Gas-Phase Reactions in the ISM:
Rate coefficients, temperature-dependences, and reaction products

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A little (personal) history

1987: **Rate Coefficients in Astrochemistry (TJ Millar & DA Williams)**

(IWMS) Experimental Measurements of the Rate Constants for Neutral-Neutral Reactions

1996: **IAU Symposium 178: Molecules in Astrophysics: Probes and Processes (E F van Dishoeck)**

(IWMS) Reactions between Neutral Species at Low Temperatures: Laboratory Results and Astrophysical Modelling

2011: **IAU Symposium 280: Gas-Phase Chemistry in the ISM: Rate coefficients, temperature-dependences, and reaction products**

Gas-phase reactions of different types included in the OSU kinetic database (version osu-09-2008) for astrochemistry.

Type of process	Example	Number in model
Gas-grain interactions:	$H + H + grain \rightarrow H_2 + grain$	14
Direct cosmic ray processes	$H_2 + \zeta \rightarrow H_2^+ + e$	11
Cation-neutral reactions	$H_2^+ + H_2 \rightarrow H_3^+ + H$	2933
Anion-neutral reactions	$C^- + NO \rightarrow CN^- + O$	11
Radiative associations (ion)	$C^+ + H_2 \rightarrow CH_2^+ + h\nu$	81
Associative detachment	$C^- + H_2 \rightarrow CH_2 + e$	46
Chemi-ionization	$O + CH \rightarrow HCO^+ + e$	1
Neutral-neutral reactions	$C + C_2H_2 \rightarrow C_3H + H$	382
Radiative association (neutral)	$C + H_2 \rightarrow CH_2 + h\nu$	16
Dissociative recombination	$N_2H^+ + e \rightarrow N_2 + H$	539
Radiative recombination	$H_2CO^+ + e \rightarrow H_2CO + h\nu$	16
Anion-cation recombination	$HCO^+ + H^- \rightarrow H_2 + CO$	36
Electron attachment	$C_6H + e \rightarrow C_6H^- + h\nu$	4
External photo-processes[a]	$C_3N + h\nu \rightarrow C_2 + CN$	175
Internal photo-processes[a]	$CO + h\nu \rightarrow C + O$	192

Kinetic information needed for Chemical Models

- **Rate coefficient and its dependence on temperature. For reaction between *A* and *B*:**

$$-d[A]/dt = -d[B]/dt = k(T)[A][B]$$

- **In models: $k(T) = \alpha (T/300)^{\beta} \exp(-\gamma / T)$ — but caution!**

- **Products of reaction**

  (a) thermodynamics **may** demonstrate that only one channel is open;

  (b) determination of ‘branching ratios’ can be ‘challenging’

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Ion-Neutral Reactions: Experimental Methods

- **'Trapping Methods':**

  (a) ICR – Ion Cyclotron Resonance: 300 K

  (b) Ion Traps: especially 22-pole trap (Gerlich): down to 10 K, especially useful for study of *radiative association*

- **'Flow Methods':**

  (a) FA – Flowing Afterglow: $82 \leq (T/\mathrm{K}) \leq 600$; later $300 \leq (T/\mathrm{K}) \leq 1800$

  (b) SIFT – Selected Ion Flow Tube: typically, down to 80 K, also one study from 18 K to 295 K

  (c) SIFDT – Selected Ion Flow Drift Tube extends measurements to much higher collision energies; up to ≡ 1800 K;

  (d) CRESU – Reaction Kinetics in Uniform Supersonic Flows: $8 \leq (T/\mathrm{K}) \leq 300$

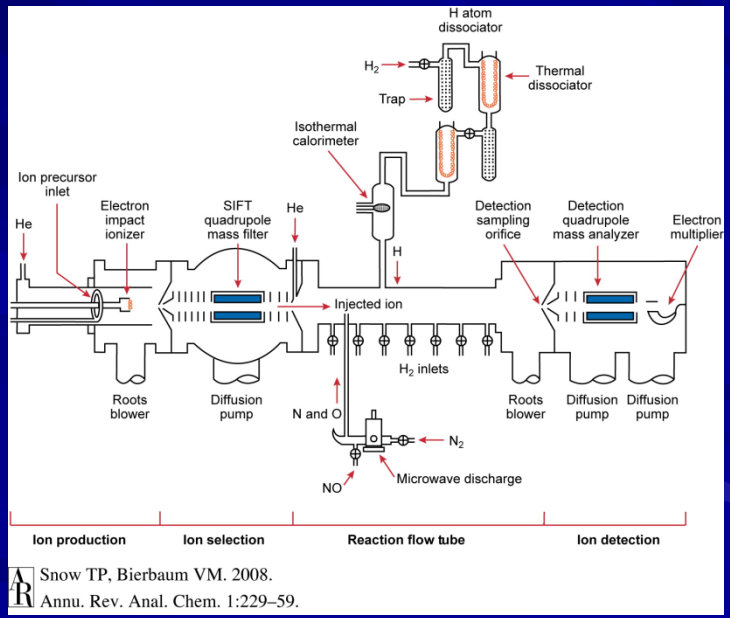
(Anicich, *Ap. J. Supplt.,* **84**, 215 (1993); Viggiano, *PCCP*, **8**, 2557 (2006))

