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Gas phase reaction kinetics at very low temperatures: recent advances on carbon chemistry using the CRESU technique

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Abstract. The review describes briefly the chemistry of interstellar clouds and focusses on how bimolecular neutral – neutral reactions may influence its evolution. Experimental techniques that give information on the reactivity and the dynamics of these processes are presented with a special attention to the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) technique, which is the only one able to deliver rate coefficients at very low temperatures for reactions between two neutral partners. Recent advances concerning the reactivity of carbon-bearing molecules are described in more detail with a special attention to the reaction kinetics of C_2 and C_4H with small stable hydrocarbons. The bibliography includes 161 references.

I. Introduction

For many years, the field of gas phase reaction kinetics involving neutral partners has been restricted to experimental studies which were carried out essentially at temperatures greater or equal to room temperature. The interest in the chemistry of the Earth stratosphere that arose in the early 1970s stimulated the adaptation of experimental equipment to extend the study of kinetics down to 200 K. This led to a significant increase, although still limited, in the number of available rate coefficients at sub-ambient temperatures.[1–3] For reasons that will be explained further, only in some very specific cases experimental data had been obtained down to 77 K.[4–7] In the last twenty years, however, the development and adjustment of new technologies opened the possibility of exploring much colder temperature areas leading to a significant amount of reaction rate constant measurements down to 13 K.[8,9] Although some experiments were also carried out at 7 K,[8] these dealt with inelastic collisions and focussed on energy transfer processes only. In the solid state, it is worth mentioning however that this record was beaten and an abundant research field on autowave chemical transformations near 4 K has been developed within the last 20 years.[10–13]

From the fundamental point of view, the new obtained data in the gas phase were like a revolution for chemical physics science as they revealed that the Arrhenius equation does not hold for a large number of neutral – neutral reactions including those for which a saturated molecule was involved. Barrierless reactions, indeed, were found to be much more frequent than suspected. Furthermore, these new experiments stimulated the development of new theories of reactive collisions.[14–31] A comparison between experiment and theory at such low energies (let us remember that 13 K corresponds to about 1 meV) was actually a decisive test of the quality of potential energy surfaces required for a correct description of chemical processes. A large number of theoretical studies was then undertaken in order to reproduce the experiments but till now, most of these works were carried out on a case-by-case basis (see for example [14,18,24,26]) and no general trends are presently known to quantify the effectiveness of a chemical process at very low temperature although some very recent attempts are shedding interesting light in this difficult task.[9,21,30–32]

Beside these fundamental considerations, studying reactivity at temperatures as low as 10 K is of major importance for the understanding of a large number of (very) cold natural environments in which a rich chemistry is taking place. Whereas the mean surface temperature of the Earth is presently about 288 K, much lower temperatures can be found as, for example, in the area of Verkhoiansk in Siberia (Russia) where the thermometer can go down to 200 K. In our own atmosphere, recent observations indicate that the temperature at the mesopause can be lower than 150 K at high latitudes.[33] Thanks to the development of space missions, ground telescopes and satellites, new horizons were revealed to our knowledge and demonstrated the existence of even colder extraterrestrial environments. The atmosphere of Giant Planets or their satellites is only several tens of a Kelvin: 70 K at the tropopause of the now well known Saturn's satellite Titan,[34] 50 K in the atmosphere of Neptune[35] or Pluto.[36] In the coma of comets, temperatures ranging from 10 K to 200 K[37] have been determined according to the distance to the Sun and the position with respect to the nucleus. Beyond the solar system, we penetrate in the so-called interstellar medium, an apparently empty space which separates stars from each other. This very tenuous environment (mean density ~ 1 atom cm^{-3}) is actually quite heterogeneous containing for example very

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Table 1. List of interstellar molecules ordered by their number of atoms.[39,40]

Number of atoms (N)									
$N = 2$		$N = 3$		$N = 4$	$N = 5$	$N = 6$	$N = 7$	$N = 8$	$N = 9$
CH (1937)	CN (1940)	H_2O (1969)	HCO^+ (1970)	NH_3 (1968)	HCO_2H (1971)	CH_3OH (1970)	CH_3CHO (1973)	HCO_2CH_3 (1975)	CH_3OCH_3 (1974)
CH^+ (1941)	OH (1963)	OCS (1971)	HCN (1971)	H_2CO (1969)	HC_3N (1971)	CH_3CN (1971)	CH_3CCH (1973)	CH_3C_3N (1984)	CH_3CH_2OH (1975)
H_2 (1970)	CO (1970)	H_2S (1972)	HNC (1973)	HNCO (1972)	CH_2NH (1973)	NH_2CHO (1971)	CH_3NH_2 (1974)	CH_3CO_2H (1997)	CH_3CH_2CN (1977)
CS (1971)	SiO (1971)	C_2H (1974)	N_2H^+ (1974)	H_2CS (1973)	NH_2CN (1975)	CH_3SH (1979)	CH_2CHCN (1975)	C_7H (1997)	HC_7N (1978)
SO (1973)	NS (1975)	HDO (1975)	SO_2 (1975)	C_3N (1977)	H_2CCO (1977)	C_2H_4 (1983)	HC_5N (1978)	$HOCH_2CHO$ (2000)	HC_9N (1978)
SiS (1975)	C_2 (1977)	HCO (1976)	HNO (1977)	HNCS (1979)	C_4H (1978)	C_5H (1986)	C_6H (1986)	C_6H_2 (2001)	CH_3C_4H (1984)
NO (1978)	HCl (1985)	HCS^+ (1981)	HOC^+ (1983)	$HOCO^+$ (1981)	SiH_4 (1984)	CH_3NC (1988)	c-C_2H_4O (1997)	CH_2CHCHO (2004)	$(CH_3)_2CO$ (1987)
AlCl (1987)	AlF (1987)	c-SiC_2 (1984)	MgNC (1986)	C_3H (1985)	c-C_3H_2 (1985)	HC_2CHO (1988)	CH_2CHOH (2001)	CH_2CCHCN (2006)	C_8H (1996)
KCl (1987)	NaCl (1987)	C_2S (1987)	C_3 (1988)	C_3O (1985)	CH_2CN (1988)	HC_3NH^+ (1994)	C_6H^- (2006)		$HC_{11}N$ (1997)
PN (1987)	SiC (1989)	CO_2 (1989)	CH_2 (1989)	H_3O^+ (1986)	C_5 (1989)	C_5N (1998)			C_6H_6 (2001)
CP (1990)	NH (1991)	C_2O (1991)	NH_2 (1993)	$HCNH^+$ (1986)	SiC_4 (1989)	C_4H_2 (2001)			$(CH_2OH)_2$ (2002)
SiN (1992)	SO^+ (1992)	N_2O (1994)	NaCN (1994)	c-C_3H (1987)	CH_4 (1991)	HC_4N (2004)			$NH_2CH_2CO_2H$ (2003)[a]
CO^+ (1993)	HF (1997)	MgCN (1995)	H_3^+ (1996)	C_3S (1987)	C_3H_2 (1991)	CH_2CNH (2006)			CH_3CH_2CHO (2004)
LiH (1998)[a]	SH (2000)	SiCN (2000)	AlNC (2002)	C_2H_2 (1989)	HCCNC (1992)	c-H_2C_3O (2006)			$CO(CH_2OH)_2$ (2005)[a]
FeO (2002)	N_2 (2004)	SiNC (2004)		HC_2N (1991)	HNCCC (1992)				CH_3C_5N (2006)
CF^+ (2006)	O_2 (2007)			H_2CN (1994)	H_2COH^+ (1996)				CH_3C_6H (2006)
PO (2007)				SiC_3 (1999)	C_4H^- (2007)				CH_3CONH_2 (2006)
				CH_3 (2000)					C_8H^- (2007)
									CH_2CHCH_3 (2007)

Note. The year of their discovery is also included in parentheses; 'c' stands for cyclic species. [a] Tentative or still controversial detections.

diluted (< 0.01 atom cm^{-3}) and hot ($\sim 10^6$ K) areas, remnants of super novae explosions where atoms have lost several of their electrons and much colder (10 K) and denser (10^4 molecules cm^{-3}) zones where an amazingly rich chemistry is now identified. The latter are called molecular clouds (or dark clouds) because most of the molecules identified in the interstellar medium were discovered in these dense enough media so that the UV light coming from neighbouring stars cannot penetrate deep inside.[38] To date, thanks to radioastronomy and satellites such as ISO (Infrared Space Observatory) or orbiting telescopes such as HST (Hubble Space Telescope), about 150 different molecules have been identified in the interstellar medium (230 including isotopomers).[39,40] This number is permanently growing and the development of the ALMA interferometer in Chile and the future space telescope Herschel (launching July 31st, 2008) will certainly considerably enrich the list. A compilation of the presently known molecules in the interstellar and circumstellar media is presented in Table 1 which also includes the year of the first detection of each molecule. More details, and particularly the references announcing the first discovery of each species, can be found at the website held by Woon.[39] How such a variety of molecules, among which a large number are organic, can be produced and survive in such harsh environments is a fundamental question that gave birth to a new field in astronomy about 40 years ago: astrochemistry.

In the present review, I will essentially focus the discussion on interstellar molecular clouds and experimental techniques that could be employed for the study of gas phase neutral–neutral reaction kinetics at very low temperature.

II. Neutral–neutral reactions in interstellar chemistry

Understanding how stars and their associated planetary system form is one of the major challenges of modern astrophysics. It is now largely accepted that molecular clouds are the cradle of stars which are generated by local gravitational collapses inside the cloud leading to a strong pressure increase which eventually will start thermonuclear reactions. In this frame, molecules play a critical role in the dynamical stability of the cloud and act as a cooling reservoir.[41] Inelastic collisions with other species, and more particularly H_2, which is by far the more abundant molecule, enable conversion of kinetic energy into radio or mm radiations which eventually can escape from the cloud which is optically thin in this wavelength range. As a consequence of molecular cooling, the thermal pressure inside the cloud is reduced and eventually will not be able to counterbalance gravitation any more leading to the collapse of the cloud.[42]

It is then essential to clearly understand the fate of interstellar molecules. With this objective in mind, astronomers started to develop gas phase photochemical models of interstellar clouds in the mid-seventies.[43–48] Their aim was to reproduce the observed abundances of these molecules taking into account all chemical and physical processes that were expected to play a role in their formation and destruction. Knowledge of a large number of parameters was required including the photon and cosmic ray fluxes coming from outside the cloud, the rate constants for reactive and inelastic collisions and the branching ratios of reactions. The most elaborated interstellar models are presently taking into account about 400 species (neutral and charged) and 4000 processes.[49,50] It is worth mentioning here that the most recent models are now starting to include gas surface processes, as the presence of important molecules such as H_2 cannot be explained by chemical schemes simply based on gas phase chemistry. The physical conditions reigning in molecular clouds (low temperatures, low pressures) restrict however the chemistry to two-body, exothermic and barrierless processes. The different families of reactions that are considered in interstellar models are listed in Table 2.

