ELSEVIER

International Journal of Mass Spectrometry 208 (2001) 73–80

International Journal of Mass Spectrometry

Pulsed injection of ions into the CRESU experiment

Thomas Speck*, Toufik I. Mostefaoui, Daniel Travers, Bertrand R. Rowe

Physique des Atomes, Lasers, Molécules et Surfaces, U.M.R. 6627 du C.N.R.S., Université de Rennes I, 35042 Rennes, France

Received 11 December 2000; accepted 14 February 2001

Abstract

A new versatile experimental technique for the study of ion–molecule reactions at very low temperatures is presented. The technique is based upon the pulsed injection of ions into a uniform and isentropic supersonic expansion (CRESU experiment). Several ion/molecule reactions have been studied in order to test the setup and the reaction between CH^+ and CO has been investigated under low temperature conditions. (Int J Mass Spectrom 208 (2001) 73–80) © 2001 Elsevier Science B.V.

Keywords: Pulsed ion source; Ion–molecule reaction; Low temperature; Uniform supersonic jet; Drift velocity

1. Introduction

Ion/molecule reactions play an important role in interstellar and atmospheric chemistry. They are favoured in low temperature regions since they are not hindered by an activation energy. Due to the low density and temperature (typically in the range 10–100 K) of interstellar clouds, exothermic, bimolecular ionic gas-phase reactions are a key route for the synthesis of interstellar molecules [1]. In planetary atmospheres, ions are frequently used as probe molecules since they are easy to detect and thus ion/molecule reactions give a deeper insight into the neutral composition [2].

During the last 20 years, therefore, many techniques such as cryogenically cooled drift tubes and ion traps, free jet flow reactors or merged ion and molecular beams have been developed that allow ion/molecule rate coefficients to be measured at very low temperatures so that data can be obtained under temperature conditions relevant to interstellar chemistry [3]. The CRESU technique (Cinétique de Réaction en Ecoulements Supersoniques Uniformes) developed by Rowe and co-workers in the early 1980s [4] uses a uniform supersonic jet as a flow reactor. Because of the slow nature of homogeneous condensation, the use of a neutral reactant with a partial pressure well above its vapour pressure at the temperature of the flow is possible. Without precooling of the buffer gas in the nozzle reservoir, a decrease in temperature down to 15 K has been achieved and with precooling by liquid nitrogen down to 8 K [5] and 13 K [6]. The lack of strong gradients and the relatively large density of the flow makes kinetic studies possible under conditions of thermodynamical equilibrium [6,7].

In the state of the art of the CRESU experiment at Rennes, ions are created by means of a 12 keV electron beam which crosses the supersonic expansion perpendicularly. With this kind of setup, some ion/

---

* Corresponding author. E-mail: Thomas.Speck@univ-rennesl.fr

PII S1387-3806(01)00383-9

molecule reactions can be investigated [8], however, the formation of a plasma creates many species that may disturb the measurement. For instance, the usage of He as a buffer gas produces He^+, He_2^+, and metastable He* which may react with the parent gas in a way that does not result in the desired daughter ion. In addition the desired ions may react with their own parent gas so that the field of ion/molecule reactions that can be investigated is limited. It is also very difficult to work with ions for which the parent gas has a very low vapour pressure such as polycyclic aromatic hydrocarbons (PAH), believed to be important in interstellar space. Such species tend to condense on the housing of the mass spectrometer, thus hindering the measurements, although this problem can be circumvented by heating the mass spectrometer.

In order to overcome these problems, a new technique, which is presented in the following, has been developed. It allows one to inject ions that are produced by a separate ion source, into the supersonic flow. The neutral counterparts coming from the ion production and metastable Helium are not therefore present in the reaction zone, these species being unable to diffuse into the kernel of the supersonic jet. Free diffusion of ions is also very slow but they can be made to drift into the jet by an electric field. In order to avoid heating effects of the ions, this field is pulsed and this results in pulsed injection/detection of ions. The simplicity of mounting the system onto different supersonic nozzles and therefore the ease of working at several different temperatures, shows a clear improvement over an earlier attempt [9] which used a continuous electric field inside the nozzle, shielded by a grounded nozzle exit. This yielded a complicated nozzle design and construction. The new setup has been tested by the study of several ion/molecule reactions, and excellent agreement has been obtained with previous results where available.

