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**Crossed-beam universal-detection reactive scattering of radical beams characterized by laser-induced-fluorescence: the case of C2 and CN**

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## Crossed-beam universal-detection reactive scattering of radical beams characterized by laser-induced-fluorescence: the case of C<sub>2</sub> and CN

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### Abstract

We have generated continuous supersonic beams of dicarbon (C<sub>2</sub>) and cyano (CN) radicals by a high-pressure radio-frequency discharge beam source starting from dilute mixtures in rare gases of suitable precursor molecules. We have subsequently characterized their internal quantum state distributions by laser-induced-fluorescence (LIF) in a new crossed molecular beam-laser apparatus. We have used these supersonic beams to study the reactive scattering of C<sub>2</sub> and CN radicals with unsaturated hydrocarbons. We report here on the C<sub>2</sub> and CN radical beam characterization by LIF and on dynamics studies of the reactions CN + C<sub>2</sub>H<sub>2</sub> (acetylene) and CN + CH<sub>3</sub>CCH (methylacetylene) by the crossed molecular beam scattering technique with universal mass spectrometric detection and time-of-flight analysis. The role of CN rovibrational excitation on the dynamics of the CN + C<sub>2</sub>H<sub>2</sub> reaction is discussed with reference to previous dynamics and kinetics studies. These reactions are of interest in the chemistry of planetary atmospheres (Titan) and the interstellar medium as well as in combustion.

*Keywords:* reaction dynamics, laser induced fluorescence, crossed molecular beam technique, radical beams, C<sub>2</sub> and CN radicals, reactions of CN with unsaturated hydrocarbons.

## 1. Introduction

The field of gas-phase *reaction dynamics* aims to understand how chemical reactions occur at the microscopic level and has experienced an increasingly strong impact in many other areas of chemistry in recent years. Experimentally, studies of reaction dynamics are carried out under single-collision conditions, which can be best obtained using molecular beams or pump-probe laser spectroscopic techniques [1]. Undoubtedly, central to the development of the field has been the “Crossed Molecular Beam” (CMB) scattering method with rotating electron-impact mass spectrometric (i.e., universal) detector and time-of-flight (TOF) analysis, as pioneered most notably by Lee and Herschbach in the late 1960s [2,3]. A further advance in our capability to investigate the dynamics of elementary reactions was made when, shortly afterwards, in the early 1970s, Zare and coworkers [4] introduced the complementary technique of Laser-Induced-Fluorescence (LIF) to the field, which permits us to probe, when applicable, the reaction products with single rotational quantum state resolution. The LIF technique proves also to be invaluable for characterizing the internal quantum state distributions of radical reactant beams [5]. Recently, in our laboratory we have used the LIF method to characterize the internal quantum state distributions of supersonic beams of C<sub>2</sub> and CN radical reactants employed in CMB experiments with universal mass spectrometric detection.

The production of supersonic beams of stable gases or liquids/solids with an appreciable vapour pressure is a trivial procedure in reactive scattering experiments. In contrast, the production of beams composed of unstable atomic/radical species can be a more complicated procedure [1,5]. The radical production technique used in our laboratory is rather general and is based on a high-pressure, high-power *radio-frequency* (RF) discharge beam source similar in design to that developed by Sibener *et al.* [6] for oxygen atoms. Atomic and molecular radicals are produced starting from dilute mixtures of suitable precursor molecules in a rare gas carrier. Here the discharge acts upon rare gas atoms at the tip of a quartz nozzle, promoting them to metastable

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3 states. These long-lived excited rare gas atoms subsequently initiate radical formation through  
4 collisions with the low concentration precursor molecules premixed in the bulk gas flow. In this  
5 way, we have been able to produce *continuous* supersonic beams [7] of a large variety of atomic –  
6 such as O(<sup>3</sup>P,<sup>1</sup>D) [8,9,10], N(<sup>4</sup>S,<sup>2</sup>D) [11,12,13], C(<sup>3</sup>P, <sup>1</sup>D) [14,15], Cl(<sup>2</sup>P) [16,17], and S(<sup>3</sup>P,<sup>1</sup>D)  
7 [18,19] - and molecular radicals – such as OH( $X^2\Pi_{3/2,1/2}$ ) [20], CN( $X^2\Sigma^+$ ) [21] and C<sub>2</sub>( $X^1\Sigma^+_g$ ) and  
8 C<sub>2</sub>( $a^3\Pi_u$ ) [22,23] (hereafter C<sub>2</sub>( $X^1\Sigma^+_g$ ) and C<sub>2</sub>( $a^3\Pi_u$ ) will be indicated with <sup>1</sup>C<sub>2</sub> and <sup>3</sup>C<sub>2</sub>,  
9 respectively)) and to study their reaction dynamics.

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20 In CMB experiments using beams of stable molecules, the internal energy content of the  
21 reactants is usually very small because an extensive cooling of the internal degrees of freedom takes  
22 place during the supersonic expansion. However, when a discharge source is used for the  
23 production of transient species (such as molecular or atomic radicals), the cooling is almost  
24 certainly incomplete. As a result, the molecular radicals might be found in a range of vibrational,  
25 rotational and even electronic energy levels, while atomic radicals can be formed in electronically  
26 excited states. Given that these energetic radicals subsequently participate in reactive collisions, it is  
27 important to know how the excess energy is partitioned between the various internal modes because  
28 it can affect the reaction mechanism. Therefore, an accurate knowledge of the internal state  
29 distributions of the reactant species would significantly enhance the interpretation of the dynamical  
30 results in CMB experiments.