Ion-Neutral Reactions: Experimental Methods

- As **mass spectrometry** is used to observe loss of ionic reactant, ionic product(s) can be observed – hence, **branching ratios**

- Methods used for reactions of cations can be adapted to study the **reactions of anions** (*Veronica Bierbaum*)

- In most studies of ion-neutral reactions, the neutral reactant is a 'stable' (i.e., non-radical) species. However, SIFT method adaapted to study of **reactions between ions and radical atoms** (*Veronica Bierbaum*)



Snow TP, Bierbaum VM. 2008.
Annu. Rev. Anal. Chem. 1:229–59.

(Snow & Bierbaum, *Ann. Rev. Anal. Chem.* 44, 367 (2006))

Ion-Neutral Reactions: *T*-dependence of rate coefficients

- For **most** ion-neutral –reactions, there is no *activation barrier*; rather the rate coefficient is determined by 'capture': that is, the ability of the long-range 'electrostatic potential' to bring the reactants into close contact 'against' the requirement to conserve angular momentum
- The 'Langevin model' assumes attraction between charge and induced dipole, leading to:

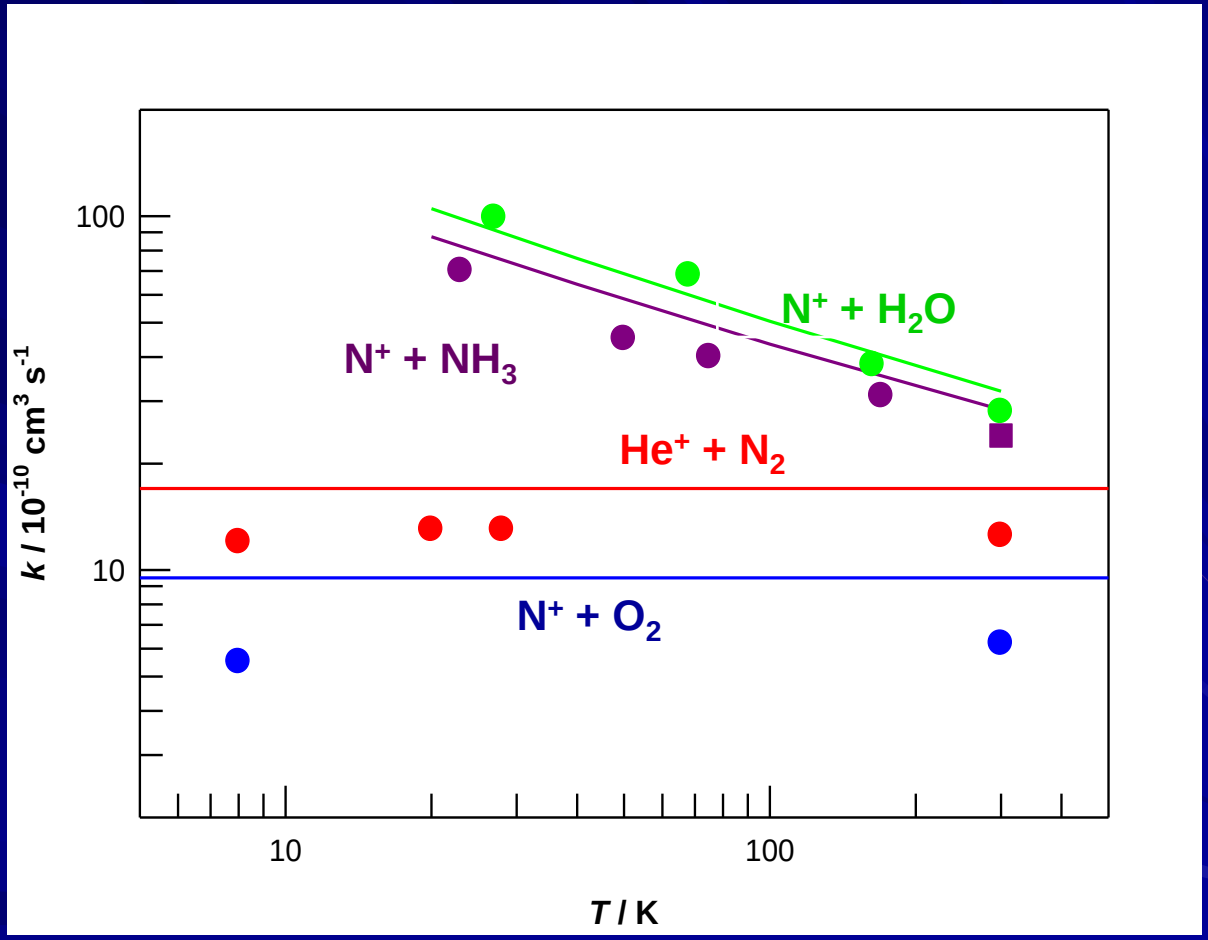
$$k_L = 2\pi e (\alpha / \mu)^{1/2}$$

- For reactions between ions and dipolar neutral molecules, the long-range potential is more complex (depends on orientation). Ratio of rate coefficient to the Langevin value has been parameterised:

$$k_D / k_L = ax + b \text{ where } x = \mu_D / (2\alpha k_B T)^{1/2}$$

Ion-Neutral Reactions: tests of simple capture models

CRESU experiments provide a good test of predictions of T-dependence for reactions between simple ions and neutral (non-polar and polar) molecules



Neutral-Neutral Reactions: Experimental Methods

- **'Discharge-Flow Methods':**

  (a) Reaction of atomic (H, O, N, Cl) and diatomic radicals:
  typically, $200 \leq (T/\mathrm{K}) \leq 500$

  (b) optical and mass spec. methods to observe loss of reactants (formation of products?)

  (c) HTFFR (Fontijn) reaches *ca*. 1320 K

- **'Pulsed Laser Photolysis Methods':**