2. Experimental

The CRESU technique has been widely used for both the study of ion/molecule and of radical–molecule reactions [10]. It has been described in detail elsewhere [11] and only the essential features are given below. The basic principle of the experiment is to use a uniform, isentropic supersonic jet as a flow reactor. This jet is produced by the expansion of a buffer gas (in the present case helium) through a Laval nozzle of suitable geometry. To obtain the desired properties (e.g. temperature) of the expansion, the pressures before and after the nozzle have to be chosen accordingly.

In order to inject ions into this supersonic jet, an ion source has been constructed that is located off to one side of the flow at the nozzle exit. It consists (Fig. 1) of a filament (usually iridium) and of an acceleration grid. These elements are surrounded by a stainless steel cylinder that is kept at earth potential. A power supply heats the filament to a temperature that is sufficient to release electrons. Gas flows past the filament and toward the exit of the source and is ionised by electron impact. The electric potential of the filament and the grid are optimised for every gas and are typically +5 and +110 V, respectively. The ions, produced under these conditions, are accelerated toward the exit of the ion source. Since the velocity of free diffusion of ions in the buffer gas is very slow compared to the velocity of the supersonic flow, however, it is necessary to drift the ions into the jet by means of an electric field. This is generated by a cone that carries a negative potential (for cations) and that is mounted on the opposite side of the flow. To allow the ions to drift into the jet centre, this potential has to be chosen in order that the drift velocity of the ions (along the electric field) is at least equal to the velocity of the expansion. The drift velocity and the electric field are coupled by the mobility, so that the applied potential also depends upon the ions to be injected. For the reactions that have been studied, voltages up to −120 V have been used. The potential on the cone is turned on and off periodically in order to release the ions and allow them to propagate and thermalise within the jet.

The translational relaxation time of an ion with helium can be estimated from a Langevin reaction rate coefficient $k_L \approx 5.5 \times 10^{-10}$ cm^3 s^{-1} (with $\mu_{red} \approx$ 3.6 a.u. and $\alpha \approx 2.05 \times 10^{-25}$ cm^3) which yields a

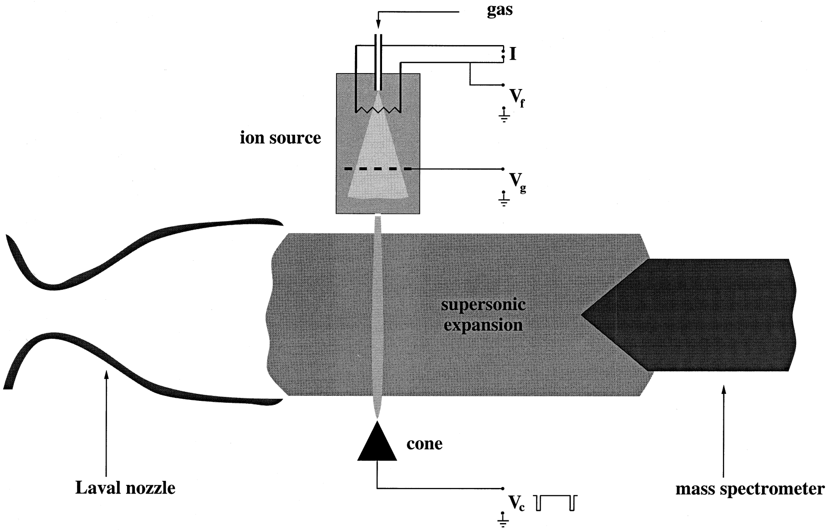

Fig. 1. Experimental setup of the pulsed ion source (see text).

value of 0.2 μs for a given gas density of typically 10^{16} cm^{-3}. For rotational excitation of most ions it is expected from statistical models that the relaxation time is very close to this value. For a gas speed of about 5 × 10^4 cm/s it corresponds to a distance of 90 μm. This is very short since typical reaction lengths are of several centimetres. Even for slower values as in the case for the rotational relaxation of N_2^+ with Ar ($k(90\ \text{K}) = (1.4 \pm 0.4) \times 10^{-11}$ cm^3 s^{-1} [12] thermalisation would still occur after about 3.5 mm. Any translational or rotational heating of the charged particles due to continuous field effects, therefore, is circumvented. Typically the cone is kept at the negative potential for 100 μs and grounded for 150 μs, which results in a frequency of operation of 4000 Hz. The whole setup is mounted right at the exit of the Laval nozzle using an attachment device and is easily assembled and dismantled for every nozzle.