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The population of the electronic and spin-orbit states of O, N and Cl atoms, produced by our  
RF discharge beam source and previously used in CMB experiments, has been determined by Stern-  
Gerlach magnetic analysis [7]. Since, after investigating the dynamics of reactions involving atomic  
species [1,24,25,26] we have recently extended our reactive scattering studies to encompass  
reactions of molecular radicals (such as C<sub>2</sub> and CN) and also radical-radical reactions (such as O +  
allyl radical [27]), it is quite important to characterize the internal states of those molecular  
transient species. Recently, we have reported on CMB experiments on the reaction C<sub>2</sub>+C<sub>2</sub>H<sub>2</sub> [22]  
which can play a role in hydrocarbon rich atmospheres, in the interstellar medium and in

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3 combustion chemistry. A peculiarity of  $C_2$ , which is one of the simplest diatomic molecules (but in  
4 contrast to the similar  $N_2$  or  $O_2$  molecules it is highly reactive), is that the first electronically excited  
5 metastable state ( $a^3\Pi_u$ ) lies only  $610\text{ cm}^{-1}$  (or  $7.3\text{ kJ mol}^{-1}$ ) above the ground state ( $X^1\Sigma_g^+$ ) [22].  $C_2$   
6 in both states is produced in the RF discharge beam source and both states can react with  
7 unsaturated hydrocarbons. As a consequence, to aid the interpretation of the data from scattering  
8 experiments on  $C_2$  reactions, we have concurrently initiated a series of experiments to characterize  
9 the rovibrational state populations and estimate the triplet-to-singlet ratio in the beams employed.  
10 We have already reported a first account of the LIF characterization of the rovibrational states of  
11  $C_2(a^3\Pi_u)$  [22]. Here we present a full account of the LIF characterization of  $C_2(X^1\Sigma_g^+, a^3\Pi_u)$  in our  
12 beams and report on the LIF characterization of continuous supersonic beams of CN radicals  
13 employed in CMB studies of the dynamics of the  $CN + C_2H_2$  and  $CN + CH_3CCH$  reactions. The  
14 CMB results on  $CN + C_2H_2$  and  $CN + CH_3CCH$  will also be reported.

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There has been a long-standing interest in the reactions of CN radicals with hydrocarbons  
because of their relevance in combustion chemistry [28]. During the last few decades the reactions  
of CN radicals with hydrocarbons have attracted a renewed attention since they are considered a  
possible source of nitriles and cyanopolyynes in hydrocarbon and nitrogen rich atmospheres and in  
the interstellar medium [29,30,31]. These species have been observed in a variety of extraterrestrial  
environments (see [30,31] and references therein) - of particular interest is the atmosphere of  
Saturn's moon Titan, subject of the recent Cassini-Huygens mission -, and they are thought to be  
potential precursors of aminoacids and nucleobases in prebiotic chemistry [29]. Undoubtedly the  
CN radical is of major astrophysical importance and has been found to act as a tracer of the physical  
conditions of sources such as comets, stellar atmospheres, and the interstellar medium. CN radicals  
also play an important role in hydrocarbon-air flames [28,32] for the production of nitrogen oxides  
and other nitrogen containing pollutants.

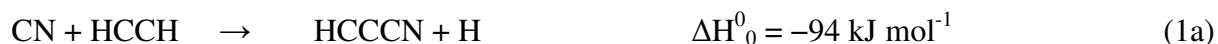
The CN radical is often considered as a pseudohalogen because of the strong C-N bond ( $748.0$   
kJ/mol) [33] and the large electron affinity ( $3.86\text{ eV}$ ) [34]. As matter of fact, the CN bond behaves

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3 as a *spectator* in many reactions. An intriguing question, however, is whether internal excitation of  
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5 CN has any effect on its reactivity, as recently pointed out in a kinetic study of the CN( $v=2$ ,  
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7  $N$ )+C<sub>2</sub>H<sub>2</sub> reaction by Olkhov and Smith [35], or on the reaction mechanism. These issues have also  
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9 been addressed in detailed studies by Macdonald and coworkers [36, 37] of the related reactions of  
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11 CN with the saturated hydrocarbons C<sub>2</sub>H<sub>6</sub> (ethane) and CH<sub>4</sub> (methane), looking at the initial  
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13 vibrational distribution of the HCN product by time resolved IR absorption spectroscopy in a flow  
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15 reactor.  
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20 The kinetics [35,38,39,40,41,42,43,44,45] and dynamics [30,31,36,37,46,47,48,49,50,51,52]  
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22 of the reactions of the CN radicals with hydrocarbons have been investigated extensively over the  
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24 years. In particular, Smith, Sims and coworkers [39,40] have measured rate constants down to very  
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26 low temperature for a variety of CN reactions with unsaturated hydrocarbons and have found them  
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28 to be very fast down to about 10 K. Leone and coworkers [45] have used tunable VUV  
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30 photoionization mass spectrometry for isomer specific product detection of CN reactions with  
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32 ethene and propene. Suits and coworkers [46] have investigated the H-atom abstraction reactions of  
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34 CN with alkanes (*n*-butane, *n*-pentane, *n*-hexane, cyclohexane) using the pulsed CMB technique  
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36 with dc slice imaging, in which the alkyl radical products were detected via single photon ionization  
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38 at 157 nm. Kaiser and coworkers have investigate a wide variety of CN reactions with unsaturated  
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40 hydrocarbons [30,31,47-52], including those with acetylene [47] and methylacetylene [48,49] using  
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42 a pulsed CMB apparatus with electron-impact mass spectrometric detection. In those experiments,  
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44 the CN beams were produced by the reaction of laser ablated species from a graphite rod with  
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46 molecular nitrogen used as seeding gas [53]. Even though the CN internal population has not been  
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48 directly characterized, CN radicals were inferred to be produced mostly in the ground vibrational  
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50 state [53], while no information is available on the rotational states of CN. Because our beam  
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52 conditions resulted in vibrationally excited CN (see Section 3), it may be of interest to compare our  
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54 results with those of Kaiser and coworkers, at comparable collision energies, to assess the possible  
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56 role of CN vibrational excitation in the CN+C<sub>2</sub>H<sub>2</sub> and CN+CH<sub>3</sub>CCH reaction dynamics.  
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According to recent *ab initio* calculations [47,49], the reaction channels which are energetically allowed under the conditions of the present study are:



Our study of the  $\text{CN} + \text{C}_2\text{H}_2$  reaction was carried out at  $E_c = 48.1 \text{ kJ mol}^{-1}$ , which is considerably higher than those explored in the studies by Huang *et al.* [47] where  $E_c$  was 21.1 and 27.0  $\text{kJ mol}^{-1}$ ; hence our results extend the dynamical information to a wider range of collision energies. Regarding the  $\text{CN} + \text{CH}_3\text{CCH}$  reaction, our collision energy of 38.3  $\text{kJ mol}^{-1}$  is only slightly higher than those ( $E_c = 13.4, 24.7, \text{ and } 34.9 \text{ kJ mol}^{-1}$ ) explored by Balucani *et al.* [49], so that the results can be compared directly. In our experiments as well as in those by Kaiser and coworkers [47,49], only the H-elimination channels could be observed for both systems. In the case of the reaction with acetylene, the H production channel was confirmed to be the only open channel in kinetic experiments [43,44]. Conversely, in the case of the reaction with methylacetylene, the  $\text{CH}_3$  elimination channel is probably important because in the similar reactions  $\text{CN} + \text{CH}_3\text{CHCH}_2$  [45] and  $\text{C}_2\text{H} + \text{CH}_3\text{CCH}$  [54] the methyl loss was identified as a major reaction pathway. Interestingly, in the case of the reaction  $\text{CN} + \text{CH}_3\text{CHCH}_2$ , the formation of HCN or HNC has not

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3 been observed [45], thus suggesting these two channels are minor in the reaction (2) as well,  
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5 especially if one considers the augmented stability of the allyl radical produced in the reactions CN  
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8 + CH<sub>3</sub>CHCH<sub>2</sub> → HCN/HNC + CH<sub>2</sub>CHCH<sub>2</sub> with respect to the CH<sub>2</sub>CCH radical produced in the  
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10 channels (2f,2g).  
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13 This paper is organized as follows. In Section 2 we describe the LIF and CMB apparatuses. In  
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15 Section 3 we report on the results of the LIF characterization of both C<sub>2</sub> and CN beams. In Section 4  
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17 we report on the results of CMB experiments for both CN+C<sub>2</sub>H<sub>2</sub> and CN+CH<sub>3</sub>CCH reactions and  
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19 we discuss the possible role of the CN internal excitation in the scattering properties. Conclusions  
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21 follow in Section 5.  
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## 27 **2. Experimental**

### 31 *a) LIF apparatus*

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33 A dedicated apparatus consisting of two main parts has been built to perform LIF measurements on  
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35 the radical beams. The LIF technique allows us to detect a wide range of radical species at the low  
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37 concentrations typically used in the reactive scattering experiments. A schematic view of this  
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39 apparatus is depicted in figure 1. The first part of the system consists of a radiofrequency discharge  
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41 radical source identical to the one employed in the CMB machine normally used for reactive  
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43 scattering experiments; this source chamber is pumped by a Freon-baffled 8000 l s<sup>-1</sup> diffusion pump  
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45 backed by a 500 m<sup>3</sup> h<sup>-1</sup> roots pump. The resultant reactant beam is collimated using a boron-nitride  
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47 skimmer (1.0 mm diameter) before passing into a main vacuum chamber (pumped by a Freon-  
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49 baffled 2400 l s<sup>-1</sup> diffusion pump backed by a 35 m<sup>3</sup> h<sup>-1</sup> mechanical pump), where it is intercepted  
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51 and probed by a tunable laser beam for LIF detection. The laser system consists of a pulsed (10 Hz),  
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53 frequency tripled Nd YAG pump laser (Quanta System, HYL 101E) at 355 nm and a dye laser  
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55 (Quanta System, D100). The laser propagates in the vacuum chamber at right angles to the radical  
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57 beam and at about 5 cm from the front of the skimmer of the beam source chamber. The optical  
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3 detection system consists of two convex lenses to collect and focus fluorescence onto the  
4 photocathode of a photomultiplier tube (THORN EMI, 9816 QB) and is placed at right angles to the  
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6 plane containing the radical beam and the probe laser, 2.5 cm above the radical beam-laser beam  
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8 crossing region (see figure 1). Care was taken to reduce sources of optical interference. Interference  
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10 filters were employed to discriminate against scattered laser light and window fluorescence when  
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12 necessary. Furthermore, window fluorescence was reduced to a minimum through the use of baffled  
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14 side-arms containing the entrance and exit windows at about 0.7 m from the observation axis.  
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16 Nevertheless, we were unable to eliminate the major source of scattered light which originated from  
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18 the RF discharge source itself, resulting in poor signal-to-noise in some experimental spectra.  
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25 Continuous supersonic beams of  $C_2$  were generated by expanding a dilute mixture of  
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27  $CO(1.5\%)/O_2(0.8\%)/$ rare gas (He or Ne) at a pressure of 100 hPa through a water-cooled quartz  
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29 nozzle with a diameter of about 0.3 mm, using a RF power of 300 W. Both C atoms and  $C_2$  are  
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31 produced in the discharge source, while no  $C_3$  is present under our experimental conditions, as  
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33 determined from mass spectrometric analysis.  $C_2$  is expected to be produced in both the ground  
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35  $X^1\Sigma_g^+$  and first excited low-lying  $a^3\Pi_u$  electronic states. For the characterization of  $^3C_2$  and  $^1C_2$   
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37 present in the  $C_2$  beam the laser dyes Coumarin 503 and Coumarin 460, pumped by the frequency  
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39 tripled Nd YAG laser at 355 nm, were used to obtain tunable wavelengths in the ranges 484-541 nm  
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41 and 442-490 nm for  $^3C_2$  and  $^1C_2$ , respectively. For the  $^1C_2$  experiments, the fundamental light from  
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43 the Coumarin 460 dye was passed through a beta-barium borate (BBO) non-linear optical crystal,  
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45 for second harmonic generation of wavelengths around 231 nm. The determination of the  
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47 population of the rovibrational levels of the  $^3C_2$  and  $^1C_2$  present in the  $C_2$  beam and an estimate of  
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49 the triplet/singlet ratio are described in Section 3.  
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55 Continuous supersonic beams of CN were generated by expanding the precursor gas mixture  
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57 of  $CO_2(0.8\%)/N_2(2.5\%)/He$  at a pressure of 100 hPa through a water-cooled quartz nozzle with a  
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59 diameter of about 0.3 mm, using a RF power of 300 W. For the characterization of the CN radical  
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the laser dye Exalite 389 (Exciton), pumped by the frequency tripled Nd YAG laser at 355 nm, was