  (a) coupled to optical methods for detection (e.g. LIF):
  typically $200 \leq (T/\mathrm{K}) \leq 600$ some experiments down to 80 K

  (b) HTPR (Fontijn) reaches *ca*. 1430 K

  (c) CRESU – Reaction Kinetics in Uniform Supersonic Flows:
  $13 \leq (T/\mathrm{K}) \leq 300$

Both methods provide data on (radical + molecule) and (radical + radical) reactions but are difficult at extremes of temperature

Measuring product yields/branching ratios is generally difficult

(http://www.iupac-kinetic.ch.cam.ac.uk; http://jpldataeval.jpl.nasa.gov)
(Baulch, D.L. et al., 2005, *J. Phys. Chem. Ref. Data*, 34, 757)

Neutral-Neutral Reactions: in the ISM and CRESU Experiments

- Of the observed 159 species in the ISM (July 2010): 17 are cations, 6 anions, 136 electrically neutral
- Of the 136 neutral species: many are free radicals (e.g., CH, CN, C_2H, C_4H, etc) and many are 'unsaturated' (C_2H_2, C_2H_4, HC_2CN, HC_4CN etc)
- Clearly scope for neutral-neutral reactions
- In CRESU experiments, radicals (C, Al, Si, B, O, CN, OH, CH, C_2H, C_2, C_4H) are formed by pulsed laser photolysis, removal followed by LIF or using chemiluminescent techniques
- Co-reactants: principally HC's, CH_4, C_2H_4, C_2H_2,……
- Radical-radical reactions difficult to study – only one $O + OH \rightarrow O_2 + H$

Neutral-Neutral Reactions: *T*-dependence of rate coefficients

- For most reactions between radicals and saturated molecules, $\gamma > 0$, $k(T)$ increases with T: e.g. CN + H_2 and C_2H + H_2
- For reactions where $k(298\ K) \geq 10^{-11}\ cm^3\ s^{-1}$: general trend is for $k(T)$ to increase as T is lowered
- However, the form of $k(T)$ is variable
- Suggests the absence of an activation barrier and that values of $k(T)$ are determined by capture
- Product yields/branching ratios difficult to measure

One example: CN + NH_3 $\rightarrow$ products

- Can we explain the *T*-dependence?
- Can we determine the products? That is HCN + NH_2 or $NCNH_2$ + H?