The reactant and product ions are monitored by a moveable quadrupole mass spectrometer, using a channeltron multiplier operated in the counting mode as a detector. For two different positions x_1 and x_2 of the mass spectrometer along the flow axis (which results in two different distances to the ion source) the ions reach the channeltron at different times. For position x_1 (respectively, x_2), a delay generator starts the counting at a given delay δt_1 (respectively, δt_2) after the grounding of the cone. Ions are then counted during a given time gate (typically 20–40 μs). The delay δt_1 is adjusted in order to match the ion time-of-flight between the source and the ion detector and therefore:

$$\frac{x_1 - x_2}{\delta t_1 - \delta t_2} = \frac{dx}{dt} = v$$

Ion/molecule reactions can occur inside the ion packet, traveling at the flow velocity v if a molecular gas, R, is added to the helium buffer. The variation of the reactant ion density I^+ is given by

$$[I^+] = [I^+]_0 \exp\left(-\frac{k[R]\delta x}{v}\right)$$

The rate coefficient k to be measured can be obtained using standard methods of flow reactors, i.e. by monitoring the relative decrease ($[I^+]/[I^+]_0$) either as a function of the position of the mass spectrometer for various reactant densities or vice versa. Typically $[I^+]/[I^+]_0$ changes by a factor of 10. Being in the pseudo-first-order limit, the rate coefficient is easily obtained.

As we have seen previously, the translational and rotational motions of the injected ions are thermalised extremely efficiently within the flow. Due to the injection of molecular ions perpendicular to the supersonic flow, however, some excitation of their other degrees of freedom is possible during the time where the electric field is applied. In [13] the equation for the centre-of-mass kinetic energy $\mathrm{KE}_{\mathrm{cm}}$ for an ion drifting in a buffer gas is given as

$$\mathrm{KE}_{\mathrm{cm}} = \frac{M_r(M_b + m)}{2(M_r + m)}\, v_d^2 + \frac{3}{2}\, kT$$

Following the above arguments and setting the drift velocity v_d to the jet velocity and by performing some simple approximations, one obtains

$$\mathrm{KE}_{\mathrm{cm}} \approx \frac{M_r(M_b + m)}{2(M_r + m)\, M_{\mathrm{gas}}}\, \frac{\gamma}{\gamma - 1}\, kT_0$$

with M_r, M_b, m being the mass of the neutral reactant, the buffer gas, and the ion, respectively, $M_{\mathrm{gas}} = \Sigma\ m_i dm_i$, $\gamma = c_p/c_v$ and T_0 the room temperature. Using appropriate values for, e.g. the reaction between O_2^+ and CH_4 in a helium buffer, one obtains an energy of roughly 760 cm^{-1} (=94 meV). This is far too low in order to excite electronic or vibrational levels in O_2^+, whereas rotational levels might get populated. As seen previously, rotational relaxation, however, is very efficient in high gas density supersonic beams, such as ours, so that injected ions should well thermalise with the buffer gas when the electric field is turned off. It should also be noted, that $\mathrm{KE}_{\mathrm{cm}}$ is an upper value for excitation since the vibrational excitation probability has not been taken into account for this estimation.