Table 2. Classes of chemical reactions that are included in chemical models of interstellar clouds.

Reaction	Reaction scheme
Ion–molecule reactions	
Charge transfer	$A^+ + B \rightarrow B^+ + A$
Radiative association	$A^+ + B \rightarrow AB^+ + h\nu$
Atomic transfer	$AB^+ + C \rightarrow A^+ + BC$
Electronic recombination reactions	
Radiative	$A^+ + e^- \rightarrow A + h\nu$
Dissociative	$AB^+ + e^- \rightarrow A + B$
Photochemical processes	
Photodissociation	$AB + h\nu \rightarrow A + B$
Photoionisation	$AB + h\nu \rightarrow AB^+ + e^-$
Neutral neutral reactions	
Atomic transfer	$A + BC \rightarrow AB + C$
Radiative association	$A + B \rightarrow AB + h\nu$
Other reactions	
Ion–ion neutralisation	$A^+ + B^- \rightarrow AB$
Neutral – negative ion reactions	$A^- + B \rightarrow AB + e^-$
	$A^- + BC \rightarrow AB^- + C$
Electron attachment	$A + e^- \rightarrow A^-$ or
	$AB + e^- \rightarrow A^- + B$

Chemistry is initiated by ionisation of molecular and atomic hydrogen, helium and carbon atoms by the VUV radiation of stars in the outer part of the cloud and cosmic rays in its inner part, which is opaque to VUV photons. A series of ion–atom (H) and ion–molecule (H_2) reactions lead to the production of bigger polyatomic ion molecules, which eventually will recombine dissociatively thus producing neutral molecules. These can also be generated by radiative association processes and neutral–neutral reactions, which is the scope of this paper. Then, although detected cations in the interstellar medium represent only about 10% of the presently known species, they play a central role in the increase of chemical complexity. Very recently, it is worth stressing that the first negative ion molecules C_8H^- (Refs 51, 52), C_6H^- (Ref. 53) and C_4H^- (Ref. 54) have been discovered in the molecular envelope of IRC +10 216 and in the dense molecular cloud TMC-1, which will certainly focus the interest of modellers on the anion chemistry in a very close future.

For about twenty years and up to the early nineties, interstellar cloud chemistry was thought to be essentially driven by ion–molecule reactions because, due to the strong attractive forces between an ion and the permanent or induced dipole on the neutral reagent, these processes were generally barrierless and very fast ($> 10^{-9}$ cm^3 s^{-1} $molecules^{-1}$). On the other hand, for many years, neutral–neutral reactions were expected to be inefficient at the very low temperature of molecular clouds as they were thought to proceed with positive activation energy barrier (E_a). The temperature dependence of the rate coefficient k was then usually described by the Arrhenius equation $k = k_0 \exp(-E_a/k_B T)$ which leads to insignificantly small rate coefficients at temperature of *ca* 10 K. Only a few radical–radical reactions such as $O + OH \rightarrow O_2 + H$ were considered in models because this class of processes could be expected to have no barrier.[47] Furthermore, at that time very few data were available at temperatures below 200 K because experimental techniques were not suited for this kind of measurements (see below). In the early nineties, as

explained further, the adaptation of the CRESU technique to the study of radical–neutral reactions shed a new light on the field and demonstrated that a large number of these processes, and more particularly those involving a saturated molecular partner, can be very efficient at temperatures as low as 13 K. This discovery was carefully considered by interstellar cloud modellers who then published dedicated articles analysing the impact of these new views.[49, 55, 56] The number of neutral–neutral processes included in models was significantly increased and rate coefficients were re-evaluated on the bases of the new experimental data (initially concerning the reactivity of the CN and CH radicals). The main consequence of this upgrading was to reduce the rate of formation of complex species because of a prompter destruction of small radicals which initiate the chemical scheme leading to complex molecules.[55]

Although a significant number of binary neutral–neutral reactions have been studied at very low temperatures now, much more data are still required. In the following section I will discuss the main difficulties faced by this kind of studies and I will show how the CRESU technique can resolve a large part of them.

III. Obtaining rate coefficients at very low temperatures

As mentioned previously, for a long time low temperature experimental rate coefficients were not available. Modellers had then to estimate or evaluate these parameters and therefore the results of simulations of the interstellar cloud chemistry were subject to very large uncertainties although they were able to reproduce some general aspects. To obtain low temperature data, one common practice (still in use nowadays) was to extrapolate the temperature dependence of a reaction for which rate coefficients were measured at room temperature and higher. As illustrated in Figure 1*a* and 1*b*, this can lead to dramatic errors at temperatures as low as 20 K. In this example, the reaction CN + C_2H_6 was initially studied by Herbert *et al*.[57] in the temperature range 297–694 K. Data are shown in Fig. 1*a* on an Arrhenius plot and seem to fit an Arrhenius dependence with modest activation energy. Figure 1b shows the attempt to extrapolate these measurements down to interstellar temperatures. As it can be seen, the extrapolated rate coefficient decreases impressively by almost 7 orders of magnitude from room temperature down to 20 K. However, experimental results obtained by Sims *et al*.[58] one year after the study by Herbert *et al*. show that the rate coefficient behaviour changes completely since a minimum was reached at about 200 K and then the rate starts again to increase leading to a difference of 6 orders of magnitude at 25 K between experiment and extrapolation. Fortunately, all situations are not as critical as this one, but this example clearly indicates that experimental data are definitely required to strongly and correctly constrain interstellar cloud models.

It is then necessary to generate a cool environment in which reaction kinetics could be studied. The simplest idea is to cryogenically cool down a slow-flow reactor cell. In that case, however, one is immediately faced with the decay of the saturated vapour pressure of gases when the temperature is reduced and, as a consequence, condensation to the refrigerated walls of the cooled vessel. The solution to prevent condensation is to limit the total concentration of the reagents in the cell to keep them at partial pressures that are below their vapour pressure at the wall temperature. However, the concentration must be high enough to perform kinetic experiments, and only gases with a significant vapour pressure at the wall temperature are then suitable. This method therefore becomes more and more limited at temperatures lower than 200 K and was never applied below the liquid nitrogen temperature of 77 K. At this temperature, only a few experiments have been conducted for a limited number of reactions involving gases such as CO (Refs 6, 7) and H_2 (Refs 4, 5) which have high enough vapour pressures at such temperatures. More details and references in relation to these techniques can be found in Ref. 3.

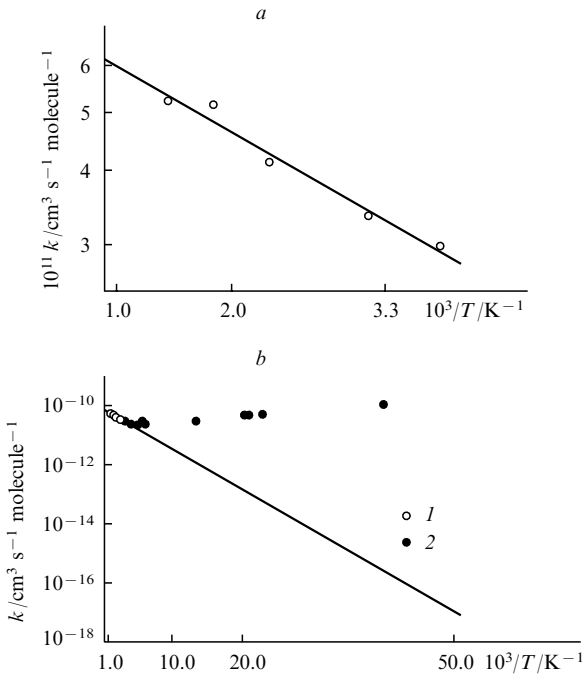


Figure 1. Arrhenius plot of the rate constant for the reaction CN + C_2H_6 in the temperature range 297–694 K (*a*)[57] and Arrhenius plot of the rate constant for the reaction CN + C_2H_6 in the temperature range 25–694 K (*b*) (*1*),[57] (*2*).[58]
The straight line is an Arrhenius extrapolation to low temperature of the data obtained by Herbert *et al*. at temperature greater than 297 K.

Generating low temperatures can also be achieved using supersonic expansions. The fundamentals of the technique here is to convert part of the internal energy of a quasi static flow into kinetic energy. There are several kinds of supersonic expansions.

The simplest is the so-called free jet, which is formed by expanding a gas from a high-pressure reservoir (typically $\sim$1 bar) into a high-vacuum chamber through a small orifice or a nozzle. The temperatures obtained with this method can be extremely low down to 0.1 K but cannot generally exceed 20 K. The density is typically less than 10^{15} cm^{-3} in most of the useable areas of the jet.[59, 60] However, the expansion is inhomogeneous, with strong spatial density and temperature gradients.[61, 62] As the expansion evolves the collision frequency decreases and therefore the different temperature moments (translation, rotation and vibration) cannot reach equilibrium.[63] The gradients of temperature and density, the low frequency of collisions and the short useable area of the jet make it difficult to perform kinetic experiments in these free-jet expansions although some ion–molecule reactions have been studied[60] because for this class of processes the long-range electrostatic forces are strong enough to attract together reagents travelling with virtually no translational velocity. Nevertheless, free jet expansions are widely employed in spectroscopy[64] for which problems of disequilibrium in the flow are not important.