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3 used in order to obtain tunable wavelengths in the range 384 – 390 nm. An interference filter  
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5 centred at 405 nm, 100 nm FWHM, was placed at the entrance of the photomultiplier tube to avoid  
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7 saturation. The determination of the population of the ro-vibrational levels of the CN radical in its  
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9 ground electronic state  $X^2\Sigma^+$  is described in Section 3. Electronically excited CN( $A^2\Pi$ ) and  
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11 CN( $B^2\Sigma^+$ ), located 110 kJ mol<sup>-1</sup> and 308 kJ mol<sup>-1</sup> above the ground  $X^2\Sigma^+$  state [55], respectively,  
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13 would decay to the ground state before reaching the laser (or secondary beam in the CMB  
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15 experiments) at the interaction center. In fact, the radiative lifetimes of the CN  $B$  and  $A$  states ( $v=0$ )  
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17 are about 50-60 ns and 11  $\mu$ s [55], respectively, which is shorter than the flight time (of about 25  
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19  $\mu$ s) of the fastest radical beams used.  
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### 27 ***b) Reactive scattering experiments***

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29 The crossed beam study of the reactions of CN radicals with methylacetylene and acetylene  
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31 was carried out with a CMB apparatus equipped with an electron impact mass spectrometer (MS)  
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33 for product detection. A detailed description of the apparatus can be found in other publications  
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35 [1,24,25] and only an outline will be given here. Figure 2 shows a schematic of the CMB apparatus.  
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37 Two continuous supersonic beams of reactants are crossed at an angle of 90° in a vacuum chamber;  
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39 a pressure of  $\sim 2 \times 10^{-6}$  hPa in operating conditions ensures single collision conditions. Inside the  
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41 reaction chamber, a three-stage differentially pumped detector (consisting of a quadrupole mass  
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43 filter and a hot tungsten filament as electron source) can rotate in the plane of the beams in order to  
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45 monitor the spatial distribution of the scattered particles; a time-of-flight (TOF) chopper wheel can  
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47 be placed at the entrance of the detector to measure the particles velocity distribution. At least five  
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49 scans per angle, with a counting time of 50 s, were performed for the angular distributions of the  
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51 possible reaction products, modulating the hydrocarbon beam with a tuning fork chopper at the  
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53 frequency of 160 Hz for background subtraction. Velocity distributions (TOF spectra) of the  
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55 reactants were determined by single-shot TOF analysis while those of the products were recorded at  
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3 selected angles with the pseudo-random technique, the counting times ranging from 2 to 3 hours for  
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5 the methylacetylene reaction, and from 40 to 90 minutes for the acetylene reaction.  
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8 The CN beam for the  $\text{CN}+\text{C}_2\text{H}_2$  experiments was generated by expanding the same precursor  
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10 gas mixture  $\text{CO}_2(0.8\%)/\text{N}_2(2.5\%)/\text{He}$ , as used in the LIF studies, at 150 hPa, the quartz nozzle  
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12 diameter was  $\phi \sim 0.3$  mm, and the RF power 300 W; the resulting beam has a peak velocity of 2480  
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14  $\text{m s}^{-1}$  and speed ratio 8.3. For the hydrocarbon beam, 125 kPa of pure acetylene were expanded  
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16 through a stainless steel nozzle ( $\phi = 0.1$  mm) heated at about 750 K; the beam had a peak velocity  
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18 of  $1117 \text{ m s}^{-1}$  and speed ratio 6.2. In these conditions the average collision energy is  $E_c = 48.1 \text{ kJ}$   
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20  $\text{mol}^{-1}$  [56] with a spread of about 30% (FWHM).  
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24 The CN beam for the  $\text{CN}+\text{CH}_3\text{CCH}$  experiments was generated by means of the RF discharge  
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26 source mentioned above, by expanding the precursor gas mixture at a pressure of 55 mbar through a  
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28 water-cooled quartz nozzle ( $\phi \sim 0.5$  mm), with a RF power of 300 W; the resulting beam has a peak  