Vibrational or electronic excitation can also be produced directly in the ion source, when the ions are formed by electron impact although it can be expected that, the present source, being operated at quite large pressures (around 1 Torr), produces ions mainly in the ground state (e.g. due to near-resonant charge exchange with the parent molecule). This relaxation, however, is not always obvious as can be seen for example in the case of protonated ions. For some ions, therefore, the good agreement with previous measurements can be taken as evidence of relaxation to the ground state or as evidence that the data are not influenced by the vibrational state. In order to test the new set-up and the effective ion thermalisation, six ion/molecule reactions which exhibit various temperature dependences, have been studied at several temperatures between 23 and 300 K: $Ar^+ + CH_4$, $Ar^+ + C_2H_6$, $Ar^+ + N_2$, $O_2^+ + CH_4$, $CH_3^+ + H_2 + He$, and $CH^+ + CO$.

3. Results and discussion

3.1. $Ar^+ + CH_4$ and $Ar^+ + C_2H_6$

The rate coefficients for these reactions have been previously determined at 300 K [14] and 700 K [15] for C_2H_6 (note that the data in [15] are obtained using a drift tube). Exothermic ion/molecule reactions with nonpolar species obey very often the collisional model and in this case the rate coefficient remains constant as a function of temperature. Since the previous measurements, therefore, are close to the Langevin values for these reactions ($k_L = 1.12 \times 10^{-9}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ and $k_L = 1.19 \times 10^{-9}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$, respectively, for CH_4 and C_2H_6), no change of the rate coefficient as a function of temperature is expected (a small variation of the rate coefficient as has been observed for $Ar^+ + CH_4$ in a flow drift apparatus [16] for high $\mathrm{KE}_{\mathrm{cm}}$ (centre-of-mass kinetic energy), which happens probably due to the population of $^2P_{1/2}$ of Ar^+, would lie within our experimental uncertainties). The experimental results that we have obtained (Table 1) agree well with this prediction within the error limits of about 30%.

3.2. $Ar^+ + N_2$

The reaction $Ar^+ + N_2$ has been studied using the pulsed ion source. This was primarily for two reasons. First, it is very easy to produce the ion Ar^+ in the source and second, this reaction, which has been widely studied elsewhere, presents a large variation of the rate coefficient with temperature and thus is a good test subject for our device. The buffer gas is helium (23, 36, 71.6, and 300 K). The measurement at

Table 1
Measured rate coefficients for CH_4 and C_2H_6 with Ar^+ for various temperatures along with corresponding Langevin rates; also presented are values obtained at 300 K [14] and at 700 K [15] (observed rate coefficients indicated; number in parentheses are powers of 10)

	Rate coefficient/cm^3 s^{-1} for the reaction of	
T (K)	$Ar^+ + CH_4$	$Ar^+ + C_2H_6$
23	9.7 (−10)	9.2 (−10)
36	1.12 (−9)	8.6 (−10)
71	1.13 (−9)	9.3 (−10)
300[a]	9.0 (−10)	. . .
700[b]	1.16 (−9)	1.15 (−9)
k_L	1.12 (−9)	1.19 (−9)

[a] See [14].
[b] See [15].

300 K was made using a new calibrated sub-sonic nozzle.

The rate coefficient has been measured in this fashion for different temperatures. Fig. 2 shows the results of these measurements in addition to some results found in the literature that have been obtained using flowing reactor techniques [17–20] in addition to results taken using the standard CRESU method [21]. Note that above room temperature the only thermal results are those of Viggiano et al. [20]. The others belong to drift tube measurements (in this case KE_{cm} has been converted to temperature but as shown in [20] there is not a real equivalence in this temperature range due to rotational population). The very good accord found between the results of this work and those in the literature indicate that the ions produced using the pulsed ion source are very well thermalised. The minimum in the rate coefficient in the vicinity of 140 K can be explained by the competition between two exit channels: $Ar + N_2^+$ $(v = 1)$ and $Ar + N_2^+$ $(v = 0)$. The former channel is weakly endothermic (0.09 eV) whereas the second is exothermic by 0.18 eV. At higher energies, only the former is present and the rate coefficient is seen to rise with temperature in accord with theoretical [22] and other experimental data. Obviously this channel becomes negligible at low temperatures due to its endothermicity. The observed increase of the rate coefficient at low temperatures is entirely due to the emergence of the channel $Ar + N_2^+$ $(v = 0)$ [21]. The discussion given in [21] concerning the results obtained using the original CRESU apparatus at Meudon, for this reaction, can be applied to the current results. The high energy, electronic metastable states of the Ar^+ ion are certainly destroyed by nitrogen even before entering the jet. In addition, the absence of curvature in the decrease of the Ar^+ signal, as a function of the N_2 flow, leads one to believe that only the single $^2P_{3/2}$ ground state is taking part in the reaction, since the two spin-orbit states react with differing rates. The absence of the $^2P_{1/2}$ state (which must certainly be produced in the source) can be explained by a very efficient deexcitation process in N_2.