A molecular beam is an extension of the free jet technique as it is obtained by extracting the centreline beam of the free jet by skimming and pumping away the excess gas. The skimming

action prevents supersonic waves from spreading back into the gas and increasing the translational temperature, and at the same time, enables one to obtain a well-collimated flow with a narrow velocity distribution. Molecular beams are very useful in studies of collisional dynamics.[65,66] As the frequency of collisions is very small in a molecular beam, data are obtained from experiments in which two collimated reagent beams intersect at fixed angle in a scattering region where single reactive or inelastic collisions occur between the components of the beams.[65–72] The species of each beam are characterised by a well-defined velocity and usually also internal quantum states. By varying the velocity of the molecular beams and their intersection angle, differential cross sections (product angular and velocity distributions) can be measured at different collisional energies. The technique provides valuable information on the nature of the products of the reaction and its mechanism.[72] Most of these so-called crossed molecular beam machines, however, work with beams at right angle and therefore the usual collisional energies are rather high with respect to those encountered in the molecular rich interstellar medium. Some devices are designed to vary the beam intersection angle which enables some reduction in the relative collision energy.[73–77] The lowest collision energy presently available was obtained by Naulin and Costes[76] who can make experiments using an apparatus for which the intersection angle can be varied from 90° down to 22°, the latter corresponding to a collision energy of 0.35 kJ mol^{-1} (*i.e.* $\sim$30 K). In this experiment, relative total cross sections (also referred as excitation function in the literature) can be integrated assuming a Maxwell distribution of relative velocities at temperature T and a Boltzmann distribution of reactant internal energies to extract a thermal rate coefficient, $k(T)$. This, however, is a relative value and has to be normalised using data obtained from other techniques. More interestingly, the technique provides the temperature dependence of the calculated rate coefficient which can be directly compared with other experimental methods.[76,78]

Absolute rate coefficients can be obtained as a function of temperature using 'collimated' supersonic flows generated by the isentropic expansion of a buffer gas through an axisymetric convergent–divergent Laval nozzle.[79] At the exit of the nozzle, the supersonic flow, typically 10 to 20 mm in diameter, moves with a bulk velocity which is parallel to the axis of the nozzle and uniform for several tens of centimetres which is also the case for temperature, pressure and hence density. The diffusion velocity is always negligible with respect to the bulk velocity, thus avoiding the major problem of condensation associated with the use of cryogenically cooled cells. As a consequence, in such expansions, heavily supersatured conditions prevail and as a matter of example condensable species such as water, ammonia[80] or even polycyclic aromatic hydrocarbons[81,82] can be maintained in the gas phase at very low temperatures. In contrast to free jet expansions and molecular beams where the concept of temperature is not really valid, the relatively high gas density (10^{16}–10^{17} molecule cm^{-3}) in the uniform supersonic flow ensures that frequent collisions take place during the expansion and subsequent flow, maintaining thermal equilibrium. It is worth stressing here that the temperature of the supersonic flow is not a tuneable parameter as it is constrained by the divergent profile of the Laval nozzle which is specifically designed to obtain a given temperature and pressure in the supersonic flow.† Hence, a series of Laval nozzles are required to match the range of temperature that needs to be explored. Clearly, uniform supersonic flows are ideal chemical reactors.[8,79,83]

Uniform supersonic flows were initially developed in a continuous flow version for the study of ion–molecule reactions by Rowe and co-workers[79] in the early eighties in the laboratoire d'Aérothermique in Meudon (France). The technique was christened as CRESU, a French acronym meaning Cinétique de Réaction en Ecoulement Supersonique Uniforme which can be translated in English by Reaction Kinetics in a Uniform Supersonic Flow. About ten years later, the methodology was adapted to the study of neutral–neutral reactions[83] at the Université de Rennes 1 (France) and in the mid-nineties mimicked at the University of Birmingham (United Kingdom).[84]

The typical temperatures than can be achieved are usually in the range 15–300 K.[8,9] However, the reservoir of the nozzle and the nozzle itself can be pre-cooled using for example liquid nitrogen. In these conditions, supersonic flows with a temperature as low as 7 K (see Refs 85, 86) can be achieved. The choice of the reactant, however, is then limited to those having a vapour pressure high enough to avoid condensation on the walls of the reservoir of the nozzle in which the flow is almost stagnant.

With respect to the determination of rate coefficients, a limitation of the CRESU technique lies in the supersonic nature of the flow which restricts the available hydrodynamic time to a few hundreds of microseconds. As a consequence, only rate coefficients greater than 5×10^{-13} cm^3 s^{-1} molecule^{-1} can usually be measured. Another aspect that is worth mentioning concerns the size of the apparatus. The supersonic flow is made of an inner isentropic core embedded into a boundary layer resulting from the viscosity of the gas. Minimising this boundary layer (and hence optimising the length of the supersonic flow) requires introducing large gas flow rates into the reservoir (typically 50 standard litres per minute). Since Laval nozzles are usually designed to obtain a low pressure into the supersonic flow (typically a fraction of a mbar) in order to avoid possible clustering, large pumping capacities are necessary for the apparatus (typically 25 000 m^3 h^{-1}). The size of pumps directly determines the size of the chamber which is 3 m long and 50 cm in diameter.

If pressures of about 1 mbar are however acceptable in the supersonic flow for the study of a given process, then a significant reduction in pumping capacities can be accepted as it is the case for the mini-CRESU that has been constructed in the Université de Bordeaux 1 by Costes and co-workers.[87] This apparatus however cannot reproduce temperatures lower than 50 K in the supersonic flow because of its limited pumping capacities. In order to reduce the cost required for the development of a CRESU continuous supersonic flow, another alternative can be to pulse the supersonic flow so that large flow rates are only introduced during a few milliseconds and therefore pumping capacities are significantly diminished. The pulsed CRESU technique was first developed at the University of Arizona (USA) by Smith and co-workers[88] and it is now also in use at the University of Berkeley (USA) in Leone's group[89] and at the University of Goettingen (Germany) in Troe's team.[90–92] Another apparatus is under development at the University of Leeds (United Kingdom) in Pilling's group. Due to their small pumping capacities, the pulsed CRESU supersonic flows are limited to temperatures greater than 50 K.

Table 3 lists the two-body neutral–neutral reactions that were experimentally studied using the continuous or pulsed version of the CRESU method.

IV. Recent results on the carbon chemistry at very low temperatures

In this section, I will discuss recent results that were obtained concerning the reactivity of neutral carbon-bearing radicals,

† It is worth mentioning here that originally, Laval nozzles were developed in the aeronautics area for their ability in maintaining a collimated gas at their exit. They are used as exhausts for the burnt gases of rockets because their design optimises the thrust when the spacecraft takes off.

Table 3. Bimolecular reactions studied using the continuous and pulsed versions of the CRESU apparatus.

Reactant	Radical	T_{min}/K [a]	Ref.	Reactant	Radical	T_{min}/K [a]	Ref.
$O(^3P_J)$	OH	39	93	C_2H_6	CN	25	58
O_2	CN	13	83, 94		CH ($v = 0$)	23	110
	CH ($v = 0$)	13	95		NH	53	105
	C_2H	15	96		C_2H	96	116
	$C_2(^1\Sigma_g^+)$	145	97		$C_2(^1\Sigma_g^+)$	24	111
	$C(^3P_J)$	15	18, 98, 99		$C_2(^3\Pi_u)$	200	113
	$Al(^2P_J)$	23	24, 100		C_4H	39	112
	$Si(^3P_J)$	15	101, 102	MeC≡CH	CN	15	117
	$B(^2P_J)$	24	103		CH ($v = 0$)	77	87
D_2	CH ($v = 0$)	13	104		C_2H	63	117
NO	CH ($v = 0$)	13	95		C_4H	39	112
	NH	53	105		$C(^3P_J)$	15	118
	$C_2(^1\Sigma_g^+)$	24	97	$CH_2{=}C{=}CH_2$	CN	15	117
	$C_2(^3\Pi_u)$	24	97		CH ($v = 0$)	77	87
	$C(^3P_J)$	15	18, 99		C_2H	63	117
	$Si(^3P_J)$	15	101		C_4H	39	see [c]
H_2O_2	OH	96	106		$C(^3P_J)$	15	118
HBr	OH	23	107, 108	$MeCH{=}CH_2$	CH ($v = 0$)	77	87
NH_3	CN	25	83		NH [b]	53	105
	CH ($v = 0$)	23	95		C_2H	15	96
	C_2H	104	109		C_4H	39	see [c]
CH_4	CH ($v = 0$)	23	110		$C(^3P_J)$	15	98
	NH	53	105		$O(^3P_J)$	23	31
	$C_2(^1\Sigma_g^+)$	24	111	C_3H_8	C_2H	96	116
	C_4H	200	112		$C_2(^1\Sigma_g^+)$	24	111
C_2H_2	CN	25	58		$C_2(^3\Pi_u)$	36	113
	CH ($v = 0$)	23	110		C_4H	39	112
	NH [b]	53	105	C_4H_2	NH [b]	53	105
	C_2H	15	96	but-1-yne	C_4H	39	see [c]
	$C_2(^1\Sigma_g^+)$	24	111	buta-1,3-diene	C_2H	104	119
	$C_2(^3\Pi_u)$	24	113		C_4H	39	see [c]
	C_4H	39	112	*cis*-but-2-ene	$O(^3P_J)$	23	31
	$C(^3P_J)$	15	14, 98	but-1-ene	CH ($v = 0$)	23	110
	$Si(^3P_J)$	15	114		C_2H	103	119, 120
	$B(^2P_J)$	23	78		C_4H	39	see [c]
C_2H_4	CN	25	58		$O(^3P_J)$	23	31
	CH ($v = 0$)	23	110	$Me_2C{=}CH_2$	C_2H	104	119
	NH [b]	53	105		$O(^3P_J)$	23	31
	C_2H	15	96	*trans*-But-2-ene	$O(^3P_J)$	23	31
	$C_2(^1\Sigma_g^+)$	24	111	n-Butane	C_2H	96	116
	$C_2(^3\Pi_u)$	24	113		C_4H	39	see [c]
	C_4H	39	112		$O(^3P_J)$	23	31
	$C(^3P_J)$	15	98	isobutane	C_2H	104	119
	$Si(^3P_J)$	15	114	benzene	C_2H	105	121
	$B(^2P_J)$	23	115	anthracene	CH ($v = 0$)	58	82
	$O(^3P_J)$	39	31	MeCN	C_2H	165	119
				EtCN	C_2H	104	119
				Pr^nCN	C_2H	104	119

[a] T_{min} is the minimum temperature at which the experiment has been carried out. [b] For these reactions, the binary nature is not firmly established. [c] Personal unpublished data.

and more particularly C_2 and C_4H, in the presence of hydrocarbon reactants. One of the main motivations for these studies lay in the involvement of these species in the photochemical cycle of diacetylene C_4H_2 in the atmosphere of Titan, a molecule considered to be an important step through the production of polyacetylene polymers and eventually the observed hazes.[122] Furthermore, both radicals have been identified in the interstellar medium [123–129] as well and can contribute to the production of more complex molecules by reacting with other hydrocarbons.