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30 velocity of  $2079 \text{ m s}^{-1}$  and speed ratio 5.5. The hydrocarbon beam was obtained by expanding 400  
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32 hPa of pure methylacetylene through a stainless steel nozzle ( $\phi=0.1$  mm), and has a peak velocity of  
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34  $741 \text{ m s}^{-1}$  and speed ratio 4.2. In these conditions the average collision energy is  $E_c = 38.4 \text{ kJ mol}^{-1}$ ;  
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36 in this case the spread is about 50% (FWHM), which is larger than for the  $\text{CN}+\text{C}_2\text{H}_2$  system  
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38 because of the lower beam speed ratios.  
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43 The quantities which are measured in a CMB experiment with MS/TOF detection are the  
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45 product intensity as a function of the scattering angle – the laboratory angular distribution,  $N(\Theta)$  –  
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47 and the product intensity as a function of the scattering angle  $\Theta$  and arrival time  $t$  – the time-of-  
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49 flight spectra,  $N(\Theta,t)$ . The measurements are carried out in the laboratory (LAB) system of  
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51 coordinates, but for the physical interpretation of the scattering data it is necessary to perform a  
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53 coordinate transformation and move to the center-of-mass (CM) reference frame [3,24,25]. Because  
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55 of the finite resolution of experimental conditions (angular and velocity spread of the reactant  
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57 beams and angular resolution of the detector), the LAB to CM transformation is not single-valued  
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59 and, therefore, analysis of the LAB data is usually performed by forward convoluting tentative CM  
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3 distributions over the experimental conditions, including the energy dependence of the integral  
4 reactive cross section, which was taken to vary as  $E^{-1/3}$ , i.e., the typical behaviour for barrierless  
5 reactions dominated by long-range attractive forces [57]. In the data analysis procedure, the product  
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8 CM angular,  $T(\theta)$  and velocity (or translational energy) distributions ( $P(u')$  or  $P(E'_T)$ ) are assumed,  
9  
10 averaged and transformed to the LAB frame for comparison with the experimental distributions; the  
11  
12 procedure is repeated until the *best-fit* of the experimental distributions is obtained. The product  
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14 angular and translational energy distributions contain basic information. By measuring the product  
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16 angular and velocity distributions, we can derive the amount of the total energy available to the  
17  
18 products,  $E_{TOT}$ . We note that, because of the energy conservation rule,  $E_{TOT}$  is given by  $(E_c -$   
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20  $\Delta H^\circ_0 + E_{INT})$  where  $E_c$  is the collision energy,  $\Delta H^\circ_0$  is the enthalpy of the reaction and  $E_{INT}$  is the  
21  
22 internal energy of the reactants. In CMB experiments the internal (rovibrational) energy of the  
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24 stable molecules is relatively small when the beams are produced by expanding pure gases at room  
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26 temperature because an extensive cooling of the internal degrees of freedom takes place during the  
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28 supersonic expansion; however, when a plasma is used for the production of molecular radicals or  
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30 unstable molecules like  $C_2$  and CN the cooling is not necessarily complete (see below) and  $E_{INT}$  can  
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32 give a sizeable contribution to the total energy.  
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### 43 **3. Results and Discussion: The LIF experiments**

#### 44 **a) LIF characterization of the $C_2(a^3\Pi_u)/(X^1\Sigma_g^+)$ beam**

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51 We began the  $C_2$  beam characterization by looking at the rovibrational spectra of the triplet  
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53 state of  $C_2$ .  $^3C_2$  radicals were excited *via* the (0, 0), (1, 1) and (2, 2) bands of the  $d^3\Pi_g - a^3\Pi_u$  Swan  
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55 system at ~ 516.5, 512.9 and 509.8 nm respectively. Emission from the  $d^3\Pi_g$  state with a lifetime of  
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57 ~ 100 ns [58] was observed in the (0, 1) (1, 2) and (2, 3) bands at 563.6, 558.6 and 554.1 nm  
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59 respectively. For the current measurements, two different interference filters were employed. The  
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first one, centred at 560 nm with a FWHM of 10 nm and a transmission factor of 0.67 at the peak