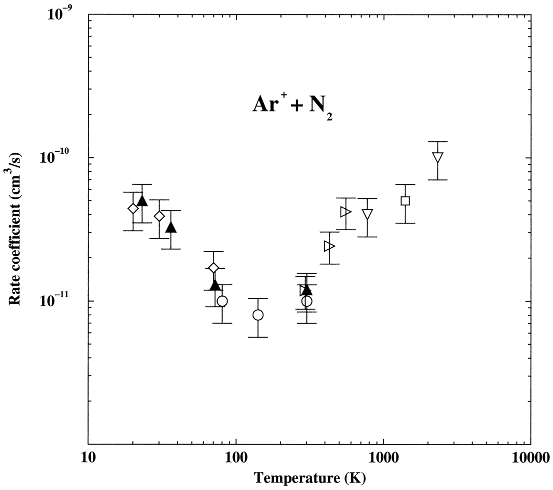

Fig. 2. Rate coefficients for the reaction $Ar^+ + N_2$ as a function of temperature. Open triangles down: [17], open boxes: [18], open circles: [19], open triangles right: [20], open diamonds: [21], filled triangles: this work.

3.3. $O_2^+ + CH_4$

After studying reactions involving atomic ions some reactions with molecular ions have been investigated. We have chosen the reaction

$$O_2^+ \, (^2\Pi_g) + CH_4 \, (^1A_1) \rightarrow CH_3O_2^+ \, (^1A_1) + H \, (^2S_{1/2}) + 4.8 \text{ eV}$$

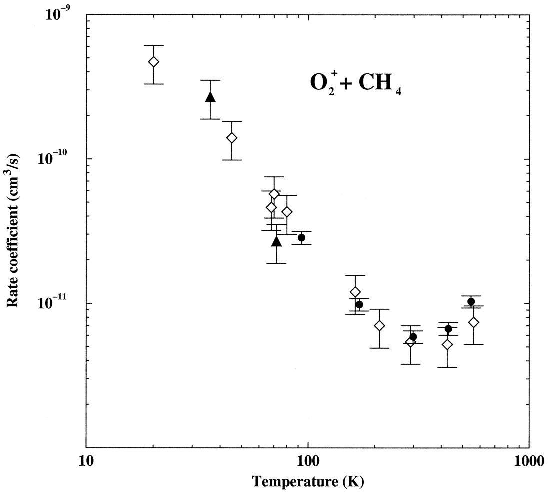

Fig. 3. Rate coefficients for the reaction $O_2^+ + CH_4$ as a function of temperature. Open diamonds: [25], filled circles: [26], filled triangles: this work.

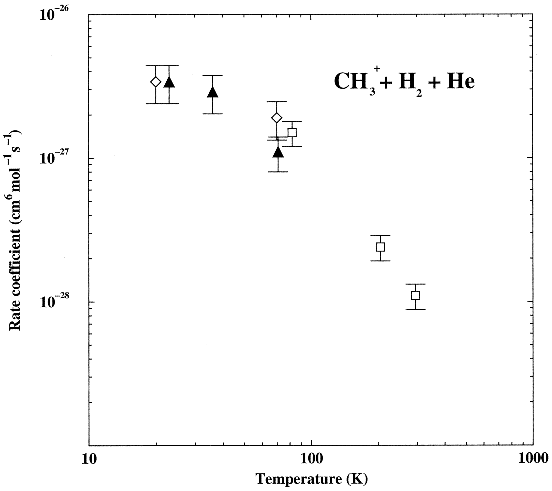

Fig. 4. Termolecular rate coefficients for the reaction $CH_3^+ + H_2 +$ He as a function of temperature. Open diamonds: [9], open boxes: [27], filled triangles: this work.