Rate coefficients were measured using the continuous CRESU apparatus available in Rennes in the temperature range 24–300 K for reactions involving C_2 (Refs 111, 113) and 39–300 K for those concerning C_4H.[112] The CRESU supersonic flow was associated to laser techniques to produce and detect the radicals *in situ* using the time resolved Pulsed Laser Photolysis–Laser Induced Fluorescence (PLP-LIF) technique. The fundamentals of the method have been described in detail elsewhere [83] and therefore a brief summary will be presented here focussing only on the specificities connected to the present studies. The PLP-LIF technique uses two pulsed lasers which are combined and co-propagate along the axis of the supersonic flow as it can be shown in Fig. 2. The first laser produces a homogeneous concentration of the

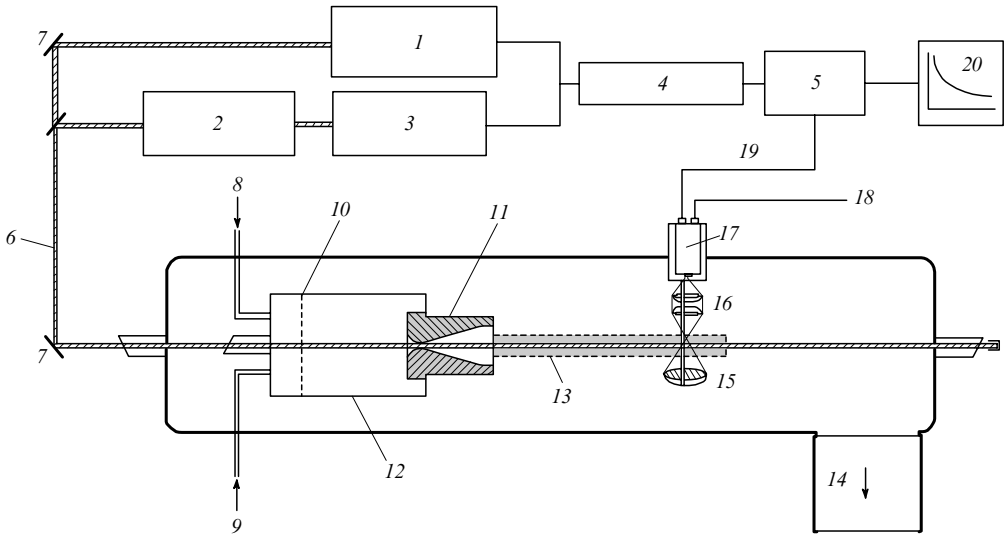


Figure 2. Sketch of the CRESU apparatus.
(*1*) Nd: YAG 266 nm or excimer 193 or 248 nm; (*2*) MOPO 730 or dye laser; (*3*) Nd: YAG 355 nm; (*4*) delay-generator; (*5*) computer interface; (*6*) laser beams; (*7*) combining optics; (*8*) precursor; (*9*) carrier/reagent gas main flow; (*10*) diffuser; (*11*) Laval nozzle; (*12*) moveable reservoir; (*13*) supersonic flow; (*14*) to pumps; (*15*) mirror; (*16*) telescope; (*17*) photomultiplier; (*18*) high voltage;(*19*) signal; (*20*) computer.

desired radical by photolysis of a suitable precursor. Then, after a variable and controlled time delay, the radical is excited to an upper electronic state by a tuneable laser acting as a probe and its fluorescence is collected by means of an optically fast telescope – mirror combination mounted within the main vacuum chamber in which it is set at right angle of the supersonic flow. Photons are then directed onto a fixed photomultiplier tube through an interference filter. Production and detection conditions for $C_2(X\,^1\Sigma_g^+)$, $C_2(a^3\Pi_u)$ and $C_4H(\widetilde{B}^2\Pi_i)$ are specified in Table 4.

For a given concentration of the reactant, the rate of loss of the radical along the flow axis is observed by scanning the delay time between the pulses from the photolysis and probe lasers using a delay generator. As the time delay between lasers increases the fluorescence signal decreases because radicals have been consumed in the reaction during their transit along the flow. A typical trace of the LIF decay can be seen in Fig 3 as well as the exponential fit which allows one to determine a first-order rate coefficient. Plotting this rate as a function of the reactant concentration, which can be varied by means of flow controllers, leads to a straight line whose slope gives the requested second-order rate coefficient. A typical second-order plot is shown in Fig. 4 as an illustration. It is worth stressing that this kind of study only scans the destruction of the reagent radical, hence no information can be extracted about the nature of the products and the branching ratios when several exit channels are open.

The C_2 radical is a peculiar molecule in the sense that its first excited electronic state $a^3\Pi_u$ ($v = 0$) is only separated from the ground state $X\,^1\Sigma_g^+$ ($v = 0$) by 610 cm^{-1} ($\sim$880 K).[130] In our experimental protocol,[97] photolysis of the precursor tetrachloroethylene at 193 nm produces mainly the triplet state which then can relax to the ground state when suitable conditions exist in the flow. Using He, Ar or N_2 as the buffer gas of the supersonic flow results in the presence of both states out of Boltzmann equilibrium in the flow. This is an uncomfortable situation for the study of the reactivity of the singlet state because introducing a reagent may result in a partial relaxation of the triplet state to the ground state in characteristic times of the same order of magnitude than the reaction of the ground state with that reagent. The LIF signal of the ground state will then be sustained by this source involving the measurement of an underestimated rate coefficient. To get rid of this complex situation, molecular oxygen was introduced in the reservoir of the nozzle at a fixed flow rate in addition to the studied reagent. We have demonstrated in a previous work [97]

Table 4. Production and detection conditions for the study of C_2 and C_4H radicals.

Radical	Precursor	Production laser	Excitation radiation,[a] dye	Collection radiation [a]	Interference filter
$C_2(X\,^1\Sigma_g^+)$	C_2Cl_4	excimer laser Lambda Physik LPX 210i 193 nm	231 nm $(D^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+)(0,0)$ coumarin 460	231 nm $(D^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+)(0,0)$	228 nm 11 nm fwhm
$C_2(a^3\Pi_u)$	C_2Cl_4	excimer laser Lambda Physik LPX 210i 193 nm	516 nm $(d^3\Pi_g \leftarrow a^3\Pi_u)(0,0)$ coumarin 307	563 nm $(d^3\Pi_g \leftarrow a^3\Pi_u)(0,1)$	561.4 nm 9 nm fwhm
C_4H	C_4H_2	excimer laser Lambda Physik LPX 210i 248 nm	408 nm $\widetilde{B}^2\Pi_i - \widetilde{X}^2\Sigma^+$ $^2\Sigma^+ - {}^2\Sigma^+$ styryl 9M (frequency doubling)	>430 nm $\widetilde{B}^2\Pi_i - \widetilde{X}^2\Sigma^+$ $^2\Sigma^+ - {}^2\Sigma^+$	low pass band filter GG435

[a] Wavelengths and the corresponding transitions (see text for details).

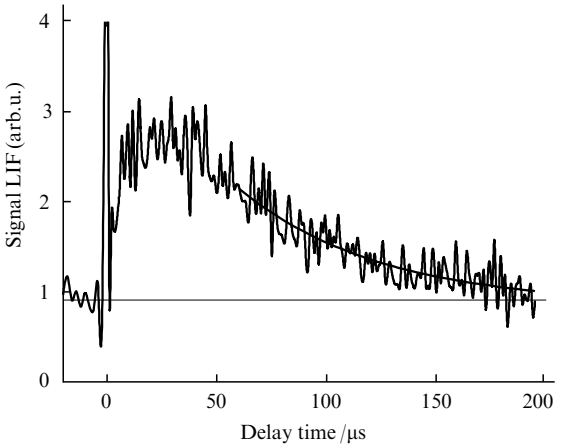


Figure 3. Decay of $C_2(X\,^1\Sigma_g^+)$ LIF signal at 36 K in the presence of C_2H_2 ($[C_2H_2] = 3.8 \times 10^{13}$ molecules cm^{-3}) and He buffer gas ($[He] = 5.3 \times 10^{16}$ atoms cm^{-3}), fit to a single exponential function.

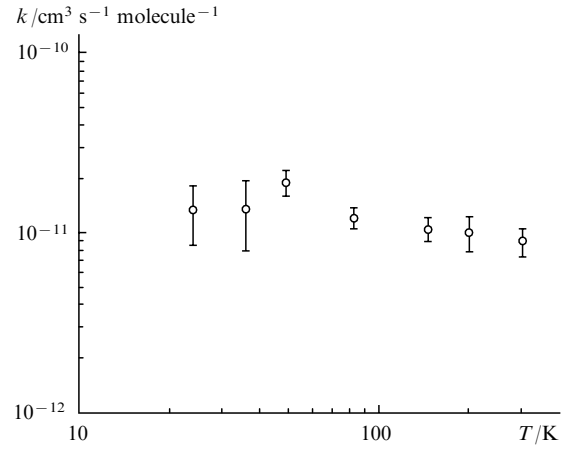


Figure 5. Second-order rate coefficients k for the removal of $C_2(X\,^1\Sigma_g^+)$ by CH_4 measured as a function of the temperature.

that O_2 was an efficient scavenger for the triplet state in the temperature range 50–200 K and therefore in this range, experiments were carried out with the singlet ground state only present in the reactor. At temperatures below 50 K, a mixture of both states was, however, present and consequences will be discussed in a further paragraph. At room temperature, oxygen was also introduced to generate an equilibrated population of triplet and singlet states before reaction with the reagent took place. The study of the removal of the triplet state was obviously made without introducing oxygen.

As mentioned in Table 4, the ground state was detected using the Mulliken bands at *ca.* 231 nm whereas the triplet state was identified through the Swan bands at about 516 nm. Five hydrocarbons were studied: CH_4, C_2H_2, C_2H_4, C_2H_6 and C_3H_8. The whole results are presented in Figs 5 to 9 where data are gathered by reactant for both singlet and triplet states. In the case of CH_4, the triplet state however is non reactive and therefore Fig. 5 contains data for the singlet state only.

As it can be observed, the reactivity of the triplet state is always lower than that of the ground state. The former is poorly removed by saturated hydrocarbons. For C_2H_6 measurements were only carried out at 200 K and 300 K because the process was not efficient enough at lower temperatures to be measurable by the CRESU apparatus. It seems however that destruction of $C_2(a^3\Pi_u)$ increases with the complexity of the hydrocarbon because measurement for propane showed a rate coefficient that is one order of magnitude greater than for C_2H_6. At the lowest temperature of the experiment however the rate coefficient was also unquantifiable. Although measurable, the removal of the triplet state with propane was still an order of magnitude lower than the reactivity of the singlet state. For unsaturated hydrocarbons, the triplet state is significantly more destroyed, but still in a less efficient way than the singlet state (about a factor of 2 to 3). Finally, it is important to stress that it is not possible in this experiment to discriminate between the pure reactivity and the possible relaxation of the triplet state to the ground state. It is then more appropriate to talk about the total removal of the triplet state rather than about the reactivity with reactants. More details can be found in Ref. 113.

With respect to the singlet ground state, the determined rate coefficients were always found to be very fast over the whole temperature range (greater than 10^{-10} cm^3 s^{-1} molecule^{-1}) except for methane for which the rate coefficient was measured to be about constant and at least one order of magnitude lower than for C_2- and C_3-based hydrocarbons. The temperature dependence is usually rather weak although a shallow maximum can be identified at about 50–70 K. Values are very close to the collisional limit and this is more particularly true for C_2H_2 and C_2H_4.

