| | E.A./eV | $H_2$ | $CH_4$ | $C_2H_6$ | $C_3H_8$ | i-$C_4H_{10}$ | n-$C_4H_{10}$ |
|---|---|---|---|---|---|---|---|
| I.E./eV | | 15.43 | 12.51 | 11.52 | 10.95 | 10.57 | 10.53 |
| $C(^3P)$ | | (17) | ? | ? | ? | ? | ? |
| $CH(^2\Pi)$ | 1.238 | (160) | 91 | 280 | 425 | 448 | 483 |
| | | | | | | | |
| $H(^2S)$ | 0.754 | $10^{-4}$ | 1.5(-7) | 2.8(-5) | 1.5(-4) | 1.1(-3) | 2.9(-4) |
| $O(^3P)$ | 1.461 | 9(-6) | 1.7(-5) | 1.4(-4) | 9.4(-3) | 0.11 | 2.6(-2) |
| $OH(^2\Pi)$ | 1.827 | 1.7(-3) | 6.1(-3) | 0.25 | 1.1 | 2.1 | 2.4 |
| $CN(^2\Sigma^+)$ | 3.862 | 2.8(-2) | 0.60 | 28 | 75 | 100 | |
| $C_2H(^2\Sigma)$ | 2.969 | 0.7 | 2.7 | 43 | 80 | 96 | 120 |

# Reactions of Radical with Saturated Molecules

- $C(^3P)$ and $CH(^2\Pi)$ react rapidly with saturated molecules – if exothermic reaction is available
- Alkanes will not react with $H(^2S)$, $O(^3P)$ or $OH(^2\Pi)$ – probably the reactions of these radicals with saturated molecules can be ignored
- Most alkanes will react rapidly with $CN(^2\Sigma^+)$ and $C_2H(^2\Sigma)$
- Reactivity of $C(^3P)$ atoms ?

Values of $k$(298 K) / $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

| | E.A./ eV | $CH_4$ | $C_2H_6$ | $C_3H_8$ | *i*- $C_4H_{10}$ | *n*- $C_4H_{10}$ |
|---|---|---|---|---|---|---|
| I.E./eV | | 12.51 | 11.52 | 10.95 | 10.57 | 10.53 |
| $C(^3P)$ | | | | | | |
| $CH(^2\Pi)$ | 1.238 | 91 | 280 | 425 | 448 | 483 |
| | | | | | | |
| $H(^2S)$ | 0.754 | 1.5(-7) | 2.8(-5) | 1.5(-4) | 1.1(-3) | 2.9(-4) |
| $O(^3P)$ | 1.461 | 1.7(-5) | 1.4(-4) | 9.4(-3) | 0.11 | 2.6(-2) |
| $OH(^2\Pi)$ | 1.827 | 6.1(-3) | 0.25 | 1.1 | 2.1 | 2.4 |
| $CN(^2\Sigma^+)$ | 3.862 | 0.60 | 28 | 75 | 100 | |
| $C_2H(^2\Sigma)$ | 2.969 | 2.7 | 43 | 80 | 96 | 120 |

# Some final thoughts !

- Examination of available rate data suggests that for any neutral-neutral reaction with *k*(298 K) > 5 x $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ there is no 'real' barrier on the MEP and *k*(10-20 K) is likely to be *ca*. 2 x $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (factor of 2 uncertainty ?)

- For radical-radical reactions *k*(10-20 K) may be lowered by 'electronic degeneracy factor'

- Theoretical point for discussion: how does two-TS model with dependence on *E* and *J* mesh with dependence of *k*(*T*) on rotational states of reactants?