as a test for our source since it has been widely studied by previous authors and it is known to display a very marked dependence with temperature. In addition, the metastable electronic state $a\ {}^4\Pi_u$, and the vibrationally excited states of O_2^+, react much more rapidly with CH_4 than the ground state. They are effectively quenched however [23,24] which will allow us to be sure that the reacting ions will be in the ground electronic and vibrational state. (They should be very efficiently quenched by oxygen in the source.) The use of oxygen in the source at relatively high pressures poses a problem due to oxidation of the filament but this can be avoided by using an iridium filament.

The measured rate coefficient is shown as a function of temperature in Fig. 3. The excellent agreement found between results, previously obtained using the CRESU, SIFT [25], and VT-SIFDT methods [26] is a very good indication that the ions are thermalised not only translationally but also vibrationally and electronically (note a slight discrepancy between SIFT and VT-SIFDT [26] data above 100 K).

3.4. $CH_3^+ + H_2 + He$

In order to study a termolecular process, we have used methane in the pulsed ion source which creates the CH_3^+ ion. It possesses more vibrational degrees of freedom than O_2^+ and therefore provides additional information concerning possible vibrational excitation in the experiment. The results obtained are shown in Fig. 4 and Table 2 along with those obtained previously by other authors [9,27].

It is seen that all the results are in good agreement and they show that this reaction displays an increase in the rate as the temperature decreases, reaching a saturation value below about 70 K. The results cannot be represented by a power law of the type $k \propto T^{-n}$, $n > 0$ as often found for association reactions. Since our results and those of the earlier CRESU measurement [9] were obtained under quite different pressure

Table 2
Termolecular rate coefficients for $CH_3^+ + H_2 +$ He (number in parentheses are powers of 10)

T (K)	Density (cm^{-3})	Rate coefficients (cm^6 s^{-1})
23[a]	4.73 (16)	3.41 (−27)
36[a]	5.28 (16)	2.85 (−27)
71[a]	6.01 (16)	1.06 (−27)
20[b]	9.64 (15)	3.4 (−27)
70[b]	9.20 (15)	1.9 (−27)

[a] Rennes apparatus.

[b] Meudon apparatus.

regimes as shown in Table 2, this saturation cannot arise from a too high buffer density (our value at 71 K is even somewhat lower than the one at 70 K from the Meudon apparatus although it has been obtained at a higher buffer gas density). This behaviour, may be explained, rather, by a freezing of the rotational states of the H_2 molecule at low temperatures due to its large rotation constant.

The agreement between the different authors leads us to believe that the results have all been obtained using ions in the same internal states, i.e. the ground state.

3.5. $CH^+ + CO$

This reaction has been reported as leading to HCO^+ as a product and is rather slow [28], with a rate coefficient of 7×10^{-12} cm^3 s^{-1} at 300 K whereas its Langevin rate coefficient is 1.4×10^{-9} cm^3 s^{-1}. The reported 300 K value is clearly in conflict however with a now well established endothermicity of 28.81 kJ mol^{-1} [29], as can be deduced from the spectroscopic measurement of the ionisation potential of CH [30], the proton affinity of CO being precisely known as 591.62 kJ mol^{-1} in very good agreement with the ionisation potential of HCO (187.95 kJ mol^{-1} [31]). Such a value implies in fact an even lower rate coefficient.

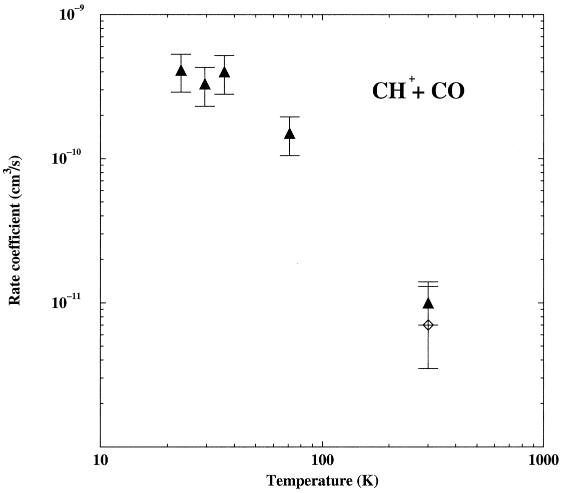

Fig. 5. Rate coefficients for the reaction $CH^+ + CO$ as a function of temperature. Open diamond: [28], filled triangles: this work.