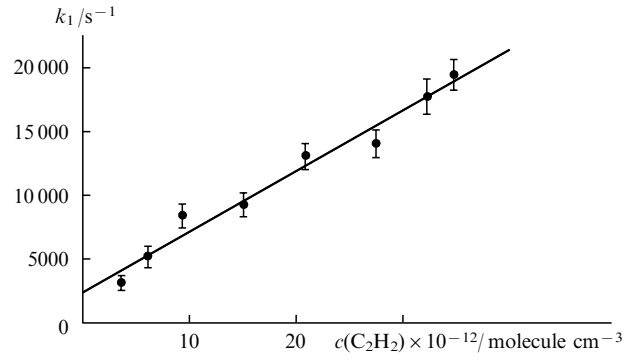


Figure 4. Plot for the removal of $C_2(X\,^1\Sigma_g^+)$ by C_2H_2 at 36 K in He, yielding a value for the second-order rate coefficient of $k = 4.7 \times 10^{-10}$ cm^3 s^{-1} molecule^{-1}.

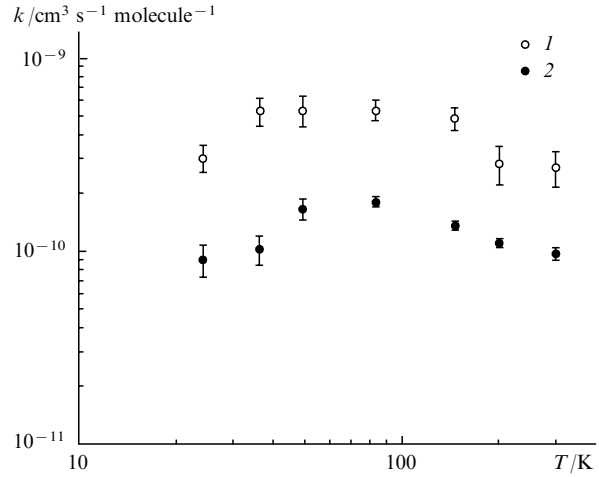


Figure 6. Second-order rate coefficients k for the removal of $C_2(X\,^1\Sigma_g^+)$ (*1*) and $C_2(a^3\Pi_u)$ (*2*) by C_2H_2 measured as a function of the temperature.

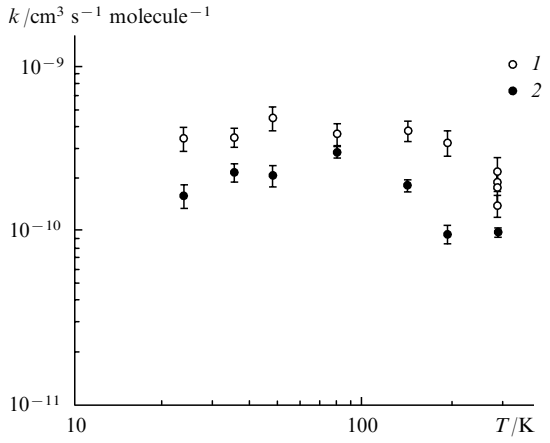


Figure 7. Second-order rate coefficients k for the removal of $C_2(X\,^1\Sigma_g^+)$ (*1*) and $C_2(a^3\Pi_u)$ (*2*) by C_2H_4 measured as a function of the temperature.

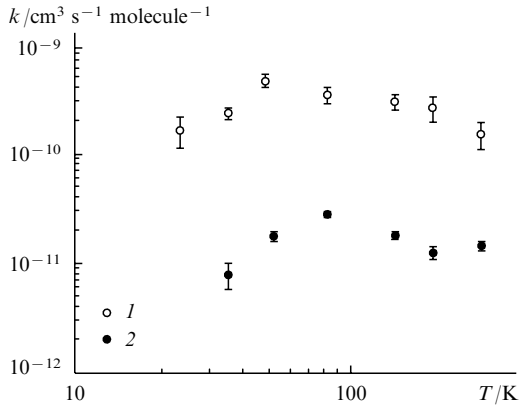


Figure 9. Second-order rate coefficients k for the removal of $C_2(X\,^1\Sigma_g^+)$ (*1*) and $C_2(a^3\Pi_u)$ (*2*) by C_3H_8 measured as a function of the temperature.

Concerning data obtained for the singlet state at temperatures below 50 K the analysis shows that the removal of the singlet state by the three saturated hydrocarbons only results from pure reactivity with these species because the removal of the triplet state is very small or immeasurable below 50 K. For unsaturated hydrocarbons the situation is more complex because the removal of the triplet and the singlet states are found to be very fast. Then the observed decay of the rate coefficient below 50 K could come from underestimated values of the rate coefficient due to relaxation of the triplet state. Since this latter process cannot be clearly evaluated, we prefer to maintain a cautious analysis and claim that these results are lower-limit rate coefficients for the reactivity of $C_2(X\,^1\Sigma_g^+)$ with C_2H_2 and C_2H_4. It is worth stressing however that this behaviour was already observed at low temperature for several reactions as for example those involving boron [78] or silicon [101, 114] atoms with hydrocarbons. As for the reaction $B + C_2H_2$,[78] a very small activation barrier can also be responsible for the observed decay.

More details concerning these studies can be found elsewhere [111] and more particularly a discussion concerning the possible consequences of these high rate coefficients for the photochemistry of Titan and Giant Planets. Briefly, these results show that reactions of C_2 with C_2H_2, C_2H_4 and C_2H_6 are significant destruction routes of the dicarbon radical which are presently not taken into account in the photochemical models of the atmospheres of these bodies. Moreover, in the chemistry of circumstellar envelopes,[131] the reactivity of C_2 with C_2H_2, which is a potential source of C_4H, has been recently updated using our new measurements because the rate coefficient which was in use was underestimated by at least a factor of four [50] (and associated website http://www.udfa.net/). Reactions with C_2H_4 and CH_4 which were absent in the chemical scheme have also been added.

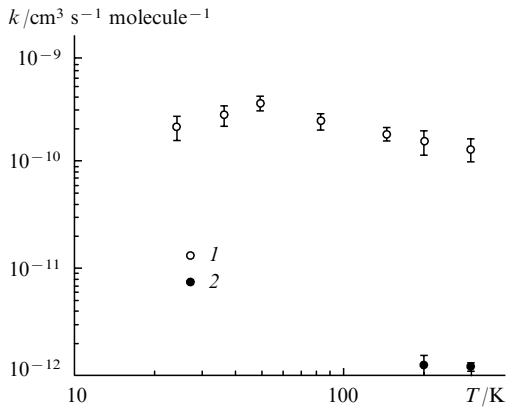


Figure 8. Second-order rate coefficients k for the removal of $C_2(X\,^1\Sigma_g^+)$ (*1*) and $C_2(a^3\Pi_u)$ (*2*) by C_2H_6 measured as a function of the temperature.

Finally, it is interesting to note that the kinetic behaviour of $C_2(X\,^1\Sigma_g^+)$ with C_2H_2, C_2H_4, C_2H_6 and C_3H_8 is quite similar to that observed for CH with the same reactants [110] indicating that the reactive mechanisms might be similar *i.e.*, insertion or addition of the radical followed by a hydrogen elimination. Regarding to the products, little information can be found in the literature. The reaction of the ground state of C_2 with CH_4 is expected to proceed *via* insertion of C_2 in the C–H bond.[132, 133] Kaiser *et al.* [134, 135] performed crossed molecular beam experiments to study the dynamics of $C_2(X\,^1\Sigma_g^+)$ and $C_2(a^3\Pi_u)$ with C_2H_2 (see Ref. 135) and C_2H_4 (see Ref. 134) at collision energies in the range 14.7–28.9 kJ mol^{-1} (*i.e.* ~1100–2300 K) and combined them with *ab initio* electronic structure calculations. They concluded that one exit channel was available and leads to 1 hydrogen atom elimination.

The C_4H radical is produced in the laboratory by photodissociation of diacetylene, C_4H_2, using UV or VUV light. One of the major difficulties concerning the study of the reactivity of this radical with hydrocarbons lies in the synthesis of diacetylene which cannot be bought from private companies. This very unstable molecule was made in our laboratory from the dehydrochloration of 1,4-dichloro-2-butyne ($C_4H_4Cl_2$). It was then stored into a 20-litre glass vessel buffered with helium under a total pressure of 1.2 bar. This mixture was then introduced in the reservoir of the Laval nozzle using a micrometric valve. The C_4H radical was produced by photolysis of C_4H_2 using an excimer laser working at 248 nm. The pencil of radicals generated all along the flow axis was detected by LIF exciting a $^2\Sigma^+ - {}^2\Sigma^+$ vibronic band of the $\widetilde{B}\,^2\Pi_i - \widetilde{X}\,^2\Sigma^+$ electronic system at a wavelength of *ca.* 408 nm. Fluorescence was collected with a photomultiplier tube through a low-pass glass filter (see Table 4).

Twelve hydrocarbons were studied including CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4 (propyne and propadiene), C_3H_6, C_3H_8, C_4H_6 (butyne and butadiene), C_4H_8 and C_4H_{10}. This work was limited to temperatures greater than 39 K because below that value rotational relaxation of C_4H was not fast enough to be completed within the available hydrodynamic time of the experiment. A sample of our results limited to CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4 (propyne) and C_3H_8 is presented in Figures 10 and 11. In all cases, reactivity increases when the temperature is lowered and, as for C_2, the rate coefficient reaches a

shallow maximum before starting to slightly decrease in some cases. It is worth noting that the rate coefficient increases with the number of carbon atoms in the molecule when considering the reagents by family (alkanes, alkenes, alkynes and dienes). As for $C_2(X\,^1\Sigma_g^+)$, the rate coefficients are very fast and close to the collision limit indicating that these processes are certainly barrierless. More details concerning these measurements can be found elsewhere.[112]

Among the studied hydrocarbons, six have been detected in the atmosphere of Titan (CH_4, C_2H_2, C_2H_4, C_2H_6 C_3H_4: propyne and C_3H_8). In photochemical models of this Saturn's moon, only reactions of C_4H with the first four reagents are taken into account probably because the abundance of propyne and propane are too small. We have compared our measurements with the values of the rate coefficients included in these models [136–140] and realised that the chosen rates were always underestimated, sometimes by more than one order of magnitude. The closest estimations were proposed in a recent model by Wilson and Atreya [140] who used rate coefficients comparable with those measured recently for reactions of C_2H with CH_4, C_2H_2, C_2H_4 and C_2H_6 (see references in Table 3). These aspects clearly show that the photochemical models should be revised. In particular, these new experimental data may affect the formation of polyaromatic polymers which are

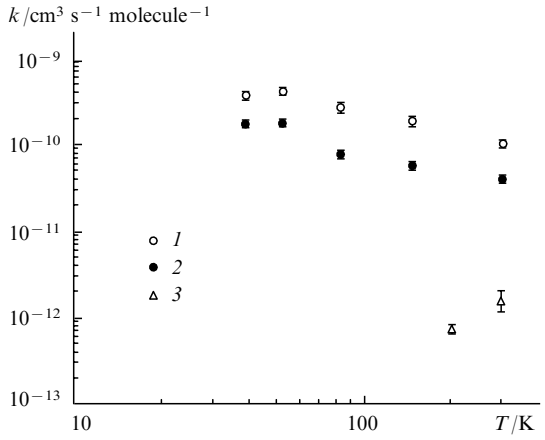


Figure 10. Second-order rate coefficients k for the reaction of C_4H with alkanes [C_3H_8 (*1*), C_2H_6 (*2*), CH_4 (*3*)] measured as a function of the temperature.