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3 was primarily used to observe fluorescence originating from the ground and first excited vibrational  
4 states of  $^3\text{C}_2$ . The second one, centred at 550 nm with a FWHM of 20 nm and a transmission factor  
5 of 0.72 at the peak was used to observe fluorescence originating from the first and second excited  
6 vibrational states of  $^3\text{C}_2$ . In this way, it was possible to obtain estimates of the rotational  
7 temperatures and relative vibrational populations (and therefore the vibrational temperature) of the  
8  $^3\text{C}_2$  formed in the beams. For measurements of the rotational temperature of the vibrational states,  
9 the relative line intensities were corrected for the changing filter transmission profile across the  
10 band. Figure 3 panel (a) shows the experimental spectrum obtained for the (0, 0) band of the  $d^3\Pi_g -$   
11  $a^3\Pi_u$  Swan system with helium as the carrier gas. Alongside the experimental spectra are presented  
12 the best fit simulations (see panel (b)) of the data using the Diatomic spectral simulation program  
13 [59] using previously published molecular constants for  $^3\text{C}_2$  as input parameters [60]. These  
14 synthetic spectra allow us to determine rotational temperatures of approximately 250 K for the (0,  
15 0) band of  $^3\text{C}_2$  with helium as carrier gas (the rotational temperature is about 200 K when using Ne  
16 as carrier gas [22]). Similar results are also found for the (1, 1) and (2, 2) band spectra. For  
17 measurements of the relative vibrational populations, it was important to account for a  
18 normalisation factor for the probe laser assuming a linear relationship between the laser energy and  
19 the fluorescence intensity in addition to the filter transmission profile. Furthermore, it was also  
20 necessary to include the transition probabilities of both the excitation transition and the fluorescence  
21 step [61]. The usual procedure for obtaining estimates of the relative vibrational populations is to  
22 integrate the area under the same rotational lines in adjacent vibrational bands for several different  
23 lines to determine an average ratio. However this analysis was inappropriate for this system, due to  
24 low concentrations of  $^3\text{C}_2$  in the molecular beam and significant overlap of spectral lines in the  
25 bandhead region of the experimental spectra. As the rotational temperatures of the vibrational bands  
26 are essentially equivalent for any particular carrier gas, better estimates of the relative populations  
27 were obtained by integrating the area under the entire P branch in each vibrational band after  
28 applying the various correction factors as described above. Furthermore, the wavelength range of

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3 each integrated band was carefully controlled so as to capture rotational levels up to and including  $J$   
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each integrated band was carefully controlled so as to capture rotational levels up to and including  $J = 23$ . In this way, the relative populations of the  $v = 0, 1$ , and  $2$  levels have been determined to be  $1, 0.54$  and  $0.44$  respectively. It is important to note that it is likely that R-branch lines from the  $(0, 0)$  and  $(1, 1)$  bands make small contributions to the relative populations of the  $v = 1$  and  $v = 2$  levels. Taking this into account leads us to estimate a vibrational temperature of  $3500 \pm 750$  K for the triplet state  $C_2$  in the molecular beam. This value was determined using the relative populations of the  $v=0$  and  $v=1$  bands; the  $v=2$  band population was somewhat too large for it to fit to the  $3500$  K distribution, so the error on the  $v=2$  population is of the order of  $\pm 50\%$ . No experimental information could be obtained about the population of  $(v > 2)$  levels.

A similar characterization has been performed for the internal states of  $^1C_2$  with helium and neon as carrier gases. In this case we have looked at the  $(0,0), (1,1), (2,2)$  and higher transitions of the Mulliken ( $D^1\Sigma_u^+ - X^1\Sigma_g^+$ ) bands at approximately  $231$  nm (see figure 3 – panel c). In this wavelength region, the vibrational bands of the singlet state coincide to a large extent, thus we have the opportunity to examine the relative populations of several bands in a single spectral scan. Unfortunately, the spectral region is also highly congested, making exact determinations more complex. However, several conclusions can be drawn from the spectral data. Examination of the R-branch profile of the  $(0, 0)$  band of  $^1C_2$  in helium, which is found to be reasonably uncongested, allows us to conclude that the rotational temperature obtained from the fit of  $400$  K is slightly higher than that found for  $^3C_2$  in helium. From the best fit simulations of the experimental data (see figure 3 – panel d) it is clear that the relative vibrational populations are comparable to those obtained in the triplet state characterisation. Thus a vibrational temperature of  $3500$  K is also appropriate to describe the  $^1C_2$  distribution. It should be noted that this vibrational temperature fits well the  $(0,0)$  and  $(1,1)$  bands, while no quantitative information was actually extracted from the  $(2,2)$  band due to the band overlap. Furthermore, as the vibration bands are coincident in this wavelength region, the long wavelength end of the singlet spectrum shows that higher vibrational



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3 states ( $v \geq 3$ ) are almost certainly present, and thus it is likely that a similar progression should also  
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5 be observable for the triplet state.  
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8 These ( $^3C_2, ^1C_2$ ) beams have been recently used to study the dynamics of the  $C_2+C_2H_2$   
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10 reaction in CMB experiments [22]. One important quantity required for the interpretation of these  
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12 reactive scattering data is the relative triplet-to-singlet  $C_2$  population ratio. This could not be  
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14 directly achieved in our LIF measurements. Nevertheless, by comparing the loss of signal intensity  
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16 of the triplet and singlet state measurements when moving from helium to neon as the carrier gas,  
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18 we could establish that the singlet/triplet state ratio remains approximately constant for experiments  
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20 conducted with the two carrier gases. The absence of an alteration of the singlet-to-triplet state  
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22 populations in the two experiments has allowed us to establish the trend of the reactive scattering  
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24 functions with increasing collision energy. Quite interestingly, the use of vibrationally excited  
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26 ( $^3C_2, ^1C_2$ ) does not seem to influence the reaction mechanism, at least as far as the product energy  
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28 release is concerned, and the reactions seem to be vibrationally adiabatic [22].  
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### 34 35 36 **b) LIF characterization of the CN radical beam** 37