We have therefore studied the temperature dependence of the reaction of CH^+ ions with CO in our experiment. CH^+ ions are produced by ionising methane gas and are injected into the flow. The bimolecular rate coefficient obeys a T^{-n} law between 300 and 36 K, whereas beyond 36 K a small saturation is observed (see Fig. 5). Considering the endothermicity this behaviour cannot be explained if the product is HCO^+ as reported elsewhere. Although our experiment is not yet designed for the measurement of branching ratio (ions are not selected), the nature of the product ions can be identified from the mass spectrum (Fig. 6). In our experiment it is clear that the reaction is termolecular, leading to the $CH \cdot CO^+$ product at mass 41. As can be seen in the mass spectrum, peaks at masses 40, 42, and 43 are also present. They probably result from other association reactions involving CO and ions such as C^+, CH_2^+, CH_3^+ that are also present in the flow. The agreement with the 300 K value for the bimolecular rate coefficient of $CH^+ + CO$ previously reported is thus fortuitous, probably due to the use of very similar values for the total pressure in both experiments. In Fig. 5 the

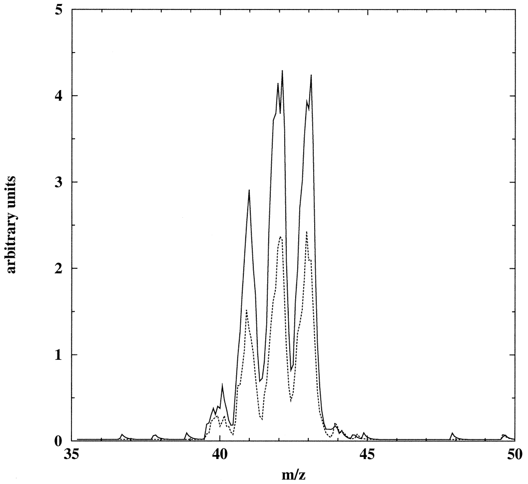

Fig. 6. Mass spectrum taken during the reaction of $CH^+ + CO$. The dotted line indicates a low density of CO and the full line a higher one. Beside the $CH \cdot CO^+$ peak there are also others present resulting from different association reactions (see text). Since all of the peaks show a dependence of CO density they must be a compound of it.

bimolecular rate coefficient is shown as a function of temperature. It is clear from the apparent bimolecular rate coefficient that the reaction is not in the low pressure limit at the lowest temperature. The large value of this rate implies however that the analogue radiative association process could be fast at the temperature of interstellar clouds.

4. Conclusion

Pulsed injection of ions into uniform supersonic flows allows us to extend the number of reactions that can be studied at very low temperatures using the CRESU method. The new technique has been tested by the study of several ion/molecule reactions and some new results have been obtained (reactions between CH^+ and CO, $Ar^+ + CH_4$, and C_2H_6). The simplicity of the setup allows measurement of the rate coefficient to be performed rather easily at different low temperatures. It is hoped that the system will allow ion–molecule reactions involving larger ions of astrophysical interest to be studied.

Acknowledgements

The national programme of “Physique et Chimie du Milieu Interstellaire (PCMI)” is thanked for their support of the present investigation. The authors also acknowledge funding by the European Community under the TMR network no. ERB FMRX-CT97-0132 “Astrophysical Chemistry.”