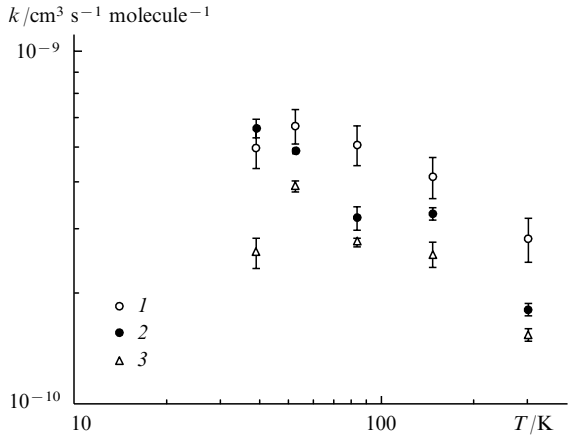


Figure 11. Second-order rate coefficients k for the reaction of C_4H with C_3H_4 (propyne) (*1*), C_2H_4 (*2*), and C_2H_2 (*3*) measured as a function of the temperature.

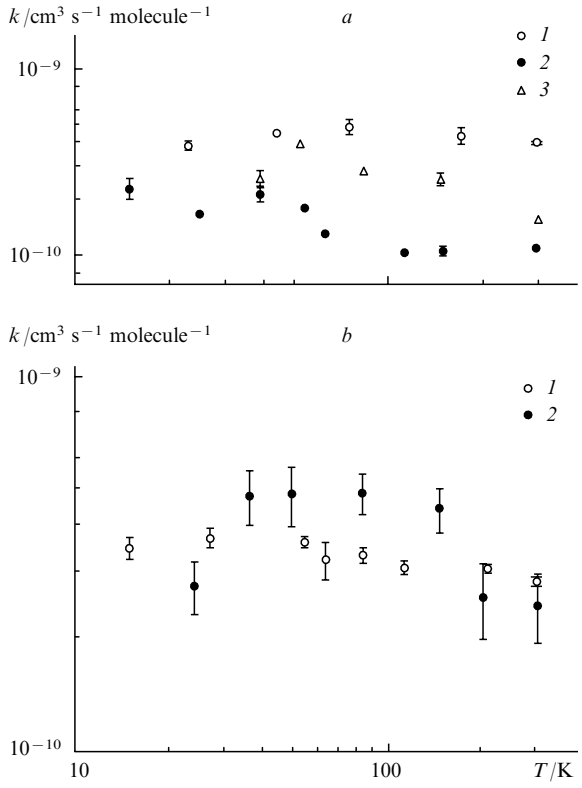


Figure 12. Second-order rate coefficients k for the reaction of C_2H_2 with CH (*1*),[110] C_2H (*2*)[96] and C_4H (*3*)[112] measured as a function of the temperature (*a*). Second-order rate coefficients k for the reaction of C_2H_2 with $C(^3P)$ (*1*)[98] and $C_2(X\,^1\Sigma_g^+)$ (*2*)[111] measured as a function of the temperature (*b*).

one possible route for the production of the thick haze that is present in the upper atmosphere of Titan.[122, 141]

At this stage of our knowledge, it is rather interesting to start comparisons of the known rate coefficients that were measured within the last 15 years at very low temperature. More particularly, some stable reagents have now been studied in the presence of a large number of differing radicals. Concerning carbon-based species the reactivity of acetylene has been studied in flow gases containing radicals such as $C(^3P)$, CH, C_2, C_2H and C_4H (see references in Table 3). The temperature evolution of the rate coefficients for these five reactions is presented in Fig. 12a and 12b. As it can be seen, rates are all fast and present temperature dependences that are rather similar. These observations may help in the estimation of rate coefficients for which the measurement is not experimentally possible and may suggest new theoretical routes to explore.

V. Perspectives

Although a lot of studies have been carried out on the experimental determination of rate coefficients at very low temperature within the last 15 years, there is still a considerable amount of work to be achieved. Beside carbon chemistry, there are several directions that are of particular interest.

Most of the present available studies concern small systems *i.e.*, atomic radicals or simple molecular radicals and reagents (see Table 3). There are still several aspects that remain unexplored however. As a matter of example, the chemistry of sulfur is completely unknown at very low temperature although molecules such as SO or SO_2 are routinely used to trace shock areas in the interstellar medium.[142, 143] The reac-

tivity of sulfur atoms is certainly of interest in the production of more complex sulfur-bearing molecules. The chemistry of metastable atoms is also important in our atmosphere and in planetary atmospheres as well. Only a few data concerning the reactivity of $O(^1D)$ are available at temperatures close to 200 K.[144–146] Extension to the lower temperatures of Titan should be valuable as well as determining rate coefficients for other atoms such as $N(^2D)$, $C(^1D)$ or $S(^1D)$. A much more difficult task resides on the experimental study of radical–radical reactions because in that case one of the partners must be produced in a large and well-defined quantity (typically 10^{13} molecules cm^{-3}) so that the characteristic time of the reaction is small enough to be measured by experimental setups such as supersonic flows. It is worth mentioning here the very recent study concerning O + OH which was conducted at temperatures as low as 39 K.[93] Future work may focus on reactions such as N + OH, O + CN, O + CH or a simpler one N + NO which are all of particular interest in interstellar chemistry.

Another important aspect that modern astrophysics revealed is the complexity of the existing interstellar molecules as illustrated by Table 1. It is important to understand how this complexity may be generated and to which level it can be brought. Although polycyclic aromatic hydrocarbons have not yet been directly observed in the interstellar medium, it is now largely accepted that they are mostly present. Their reactivity with other molecules is then of particular interest because insertion mechanisms could contribute to the building up of new species containing an increasing number of aromatic cycles. The study of dimerisation and eventually nucleation of PAHs can also give new insights in the generation of nanoparticles by extension of interstellar dust. Finally, reactions of simple stable C_2, C_3 and C_4-based hydrocarbons with radicals should also be completed although it is rather well documented now.

Measuring rate coefficients, although being of crucial importance, is only a partial answer to the understanding of a chemical process. Obviously, the identification of the products and the quantification of the branching ratios are vital as well. This aspect is much more difficult with the available experimental techniques dedicated worldwide to the investigation of gas phase kinetics. Although products can be identified by several methods such as LIF or mass spectrometry, the determination of their concentration is usually not possible. Some recent works are noteworthy however. Reactions for which only one exit channel is open can be used as references to determine the quantity of products of another process. This idea was used by the group of Seakins in Leeds (UK)[147,148] and Loison in Bordeaux (France)[149–153] to obtain the branching ratio of channels containing hydrogen atoms. Calibration reactions such as

$$CN + H_2 \longrightarrow HCN + H,$$

$$CH + CH_4 \longrightarrow C_2H_4 + H \text{ or}$$

$$C + C_2H_4 \longrightarrow C_3H_3 + H$$

can be used whereas H atoms are detected by VUV-LIF. These studies however are only available at room temperature and it would be worth to extend them at interstellar temperatures. The development of infrared lasers opens new possibilities for the determination of branching ratios. Multipass cells can be coupled to infrared light to detect molecular radicals by absorption techniques and quantify their concentration. Using this method, Hershberger and co-workers[154–159] obtained a significant amount of results at room temperature and above. One of the major problems here lies in the vibrational population of the produced molecules which may not be in equilibrium and therefore relaxation processes could interfere in the measurements. This was solved by the authors using SF_6 as a buffer gas,[160] a technique which is inapplicable to CRESU supersonic flows because of potential polymerisation of large concentrations of SF_6 during the expansion. A more promising technique lies on the photoionisation of products at threshold using VUV light and collection of the ions by a time-of-flight mass spectrometer. VUV can be generated by wave mixing laser techniques. This however is rather limited because of the restricted accordability of the generated light. Furthermore, the quantity of photons is generally rather small. A more appropriate tool for this kind of study is light produced from a synchrotron. Recent works have been undertaken at room temperature coupling a slow flow cell reactor to the ALS synchrotron in Berkeley.[161] By scanning the VUV light it is possible to detect products according to their ionisation potential which allows one to separate isomers. Provided that ionisation cross sections are known, the concentration of the products can be extracted from the experiment. Using a reduced version of the CRESU apparatus, it could be possible to couple it to a synchrotron (SOLEIL in France) and then make this kind of experiments at low temperatures.

Another challenge of experimental gas kinetics would be to be able to study the reactivity of molecules at even colder temperatures. The CRESU technique is well designed for this kind of task although the continuous version will request considerable pumping capacities to reach temperatures as low as a few Kelvin. Let's remind that the technique is presently limited to temperatures greater than 15 K for a reservoir kept at room temperature. Using a pulsed version of the CRESU apparatus coupled to the pumping capacities which are available in Rennes will make it possible however to obtain temperatures lower than 5 K reducing by a factor of 3 the present limit. This idea is in development in our lab and would open new horizons. More particularly it would allow one to compare theory and experiments in these extreme conditions. Indeed, theoretical predictions indicate that peculiar behaviours of the rate coefficients below 10 K should occur. As a matter of example, capture theories are expecting a maximum of the rate coefficient close to that temperature and then a significant decrease for colder conditions.

As it can be seen through these pages, the field of gas kinetics at low temperature is very active and has still unexplored areas. The development of new technologies however should allow experimentalists to push the limits even further and exciting results are expected in the future.