Neutral-Neutral Reactions: branching ratios

- No ‘universal’ method
- *Ab initio* calculations
- Experiments on reactions that yield H atoms

a) Bordeaux group (Bergeat, Loison, et al) use a flow system and create CH radicals ($CHBr_3 + 3\ K \rightarrow CH + 3KBr$) and observe H atoms by ‘resonance fluorescence’

b) Leeds group (Blitz, Seakins, et al) carry out time-resolved experiments $CHBr_3 + 3\ h\nu \rightarrow CH + 3Br$) and observe H atoms by LIF ‘laser-induced fluorescence’

Note that a number of important low *T* reactions involve addition of radical followed by H-atom elimination

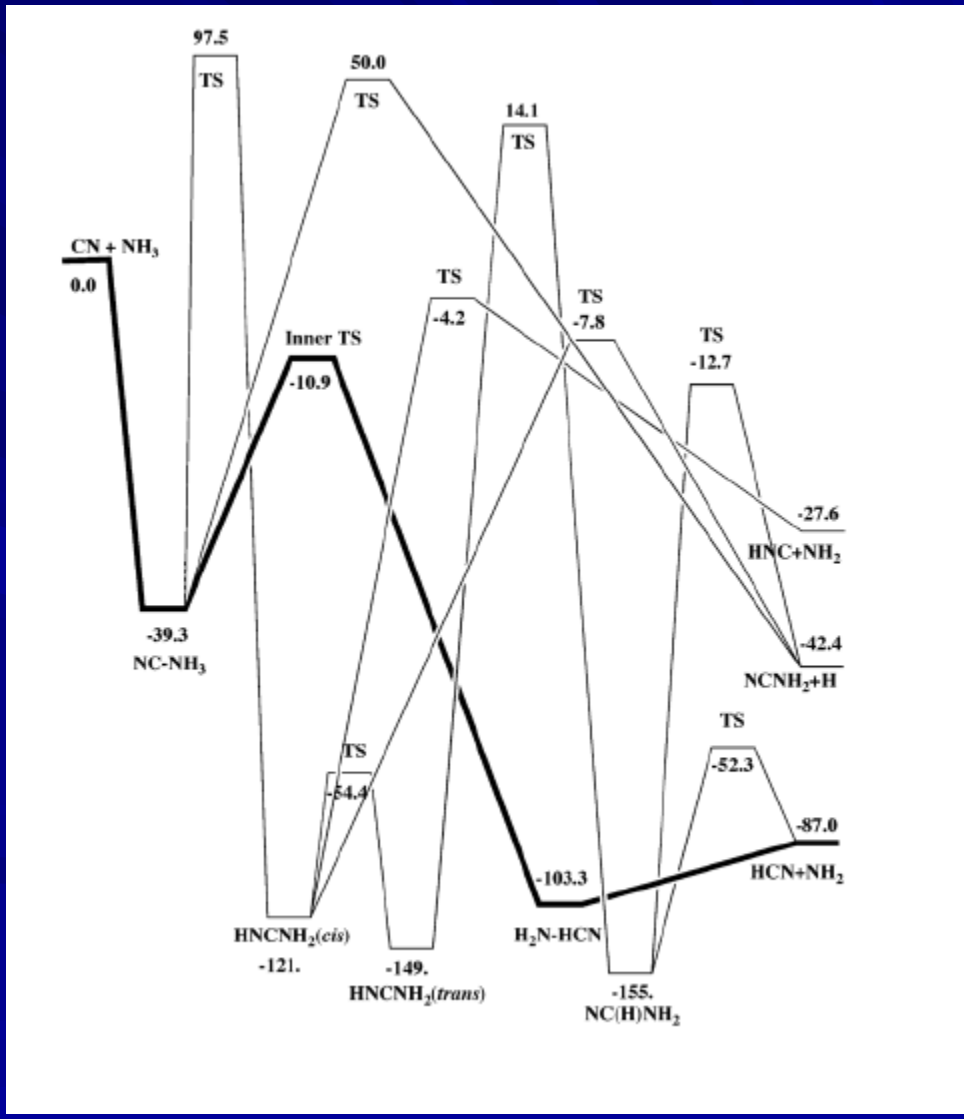
e.g. $CH + C_2H_2 \rightarrow C_3H + H$

Neutral-Neutral Reactions: Theory and Experiments on $CN + NH_3 \rightarrow$ products

- *Ab initio* calculations of reaction path (Dahbia Talbi)

