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Crossed molecular beam study of gas phase reactions relevant to the chemistry of planetary atmospheres: The case of $C_2 + C_2H_2$

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Abstract

The reaction between dicarbon (C_2) and acetylene was recently suggested as a possible competitive reaction in the atmospheres of Titan, Saturn and Uranus by rate constant measurements at very low temperatures [see Canosa, A., Páramo, A., Le Picard, S.D., Sims, I.R., 2007. An experimental study of the reaction kinetics of $C_2(X^1\Sigma_g^+)$ with hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6 and C_3H_8) over the temperature range 24–300 K: implications for the atmospheres of Titan and the Giant Planets. Icarus 187, 558–568]. We have investigated the reaction of the two low lying electron states of C_2 and acetylene by the crossed molecular beam (CMB) technique with mass spectrometric detection. C_4H, already identified as a primary product in previous CMB experiments, is confirmed as such, even though the mechanism of formation is inferred to be partly different with respect to the previous study. An experimental setup has been devised to characterize the internal population of C_2 and refine the interpretation of the scattering results. The implications for the modelling of the atmospheres of Giant Planets and Titan, as well as cometary comae and the interstellar medium, are discussed.

Keywords: Experimental techniques; Jovian planets; Titan; Atmospheres; Composition; Comets

1. Introduction

The recent exploration of the bodies of our solar system has provided unprecedented, detailed information on the chemical composition of planetary atmospheres. The detection of relatively complex molecules can be seen as proof that a certain chemical evolution has taken (and is still taking) place over a large number of years, converting a few simple gas-phase parent molecules into larger ones (see, for instance, Coustenis, 2005; Strobel, 2005; Encrenaz, 2005). Analogously to the atmosphere of our own planet, in fact, the atmospheres of the other planets (or satellites like Titan) can be described as giant photoreactors, where the energy deposited mainly by solar photons, but also by cosmic rays and other energetic particles, drives a somewhat complex gas-phase chemistry.

Understanding the chemical evolution of planetary atmospheres requires a multi-disciplinary approach. In addition to large-scale effects and transport phenomena, a realistic model needs to consider all the relevant reactions, which should be identified and included with the appropriate parameters, possibly determined in laboratory experiments. Neutral–neutral gas-phase reactions play a major role in the chemistry of planetary atmospheres up to the ionospheres. Provided that it is thermodynamically feasible, a neutral–neutral gas-phase reaction will be relevant if it is "competitive", that is, fast under the conditions of interest. For this reason, the knowledge of accurate rate constants of the possibly relevant uni-, bi- and, when necessary, ter-molecular reactions is a crucial