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References

1. R Atkinson, D L Baulch, R A Cox, J N Crowley, R F Hampson, R G Hynes, M E Jenkin, M J Rossi, J Troe *Atmos. Chem. Phys.* **6** 3625 (2006)
2. R Atkinson, D L Baulch, R A Cox, J N Crowley, R F Hampson, R G Hynes, M E Jenkin, M J Rossi, J Troe *Atmos. Chem. Phys.* **4** 1461 (2004)
3. I W M Smith *Chem. Rev.* **103** 4549 (2003)

4. D W Trainor, D O Ham, F Kaufman *J. Chem. Phys.* **58** 4599 (1973)
5. D O Ham, D W Trainor, F Kaufman *J. Chem. Phys.* **53** 4395 (1970)
6. M J Frost, P Sharkey, I W M Smith *J. Phys. Chem.* **97** 12254 (1993)
7. M J Frost, P Sharkey, I W M Smith *Faraday Discuss.* **91** 305 (1991)
8. I W M Smith, B R Rowe *Acc. Chem. Res.* **33** 261 (2000)
9. I W M Smith *Angew. Chem., Int. Ed.* **45** 2842 (2006)
10. V V Barelko, I M Barkalov, V I Goldanskii, D P Kiryukhin, A M Zanin *Adv. Chem. Phys.* **74** 339 (1988)
11. V V Barelko, I M Barkalov, V I Gol'danskii, A M Zanin, D P Kiryukhin *Usp. Khim.* **59** 353 (1990) [*Russ. Chem. Rev.* **59** 205 (1990)]
12. D P Kiryukhin, I M Barkalov *Vysokomol. Soedin., Ser. B* **42** 244 (2000) [a]
13. D P Kiryukhin, I M Barkalov *Usp. Khim.* **72** 245 (2003) [*Russ. Chem. Rev.* **72** 217 (2003)]
14. D C Clary, E Buonomo, I R Sims, I W M Smith, W D Geppert, C Naulin, M Costes, L Cartechini, P Casavecchia *J. Phys. Chem. A* **106** 5541 (2002)
15. A I Maergoiz, E E Nikitin, J Troe, V G Ushakov *J. Chem. Phys.* **105** 6277 (1996)
16. A I Maergoiz, E E Nikitin, J Troe, V G Ushakov *J. Chem. Phys.* **108** 5265 (1998)
17. A I Maergoiz, E E Nikitin, J Troe, V G Ushakov *J. Chem. Phys.* **108** 9987 (1998)
18. W D Geppert, D Reignier, T Stoecklin, C Naulin, M Costes, D Chastaing, S D Le Picard, I R Sims, I W M Smith *Phys. Chem. Chem. Phys.* **2** 2873 (2000)
19. D C Clary *Annu. Rev. Phys. Chem.* **41** 61 (1990)
20. J Troe *Z. Phys. Chem.-Int. J. Res. Phys. Chem. Chem. Phys.* **218** 457 (2004)
21. Y Georgievskii, S J Klippenstein *J. Chem. Phys.* **122** 194103 (2005)
22. E I Dashevskaya, A I Maergoiz, J Troe, I Litvin, E E Nikitin *J. Chem. Phys.* **118** 7313 (2003)
23. T Stoecklin, C E Dateo, D C Clary *J. Chem. Soc., Faraday Trans.* **87** 1667 (1991)
24. D Reignier, T Stoecklin, S D Le Picard, A Canosa, B R Rowe *J. Chem. Soc., Faraday Trans.* **94** 1681 (1998)
25. J Troe, J C Lorquet, J Manz, R A Marcus, M Herman *Advances in Chemical Physics. Chemical Reactions and their Control on the Femtosecond Time Scale. The 20th Solvay Conference on Chemistry* (New York: Wiley, 1997) Vol. 101, p. 819
26. L B Harding, A I Maergoiz, J Troe, V G Ushakov *J. Chem. Phys.* **113** 11019 (2000)
27. A Faure, L Wiesenfeld, P Valiron *Chem. Phys.* **254** 49 (2000)
28. J Troe *J. Chem. Soc., Faraday Trans.* **90** 2303 (1994)
29. J Troe, V G Ushakov *J. Chem. Phys.* **115** 3621 (2001)
30. A Fernandez-Ramos, J A Miller, S J Klippenstein, D G Truhlar *Chem. Rev.* **106** 4518 (2006)
31. H Sabbah, L Biennier, I R Sims, Y Georgievskii, S J Klippenstein, I W M Smith *Science* **317** 102 (2007)
32. I W M Smith, A M Sage, N M Donahue, E Herbst, D Quan *Faraday Discuss.* **133** 137 (2006)
33. O Gusev, M Kaufmann, K U Grossmann, F J Schmidlin, M G Shepherd *J. Atmos. Solar-Terr. Phys.* **68** 1684 (2006)
34. M Fulchignoni, F Ferri, F Angrilli, A J Ball, A Bar-Nun, M A Barucci, C Bettanini, G Bianchini, W Borucki, G Colombatti, M Coradini, A Coustenis, S Debei, P Falkner, G Fanti, E Flamini, V Gaborit, R Grard, M Hamelin, A M Harri, B Hathi, I Jernej, M R Leese, A Lehto, P F L Stoppato, J J Lopez-Moreno, T Makinen, J A M McDonnell, C P Mckay, G Molina-Cuberos, F M Neubauer, V Pirronello, R Rodrigo, B Saggin, K Schwingenschuh, A Seiff, F Simoes, H Svedhem, T Tokano, M C Towner, R Trautner, P Withers, J C Zarnecki *Nature (London)* **438** 785 (2005)
35. R V Yelle, F Herbert, B R Sandel, R J Vervack, T M Wentzel *Icarus* **104** 38 (1993)
36. D F Strobel, X Zhu, M E Summers, M H Stevens *Icarus* **120** 266 (1996)
37. S D Rodgers, S B Charnley, W F Huebner, D C Boice *Comets II*. (Eds M Festou, H U Keller, H A Weaver) (Tucson: University Arizona Press, 2005) p. 505
38. J Lequeux, E Falgarone, C Ryter *The Interstellar Medium* (Berlin, Heidelberg: Springer, 2005)
39. D E Woon www.astrochymist.org/astrochymist_ism.html (2007)
40. www.astrochemistry.net (2007)
41. P F Goldsmith, W D Langer *Astrophys. J.* **222** 881 (1978)
42. J Rawlings *Astrophys. Space Sci.* **285** 777 (2003)
43. W D Watson *Rev. Mod. Phys.* **48** 513 (1976)
44. Y P Viala, C M Walmsley *Astron. Astrophys.* **50** 1 (1976)
45. G F Mitchell, J L Ginsburg, P J Kuntz *Astrophys. J.* **212** 71 (1977)
46. J H Black, A Dalgarno *Astron. Astrophys., Suppl. Ser.* **34** 405 (1977)
47. E Herbst, W Klemperer *Astrophys. J.* **185** 505 (1973)
48. T J Millar, D A Williams *Astron. Astrophys.* **173** 527 (1975)
49. I W M Smith, E Herbst, Q Chang *Astron. Astrophys.* **350** 323 (2004)
50. J Woodall, M Agúndez, A J Markwick-Kemper, T J Millar *Astron. Astrophys.* **466** 1197 (2007)
51. S Brûnken, H Gupta, C A Gottlieb, M C McCarthy, P Thaddeus *Astrophys. J.* **664** L43 (2007)
52. A J Remijan, J M Hollis, F J Lovas, M A Cordiner, T J Millar, A J Markwick-Kemper, P R Jewell *Astrophys. J.* **664** L47 (2007)
53. M C McCarthy, C A Gottlieb, H Gupta, P Thaddeus *Astrophys. J.* **652** L141 (2006)
54. J Cernicharo, M Guélin, M Agúndez, K Kawaguchi, M C McCarthy, P Thaddeus *Astron. Astrophys.* **467** L37 (2007)
55. E Herbst, H H Lee, D A Howe, T J Millar *Astron. Astrophys.* **268** 335 (1994)
56. R P A Bettens, H H Lee, E Herbst *Astrophys. J.* **443** 664 (1995)
57. L Herbert, I W M Smith, R D Spencer-Smith *Int. J. Chem. Kinet.* **24** 791 (1992)
58. I R Sims, J L Queffelec, D Travers, B R Rowe, L B Herbert, J Karthäuser, I W M Smith *Chem. Phys. Lett.* **211** 461 (1993)
59. M A Smith, M Hawley *Advances in Gas Phase Ion Chemistry* (Amsterdam: Elsevier, 1992) Vol. 1, p. 167
60. M A Smith *Unimolecular and Bimolecular Reaction Dynamics* (Eds C Y Ng, T Baer, I Powis) (New York: Wiley, 1994) p. 183
61. B Maté, A Graur, T Elizarova, I Chirokov, G Tejeda, J M Fernández, S Montero *J. Fluid Mech.* **426** 177 (2001)
62. T L Mazely, M A Smith *J. Chem. Phys.* **89** 2048 (1988)
63. L K Randeniya, M A Smith *J. Chem. Phys.* **93** 661 (1990)
64. M Herman, R Georges, M Hepp, D Hurtmans *Int. Rev. Phys. Chem.* **19** 277 (2000)
65. P Casavecchia *Rep. Prog. Phys.* **63** 355 (2000)
66. R D Levine *Molecular Reaction Dynamics* (Cambridge: Cambridge University Press, 2005)
67. Y T Lee, J D McDonald, P R Le Breton, D R Herschbach *Rev. Sci. Instrum.* **40** 1402 (1969)
68. Y T Lee *Atomic and Molecular Beam Methods* (Ed. G Scoles) (New York: Oxford University Press, 1988) p. 553
69. K P Liu *Int. Rev. Phys. Chem.* **20** 189 (2001)
70. K P Liu *Annu. Rev. Phys. Chem.* **52** 139 (2001)
71. R I Kaiser *Chem. Rev.* **102** 1309 (2002)
72. N Balucani, G Capozza, F Leonori, E Segoloni, P Casavecchia *Int. Rev. Phys. Chem.* **25** 109 (2006)
73. G Hall, K Liu, M J McAuliffe, C F Giese, W R Gentry *J. Chem. Phys.* **81** 5577 (1984)
74. W R Gentry *Atomic and Molecular Beam Methods* (Ed. G Scoles) (New York: Oxford University Press, 1988) p. 54
75. R G Macdonald, K Liu *J. Chem. Phys.* **91** 821 (1989)
76. C Naulin, M Costes *Chem. Phys. Lett.* **310** 231 (1999)
77. P Casavecchia, G Capozza, E Segoloni *Modern Trends in Chemical Reaction Dynamics: Experiment and Theory* Pt II (Eds X Yang, K Liu) (Singapore: World Sci., 2004) p. 329
78. W D Geppert, F Goulay, C Naulin, M Costes, A Canosa, S D Le Picard, B R Rowe *Phys. Chem. Chem. Phys.* **6** 566 (2004)