No low energy path to $NCNH_2 + H$; reaction proceeds 100% to $HCN + NH_2$

- Calculations of $k(T)$ using two-transition state method of Klippenstein & Georgievskii

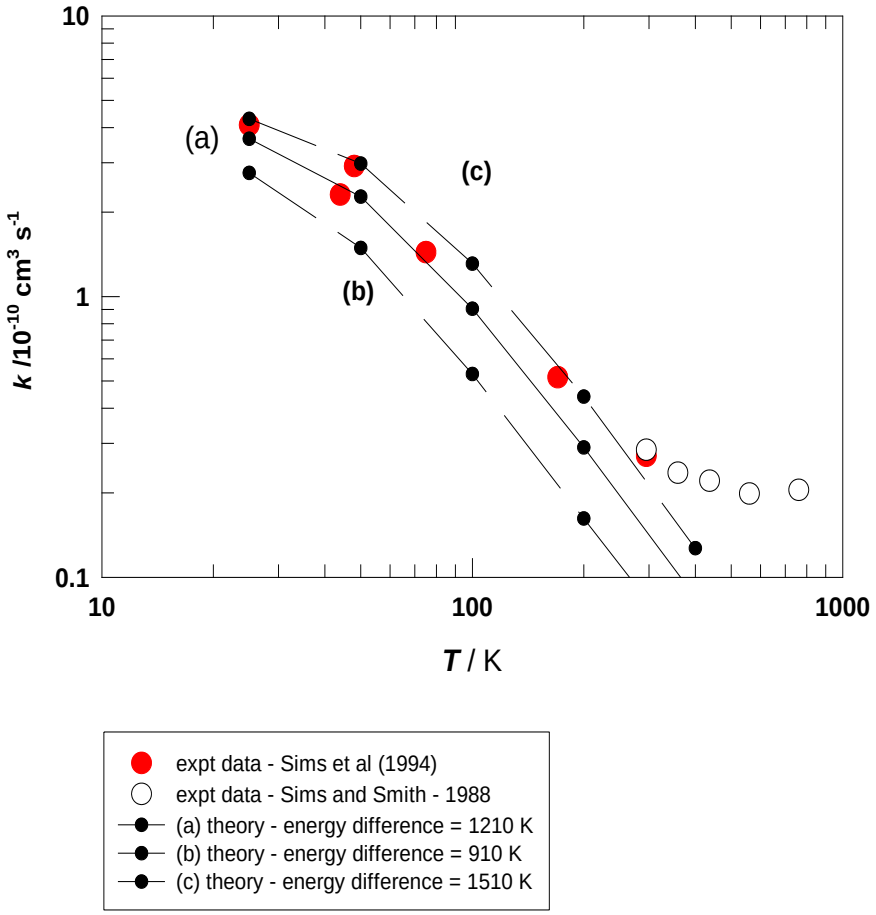


(D Talbi & IWMS, *PCCP*, **11**, 8477 (2009))

Neutral-Neutral Reactions: Theory and Experiments on $CN + NH_3 \rightarrow$ products

Large points show experimental rate coefficients from 23 to ca. 750 K

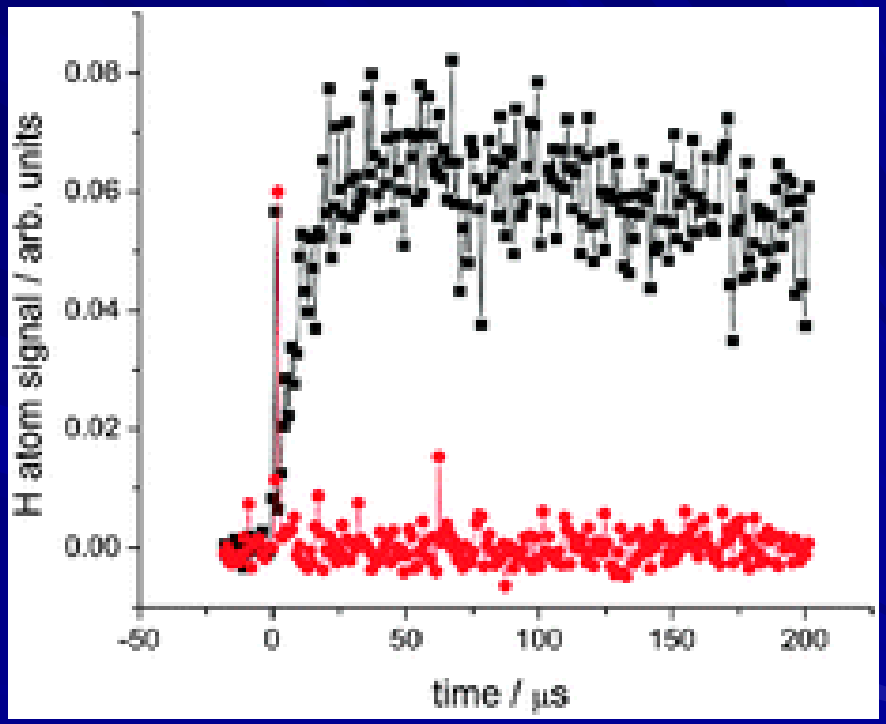
Small points and lines show results of TST calculations with different choices for the inner transition state barrier