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39 When discharging CO (or  $CO_2$ ) /  $N_2$  / He (or (Ne) gas mixtures, in addition to formation of  
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41 C and  $C_2$  species, CN radicals are also produced. The mechanism leading to formation of CN is not  
42  
43 clear, but presumably involves reactions of C atoms with molecular nitrogen (with one or both  
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45 species in an electronically excited state), electronically excited atomic/molecular nitrogen with CO  
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47 (or  $CO_2$ ) and/or C+N recombination in the plasma before the supersonic expansion is completed.  
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49 Because of the high energetic processes occurring in the hot plasma, we expect the CN radicals to  
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51 be formed in highly excited rovibrational states, as well as in electronically excited states. While the  
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53 electronically excited states decay to the ground electronic state because of their short lifetimes  
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55 [55], the rotational excited states are not expected to be completely quenched because of the  
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57 characteristics of the RF discharge source (hot plasma and moderate supersonic expansion), and the  
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59 vibrational excited states are not expected to relax because of their large energy spacing.  
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3 Characterization of the CN radicals was undertaken using LIF of a beam similar to the one used in  
4 the CMB experiments. Experiments were only performed on CN/He beams due to the low signal  
5 levels for CN/Ne mixtures (never used in CMB experiments). Slightly different expansion  
6 conditions and RF power proved not to affect significantly the internal quantum state distribution,  
7 so that the CN beams interrogated by LIF and those used in CMB experiments have very similar  
8 rovibrational distributions. We measured the rovibrational distribution of the ground electronic  $^2\Sigma^+$   
9 state of CN primarily via the (0, 0), (1, 1), (2, 2) and (3, 3) bands of the  $B^2\Sigma^+ - X^2\Sigma^+$  system at  
10 387.7, 386.5, 385.5 and 384.7 nm, respectively. The experimental spectrum recorded in the  
11 wavelength range of 384.0-388.5 nm is reported in figure 4(a), while an expanded view (from 386.5  
12 to 388.5 nm) is shown in figure 4(c). The experimental spectra were then simulated using the  
13 LIFBASE spectral simulation program [62]. The simulation also contained contributions from  
14 higher vibrational levels ( $4 \leq v \leq 9$ ) which fall in the 384 – 389 nm wavelength range in order to  
15 realistically reproduce the observed spectral lines. The simulations are reported in the figures 4(b)  
16 and (d).

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37 The rotational distributions for low vibrational levels were clearly seen to be bimodal, as  
38 exemplified in figure 5(a) for the rotational distribution of CN( $v=0$ ). A rotational temperature of  
39 approximately 250 K, in fact, accounts for low rotational quantum numbers ( $N < 10$ ) with a peak in  
40 the population at  $N = 6$ . In contrast, the rotational populations in higher quantum numbers were  
41 found to exceed those of a thermalised distribution (at 250 K, the rotational population falls to zero  
42 at  $N \sim 24$ ) with a minimum in the population at approximately  $N = 22 - 28$ . A second maximum in  
43 the population distribution was seen to occur at around  $N = 39 - 44$  (corresponding to  
44 approximately 42 kJ mol<sup>-1</sup> of rotational energy from the  $v = 0$  level), with peak values  
45 corresponding to a third of the primary maximum. The tail of the rotational distribution occurred at  
46 approximately  $N = 60$  (corresponding to 82 kJ mol<sup>-1</sup>). It is worth noting that bimodal rotational  
47 distributions have also been obtained for CN radicals generated from photolysis of precursor  
48 molecules such as (CN)<sub>2</sub>, ClCN and BrCN, as used in the flow studies of Macdonald and coworkers  
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[36,37]. Studies of rotational relaxation of high rotational levels of CN, as produced for instance from the BrCN photolysis at 193 nm, found that the initial CN N-levels relaxed to a 300 K Boltzmann distribution (peaking at  $N=8$ ), and at one peaking near  $N\sim 65$ , corresponding closely to the initial maximum in the CN(N) distribution [63]. It was observed that N states below  $N\sim 40$  were thermalized quickly, within a few gas kinetic collisions; however, for  $N>67$ , these states are essentially metastable and very high N states were present even after a 1000 gas kinetic collisions with Ar or He. It was noted that other collision partners such as NO were much more efficient at relaxing these high CN(N) states. In our case similar effects are expected to occur, with expectedly somewhat more relaxation taking place because of the presence of molecular partners such as CO<sub>2</sub>/CO and N<sub>2</sub>, besides He (during the supersonic expansion, hundreds of collision take place).

Identical rotational distributions were used for all vibrational levels in the simulation due to the difficulty of fitting to the low signal to noise and congested wavelength region of the experimental spectrum. Nevertheless, the vibrational populations were found to be reasonably well described by a thermalised distribution (shown in figure 5(b)) with a vibrational temperature of 6500 K. By analyzing the present experimental results, therefore, we can conclude that enough inelastic collisions occur upon exiting the discharge source to partially relax the CN rotational populations, whereas the vibrational populations remain largely unaffected and are seen to maintain a hot distribution.