References

[1] E. Herbst, W. Klemperer, Astrophys. J. 185 (1973) 505.
[2] A.A. Viggiano, R.A. Perry, D.L. Albritton, E.E. Ferguson, F.C. Fehsenfeld, J. Geophys. Res. 85 (1980) 455.
[3] M.A. Smith, Unimolecular and Bimolecular Reaction Dynamics, Wiley, New York, 1994, pp. 183–251.
[4] B.R. Rowe, G. Dupeyrat, J.B. Marquette, P. Gaucherel, J. Chem. Phys. 80 (1984) 4915.
[5] B.R. Rowe, J.B. Marquette, G. Dupeyrat, E.E. Ferguson, Chem. Phys. Lett. 113 (1985) 403.
[6] I.R. Sims, J.C. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, P. Bocherel, B.R. Rowe, I.W.M. Smith, J. Chem. Phys. 100 (1994) 4229.
[7] G. Dupeyrat, J.B. Marquette, B.R. Rowe, Phys. Fluids 28 (1984) 1273.
[8] J.L. LeGarrec, V. Lepage, B.R. Rowe, E.E. Ferguson, Chem. Phys. Lett. 270 (1997) 66.
[9] B.R. Rowe, J.B. Marquette, C.J. Rebrion, J. Chem. Soc., Faraday Trans. 2 85 (1989) 1631.
[10] I.W.M. Smith, B.R. Rowe, Acc. Chem. Res. 33 (2000) 261.
[11] B.R. Rowe, A. Canosa, V. Lepage, Int. J. Mass Spectrom. Ion Processes 149 (1995) 573.
[12] S. Schlemmer, T. Kuhn, E. Lescop, D. Gerlich, Int. J. Mass. Spectrom. 185/186/187 (1999) 589.
[13] M. McFarland, D.L. Albritton, F.C. Fehsenfeld, E.E. Ferguson, A.L. Schmeltekopf, J. Chem. Phys. 59 (1973) 6620.
[14] R.C. Bolden, R.S. Hemsworth, M.J. Shaw, N.D. Twiddy, J. Phys. B 3 (1970) 45.
[15] H. Chatham, D. Hils, R. Robertson, A.C. Gallagher, J. Chem. Phys. 79 (1983) 1301.
[16] H. Störi, E. Alge, H. Villinger, F. Egger, W. Lindiger, Int. J. Mass Spectrom. Ion Phys. 30 (1979) 263.
[17] I. Dotan, W. Lindinger, J. Chem. Phys. 76 (1982) 4972.
[18] W. Lindinger, F. Howorka, P. Lukac, S. Kuhn, H. Villinger, E. Alge, H. Ramler, Phys. Rev. A 23 (1981) 2319.
[19] D. Smith, N.G. Adams, Phys. Rev. A 23 (1981) 2327.
[20] A.A. Viggiano, J.M. Van Doren, R.A. Morris, J.F. Paulson, J. Chem. Phys. 93 (1990) 4761.
[21] C. Rebrion, B.R. Rowe, J.B. Marquette, J. Chem. Phys. 91 (1989) 6142.
[22] G. Parlant, E.A. Gislason, J. Chem. Phys. 86 (1987) 6183.
[23] M. Durup-Ferguson, H. Böringer, D.W. Fahey, F.C. Fehsenfeld, E.E. Ferguson, J. Chem. Phys. 81 (1984) 2657.
[24] W. Lindinger, D.L. Albritton, F.C. Fehsenfeld, J. Chem. Phys. 70 (1979) 2038.
[25] B.R. Rowe, G. Dupeyrat, J.B. Marquette, D. Smith, N.G. Adams, E.E. Ferguson, J. Chem. Phys. 80 (1984) 241.
[26] A.A. Viggiano, R.A. Morris, J.M. Van Doren, J.F. Paulson, J. Chem. Phys. 96 (1992) 275.
[27] D. Smith, N.G. Adams, E. Alge, J. Chem. Phys. 77 (1982) 1261.
[28] D. Smith, N.G. Adams, Int. J. Mass Spectrom. Ion Phys. 23 (1977) 123.
[29] M.W. Chase Jr., C.A. Davies, J.R. Downey Jr., D.J. Frurip, R.A. McDonald, A.N. Syverud, J. Phys. Chem. Ref. Data 14, Suppl. 1 (1985).
[30] G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 1, Spectra of Diatomic Molecules, Van Nostrand, New York, 1950.
[31] E. Mayer, E.R. Grant, J. Chem. Phys. 103 (1995) 10513.