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aspect in the construction of a successful model. Laboratory experiments on reaction kinetics provide us with the rate constants and their dependence on temperature, but are rarely able to determine the nature of the products and their branching ratio. Nevertheless, this information is also fundamental, because the products of one reaction yield the reagents of a subsequent one. In this respect, a powerful approach is the one used in the research field of reaction dynamics, as it provides us with the most detailed knowledge of a gas-phase reaction and aims to verify whether a specific reaction pathway, and the related products, are easily accessible by the system. Several experimental techniques have been developed to achieve this (see, for instance, Levine and Bernstein, 1987; see also Casavecchia, 2000; Casavecchia et al., 1999). In our laboratory, we make use of the crossed molecular beam (CMB) technique with mass spectrometric (MS) detection. This technique, first developed in the late 1960s to address fundamental aspects, has more recently achieved the capability of studying elementary reactions of relevance in astrochemistry, as a result of improvements in the production of beams of unstable species and vacuum technology (Balucani et al., 2006, 2007; Balucani and Casavecchia, 2006a; Kaiser, 2002; Kaiser and Balucani, 2001; and references therein). The salient aspect of a CMB experiment is that the reactions are investigated under single collision conditions. The reactants are confined into separate beams which cross each other at a specific angle, that is, the species of each beam, characterized by a well-defined velocity, are made to collide only with the molecules of the other beam, allowing us to observe the consequences of well-defined single molecular collisions. The products are therefore formed only at the collision centre and then fly undisturbed towards the detector because of the large mean free path achieved by operating at a very low pressure (10^{-5} Pa). In CMB experiments, the product detection can be performed by means of spectroscopic techniques, but it is the coupling with MS detection that makes the method universal, that is, applicable to the study of (at least in principle) any reaction. All species can be ionized in the tunable electron impact ionizer which precedes the quadrupole mass filter and, therefore, it is possible to determine the mass (and, since the nature of the reactants is well-defined, the gross formula) of all possible species produced in a reaction by selecting different mass-to-charge ratios (m/z) in the mass filter. Some problems, such as dissociative ionization and background noise, have restricted the sensitivity of the method, but we have recently succeeded in overcoming most of these problems by means of the soft electron ionization (EI) approach (Balucani et al., 2006). The use of MS detection is anyhow advantageous compared to spectroscopic techniques, the applicability of which requires the knowledge of the optical properties of the products—while, in many cases, their nature itself is unknown. An advantage of CMB experiments with respect to common MS flow reactors is the possibility to measure product angular and velocity distributions, which allows one to directly derive the amount of the total energy available to the products and, therefore, the energetics of the reaction. This is crucial when more isomers with the same gross formula can be produced (Casavecchia et al., 2001; Balucani et al., 2006). In general, the CMB technique allows one to determine: (a) the nature of the primary reaction products, (b) the branching ratios of competing reaction channels, (c) the microscopic reaction mechanisms (d) the product energy partitioning. More generally, we can say that it is possible to obtain information on the underlying potential energy surfaces (PES) governing the transformation from reactants to products. The benefits of the CMB technique strongly motivate its extension to the study of reactions of interest in astrochemistry. In recent years, the CMB method with MS detection has indeed been applied to the study of astronomically relevant reactions. In this way, some reactions of atomic species—such as oxygen (Capozza et al., 2004; Casavecchia et al., 2005; Balucani et al., 2004a), carbon (Costes et al., 2006; Kaiser, 2002 and references therein; Leonori et al., 2008) and nitrogen atoms (Balucani and Casavecchia, 2006a, b; Casavecchia et al., 2001; Balucani et al., 2000b, c, 2002)—and simple radicals—such as OH (Alagia et al., 1995, 1993a, b), CN (Casavecchia et al., 2001; Balucani et al., 2000a; Kaiser and Balucani, 2001 and references therein), C_2H (Kaiser et al., 2001b, Stahl et al., 2001) and C_6H_5 radicals (Kaiser et al., 2000)—and C_2/C_3 (Kaiser et al., 2001a, 2003; Balucani, et al., 2001; Gu et al., 2006a, b, 2007; Guo et al., 2006a, b) have been characterized.

In this report, after a brief introduction on the experimental method, we will present some of the results obtained in our laboratory on the reaction $C_2+C_2H_2$, which can play a role in hydrocarbon-rich atmospheres (see, for instance, the recent model of Titan's atmosphere by Lavvas et al., 2008). C_2 is one of the simplest diatomic molecules, but, in contrast to the similar N_2 or O_2 molecules, it is highly reactive. Another peculiarity of C_2 is that the first electronically excited metastable state ($a^3\Pi_u$) lies only 610 cm^{-1} (or 7.3 kJ/mol) above the ground state ($X^1\Sigma_g^+$) (hereafter $C_2(X^1\Sigma_g^+)$ and $C_2(a^3\Pi_u)$ will be indicated with $^1C_2$ and $^3C_2$, respectively). C_2 has been identified in the interstellar medium (see for instance van Dishoeck and Black, 1982) and cometary comae (see for instance Altwegg et al., 1999; Geiss et al., 1999; Sorkhabi et al., 1997a, b), while its detection in planetary atmospheres has never been reported in the literature until now. However, several formation and destruction processes of C_2 are included in the photochemical models of planetary atmospheres where C_2H_2 has been observed (see, for example, Yung et al., 1984, Toublanc et al., 1995; Lara et al., 1996, Lebonnois et al., 2001; Wilson and Atreya, 2004; Lavvas et al., 2008; Moses et al., 2000; Romani et al., 1993; Bishop et al. 1998; Atreya, 1990), since C_2 is expected to be produced (directly or in two steps) by acetylene photodissociation (see Section 6). Because of the very low energy content of the $a^3\Pi_u$ excited state, which can be