Neutral-Neutral Reactions: Theory and **Experiments on** **CN + NH_3 → products**

- CN produced by PLP from ICN
- H atoms observed by LIF

- **from CN + C_2H_2**
- **from CN + NH_3**



Yield of H atoms from CN + NH_3 < 5%

Gas-Phase Chemistry: role of modelling

- Main aim is to reproduce the observed molecular abundances in different regions of ISM
- Inclusion of errors on the rate coefficients allows one to identify significant discrepancies
- Modelling can also be used to identify ‘important reactions’
- In KIDA (Kinetic Database for Astrochemistry) efforts are made to give estimate of uncertainties
- In KIDA, ‘data sheets’ are provided for important reactions

http://kida.obs.u-bordeaux1.fr : Valentine Wakelam and others

Gas-Phase Chemistry: some ‘take home messages’

- Ion-neutral reactions measured over wide *T*-range and quite well-understood – it seems that charge exchange be treated by same (Langevin) methods as atom/ion transfers?

- Extension of CRESU experiments to lower temperatures: 5 K?

- Low temperature trapping experiments on radiative association largely restricted to cation + H_2 reactions. No measurements on neutral-neutral associations: e.g. $C + H_2 \rightarrow CH_2 + h\nu$

- More details in IWM Smith, *Ann Rev Astronom Astrophys,* to be published this year.

Radical-Molecule Reactions: CN, C_2H + H_2

$$k(T) = \alpha\,(T / 300)^{\beta} \exp(-\gamma / T)$$

	$CN + H_2 \rightarrow HCN + H$	$C_2H + H_2 \rightarrow HCCH + H$
α / $cm^3\ s^{-1}$	5.0×10^{-13}	1.95×10^{-12}
β	2.60	2.32
γ / K	960	444
k (1000 K)/ $cm^3\ s^{-1}$	4.4×10^{-12}	2.0×10^{-11}

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^+	HDO	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	
NH	SiO	H_2O	MgNC	H_2CS	H_2C_3	CH_3CN	*c*-CH_2OCH_2	C_7H	CH_3C_4H	CH_3CH_2CHO
OH	SiS	H_2S	NaCN	*l*-C_3H	*l*-C_3H_2	CH_3NC	CH_2CHCN	$HOCH_2CHO$	C_8H	$(CH_2OH)_2$
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_3CONH_2	
CN	PO	HNC	SiCN	$HCNH^+$	H_2NCN	HC_3NH^+	H_2CCHOH	H_2C_6	C_8H^-	
CO	SH	HCO	CO_2	H_2CN	CH_2CO	H_2C_4	C_6H^-	CH_2CHCHO	CH_3CHCH_2	N = 11
CS	AlF	HCO^+	*c*-SiC_2	*c*-C_3H	HCOOH	C_5H		CH_2CCHCN		HC_8CN
CP	FeO	HOC^+	SiNC	HCCN	C_4H	C_5N				$HCOOC_2H_5$
NO	SiC	HN_2^+	AlNC	HNCO	HC_2CN	HC_4H				N = 12
NS	CF^+	HNO	HCP	$HOCO^+$	HC_2NC	HC_3CN				C_6H_6
SO	N_2	HCS^+	C_2P	HNCS	C_4Si	*c*-C_3H_2O				C_3H_7CN
HCl	LiH	C_3	AlOH	C_2CN	C_5	H_2CCHNH				N = 13
NaCl	SiH	C_2O	H_2O^+	C_3O C_3S	C_4N	C_5N^-				$HC_{10}CN$
KCl AlO	O_2	C_2S	H_2Cl^+	SiC_3 PH_3	H_2COH^+					$C_2H_5OCH_3$
OH^+	CN^-			C_3N^-	C_6H^-					

CRESU apparatus configured for radical-neutral reactions