79. G Dupeyrat, J B Marquette, B R Rowe *Phys. Fluids* **28** 1273 (1985)
80. J B Marquette, B R Rowe, G Dupeyrat, G Poissant, C Rebrion *Chem. Phys. Lett.* **122** 431 (1985)
81. F Goulay, C Rebrion-Rowe, J L Le Garrec, S D Le Picard, A Canosa, B R Rowe *J. Chem. Phys.* **122** 104308 (2005)
82. F Goulay, C Rebrion-Rowe, L Biennier, S D Le Picard, A Canosa, B R Rowe *J. Phys. Chem. A* **110** 3132 (2006)
83. I R Sims, J-L Queffelec, A Defrance, C Rebrion-Rowe, D Travers, P Bocherel, B R Rowe, I W M Smith *J. Chem. Phys.* **100** 4229 (1994)
84. P L James, I R Sims, I W M Smith *Chem. Phys. Lett.* **272** 412 (1997)
85. P L James, I R Sims, I W M Smith *Chem. Phys. Lett.* **276** 423 (1997)
86. P L James, I R Sims, I W M Smith, M H Alexander, M Yang *J. Chem. Phys.* **109** 3882 (1998)
87. N Daugey, P Caubet, B Retail, M Costes, A Bergeat, G Dorthe *Phys. Chem. Chem. Phys.* **7** 2921 (2005)
88. D B Atkinson, M A Smith *Rev. Sci. Instrum.* **66** 4434 (1995)
89. S Lee, R J Hoobler, S R Leone *Rev. Sci. Instrum.* **71** 1816 (2000)
90. E Vohringer-Martinez, B Hansmann, H Hernandez, J S Francisco, J Troe, B Abel *Science* **315** 497 (2007)
91. T Spangenberg, S Köhler, B Hansmann, U Wachsmuth, B Abel, M A Smith *J. Phys. Chem. A* **108** 7527 (2004)
92. B Hansmann, B Abel *ChemPhysChem.* **8** 343 (2007)
93. D Carty, A Goddard, S Köhler, I R Sims, I W M Smith *J. Phys. Chem. A* **110** 3101 (2006)
94. I R Sims, J L Queffelec, A Defrance, C Rebrion-Rowe, D Travers, B R Rowe, I W M Smith *J. Chem. Phys.* **97** 8798 (1992)
95. P Bocherel, L B Herbert, B R Rowe, I R Sims, I W M Smith, D Travers *J. Phys. Chem.* **100** 3063 (1996)
96. D Chastaing, P L James, I R Sims, I W M Smith *Faraday Discuss.* **109** 165 (1998)
97. A Pàramo, A Canosa, S D Le Picard, I R Sims *J. Phys. Chem. A* **110** 3121 (2006)
98. D Chastaing, P L James, I R Sims, I W M Smith *Phys. Chem. Chem. Phys.* **1** 2247 (1999)
99. D Chastaing, S D Le Picard, I R Sims *J. Chem. Phys.* **112** 8466 (2000)
100. S D Le Picard, A Canosa, D Travers, D Chastaing, B R Rowe, T Stoecklin *J. Phys. Chem. A* **101** 9988 (1997)
101. S D Le Picard, A Canosa, D Reignier, T Stoecklin *Phys. Chem. Chem. Phys.* **4** 3659 (2002)
102. S D Le Picard, A Canosa, G Pineau des Forêts, C Rebrion-Rowe, B R Rowe *Astron. Astrophys.* **372** 1064 (2001)
103. S D Le Picard, A Canosa, W D Geppert, T Stoecklin *Chem. Phys. Lett.* **385** 502 (2004)
104. R A Brownsword, A Canosa, B R Rowe, I R Sims, I W M Smith, D W A Stewart, A C Symonds, D Travers *J. Chem. Phys.* **106** 7662 (1997)
105. C Mullen, M A Smith *J. Phys. Chem. A* **109** 1391 (2005)
106. A B Vakhtin, D C McCabe, A R Ravishankara, S R Leone *J. Phys. Chem. A* **107** 10642 (2003)
107. V Jaramillo, S Gougeon, S D Le Picard, A Canosa, M Smith, B R Rowe *Int. J. Chem. Kinet.* **34** 339 (2002)
108. I R Sims, I W M Smith, D C Clary, P Bocherel, B R Rowe *J. Chem. Phys.* **101** 1748 (1994)
109. B Nizamov, S R Leone *J. Phys. Chem. A* **108** 3766 (2004)
110. A Canosa, I R Sims, D Travers, I W M Smith, B R Rowe *Astron. Astrophys.* **323** 644 (1997)
111. A Canosa, A Páramo, S D Le Picard, I R Sims *Icarus* **187** 558 (2007)
112. C Berteloite, S D Le Picard, P Birza, M C Gazeau, A Canosa, Y Benilan, I R Sims *Icarus* (2008) (in the press)
113. M A Páramo-Martínez, Ph.D. School of Chemistry, University of Birmingham, Birmingham, UK, 2005
114. A Canosa, S D Le Picard, S Gougeon, C Rebrion-Rowe, D Travers, B R Rowe *J. Chem. Phys.* **115** 6495 (2001)
115. A Canosa, S D Le Picard, W D Geppert *J. Phys. Chem. A* **108** 6183 (2004)
116. J E Murphy, A B Vakhtin, S R Leone *Icarus* **163** 175 (2003)
117. D Carty, V Le Page, I R Sims, I W M Smith *Chem. Phys. Lett.* **344** 310 (2001)
118. D Chastaing, S D Le Picard, I R Sims, I W M Smith, W D Geppert, C Naulin, M Costes *Chem. Phys. Lett.* **331** 170 (2000)
119. B Nizamov, S R Leone *J. Phys. Chem. A* **108** 1746 (2004)
120. A B Vakhtin, D E Heard, I W M Smith, S R Leone *Chem. Phys. Lett.* **348** 21 (2001)
121. F Goulay, S R Leone *J. Phys. Chem. A* **110** 1875 (2006)
122. E H Wilson, S K Atreya *Planet. Space Sci.* **51** 1017 (2003)
123. E J Bakker, E F van Dishoeck, L B F M Waters, T Schoenmaker *Astron. Astrophys.* **323** 469 (1997)
124. C Cecchi-Pestellini, A Dalgarno *Mon. Not. R. Astron. Soc.* **331** L31 (2002)
125. T Oka, J A Thorburn, B J McCall, S D Friedman, L M Hobbs, P Sonnentrucker, D E Welty, D G York *Astrophys. J.* **582** 823 (2003)
126. S P Souza, B L Lutz *Astrophys. J.* **216** L49 (1977)
127. M Guelin, S Green, P Thaddeus *Astrophys. J.* **224** L27 (1978)
128. M B Bell, T J Sears, H E Matthews *Astrophys. J.* **255** L75 (1982)
129. M B Bell, P A Feldman, H E Matthews *Astrophys. J.* **273** L35 (1983)
130. E A Ballick, D A Ramsay *Astrophys. J.* **137** 84 (1963)
131. T J Millar, E Herbst *Astron. Astrophys.* **288** 561 (1994)
132. W M Pitts, L Pasternack, J R Mcdonald *Chem. Phys.* **68** 417 (1982)
133. D A Horner, L A Curtiss, D M Dieter *Chem. Phys. Lett.* **233** 243 (1995)
134. R I Kaiser, T N Le, T L Nguyen, A M Mebel, N Balucani, Y T Lee, F Stahl, P V Schleyer, H F Schaefer *Faraday Discuss.* **119** 51 (2001)
135. R I Kaiser, N Balucani, D O Charkin, A M Mebel *Chem. Phys. Lett.* **382** 112 (2003)
136. Y L Yung, M Allen, J P Pinto *Astrophys. J., Suppl. Ser.* **55** 465 (1984)
137. D Toublanc, J P Parisot, J Brillet, D Gautier, F Raulin, C P Mckay *Icarus* **113** 2 (1995)
138. L M Lara, E Lellouch, J J López-Moreno, R Rodrigo *J. Geophys. Res.* **101** 23261 (1996)
139. S Lebonnois, D Toublanc, F Hourdin, P Rannou *Icarus* **152** 384 (2001)
140. E H Wilson, S K Atreya *J. Geophys. Res. Planet.* **109** E06002 (2004)
141. S K Atreya, E Y Adams, H B Niemann, J E Mick-Montelara, T C Owen, M Fulchignoni, F Ferri, E H Wilson *Planet. Space Sci.* **54** 1177 (2006)
142. G Pineau des Forêts, E Roueff, P Schilke, D R Flower *Mon. Not. R. Astron. Soc.* **262** 915 (1993)
143. F F S van der Tak, A M S Boonman, R Braakman, E F van Dishoeck *Astron. Astrophys.* **412** 133 (2003)
144. E J Dunlea, A R Ravishankara *Phys. Chem. Chem. Phys.* **6** 2152 (2004)
145. E J Dunlea, A R Ravishankara *Phys. Chem. Chem. Phys.* **6** 3333 (2004)
146. M A Blitz, T J Dillon, D E Heard, M J Pilling, I D Trought *Phys. Chem. Chem. Phys.* **6** 2162 (2004)
147. N Choi, M A Blitz, K McKee, M J Pilling, P W Seakins *Chem. Phys. Lett.* **384** 68 (2004)
148. K McKee, M A Blitz, K J Hughes, M J Pilling, H -B Qian, A Taylor, P W Seakins *J. Phys. Chem. A* **107** 5710 (2003)
149. J C Loison, A Bergeat *Phys. Chem. Chem. Phys.* **6** 5396 (2004)
150. N Galland, F Caralp, Y Hannachi, A Bergeat, J-C Loison *J. Phys. Chem. A* **107** 5419 (2003)
151. P Fleurat-Lessard, J C Rayez, A Bergeat, J-C Loison *Chem. Phys.* **279** 87 (2002)
152. A Bergeat, J C Loison *Phys. Chem. Chem. Phys.* **3** 2038 (2001)
153. A Bergeat, T Calvo, F Caralp, J H Fillion, G Dorthe, J C Loison *Faraday Discuss.* **119** 67 (2001)
154. C A Taatjes, J F Hershberger *Annu. Rev. Phys. Chem.* **52** 41 (2001)

155. W D Thweatt, M A Erickson, J F Hershberger *J. Phys. Chem. A* **108** 74 (2004)
156. J P Meyer, J F Hershberger *J. Phys. Chem. B* **109** 8363 (2005)
157. J P Meyer, J F Hershberger *J. Phys. Chem. A* **109** 4772 (2005)
158. W Feng, J P Meyer, J F Hershberger *J. Phys. Chem. A* **110** 4458 (2006)
159. W Feng, J F Hershberger *J. Phys. Chem. A* **110** 12184 (2006)
160. W F Cooper, J F Hershberger *J. Phys. Chem.* **96** 771 (1992)
161. G Meloni, P Zou, S J Klippenstein, M Ahmed, S R Leone, C A Taatjes, D L Osborn *J. Am. Chem. Soc.* **128** 13559 (2006)

[a] — *Polym. Sci. (Engl. Transl.)*