#### 4. Results and Discussion: The crossed molecular beam experiments

##### a) $CN + C_2H_2$

In figure 6 is shown the product laboratory angular distribution detected at  $m/z=51$  (corresponding to the ion C<sub>3</sub>HN<sup>+</sup>) together with the relevant velocity vector (“Newton”) diagram. The error bars (representing  $\pm 1$  standard deviation) are also reported when they exceed the size of the dots indicating the intensity averaged over the different scans. In the Newton diagram of figure 6 are also shown the Newton circles relative to the two possible isomers HCCCN (channel 1a,

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3 dashed lines) and HCCNC (channel 1b, dotted lines) in the assumption that all the available energy  
4 is converted into product translational energy. The Newton circles delimit the LAB angular range  
5 within which each specific isomer can be scattered. The quite different exothermicities of the two  
6 channels imply a different extension of the Newton circles and of the relative scattering angular  
7 ranges. In figure 7 are shown the TOF spectra measured at selected angles. The LAB angular  
8 distribution is relatively narrow, but is characterized by a broad peak which is located slightly to the  
9 left of the center-of-mass angle ( $\Theta_{CM}=24.3^\circ$ ). The TOF spectra are also relatively sharp and  
10 centered around the CM velocity (see figure 7). The solid lines in figures 6 and 7 represent the  
11 curves calculated with the best-fit functions depicted in figure 8. The grey areas in figure 8 delimit  
12 the range of CM functions which still afford an acceptable fit of the data, *i.e.*, they represent the  
13 error bars of the present determination. The best CM angular distribution (figure 8, top panel)  
14 exhibits a significant intensity in the whole angular range, with a marked preference for the forward  
15 hemisphere with a best-fit ratio  $T(180^\circ)/T(0^\circ)$  of 0.66. The best-fit ratio can vary by about  $\pm 0.10$   
16 within the error bars. This shape is consistent either with the competition of two reaction  
17 mechanisms (a direct one generating forward scattering and an indirect one generating a backward-  
18 forward symmetric angular distribution) or with the formation of a bound intermediate with a  
19 lifetime  $\tau$  comparable to its rotational period  $\tau_R$  (*osculating* model of chemical reaction [64,65,66]).  
20 If the latter is the case, from the difference of the intensity at the two poles it is possible to give an  
21 estimate of the complex lifetime relative to its rotational period by means of the equation  
22  $T(180^\circ)/T(0^\circ) = e^{-\tau_R/2\tau}$ , where  $T(0^\circ)$  and  $T(180^\circ)$  are the values assumed by  $T(\theta)$  at the two poles.  
23 With the observed asymmetry of the CM angular distribution, therefore, the  $\tau/\tau_R$  ratio is 1.2. As far  
24 as the best-fit  $P(E'_T)$  is concerned (figure 8, bottom), we note that the peak is broad (extending from  
25 about 30 to 60  $\text{kJ mol}^{-1}$ ) and quite displaced from  $E'_T=0$ , which might indicate the presence of an  
26 exit barrier, but the  $P(E'_T)$  show some intensity also at very small  $E'_T$  values. The fit of both angular  
27 and TOF distributions was very sensitive to the rise and the peak position, while it was less  
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3 sensitive to the tail of the  $P(E'_T)$ , as clearly visible from the shape of the grey area. Nevertheless, it  
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5 is quite clear that the extra amount of energy carried by the CN vibrational excitation is not needed  
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7 to fit the experimental distributions (see the arrows in the bottom panel of figure 8 indicating the  
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9 total available energy for the reaction involving the vibrationally excited states of CN). The average  
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11 product translational energy, defined as  $\langle E'_T \rangle = \sum P(E'_T)E'_T / \sum P(E'_T)$  is about  $57 \text{ kJ mol}^{-1}$   
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13 corresponding to a fraction of the total available energy,  $\langle f_T \rangle = \langle E_T \rangle / E_{TOT}$ , of about 0.4, where  
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15  $E_{TOT}(=E_c - \Delta H^0_0)$  is the one associated to the reaction of CN in its ground rovibrational level ( $v=0$ ,  
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17  $N=0$ ) leading to the more stable isomer HCCCN. The present experimental results are consistent  
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19 with those obtained by Huang *et al.* [47] in pulsed CMB experiments at the lower collision energies  
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21 of 21.1 and 27.0  $\text{kJ mol}^{-1}$ . At those lower  $E_c$ s, the CM angular distributions already showed a less  
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23 pronounced preference for forward scattering, in agreement with the trend predicted by the  
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25 *osculating* model of chemical reaction with increasing  $E_c$  [64-66]. Quite interestingly, at the lower  
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27  $E_c$  investigated by Huang *et al.* the best-fit  $T(\theta)$  has a maximum around  $\theta=60^\circ-95^\circ$  and that was  
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29 taken as an evidence of a “bent displacement” of the H atom during the complex fission. Also the  
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31 main characteristics of the best fit  $P(E'_T)$  of Ref. [47] are consistent with the present determination  
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33 with the  $\langle f_T \rangle$  ranging from 0.33 to 0.36. Nevertheless, an important difference with respect to the  
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35 experiments of Huang *et al.* is that under the conditions of the present experiment, the formation of  
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37 the HCCNC isomer is also possible. As a matter of fact, not only is the experimental  $E_c$  sufficient to  
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39 compensate for the endothermicity of that channel ( $+13 \text{ kJ mol}^{-1}$ ), but it is also sufficient to  
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41 overcome the exit barriers of  $+36$  or  $+19 \text{ kJ mol}^{-1}$  which have been theoretically predicted along the  
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43 two reaction pathways leading to HCCNC+H (see figure 9 of Ref. [47]). In addition to the increased  
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45  $E_c$ , in our study the CN radical is also internally excited (see Section 3-b) with an average  
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47 vibrational and rotational energy content of 41 and 16  $\text{kJ mol}^{-1}$ , respectively, so that  $E_{TOT}$  is equal to  
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49  $106 \text{ kJ mol}^{-1}$ . As a consequence, in our experiment we expect a contribution from channel (1b).  
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Quite interestingly, the initial vibrational excitation of the CN bond does not seem to influence the main reaction outcomes. This is witnessed by two facts: on one side there is no need

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3 to consider the extra amount of energy added by CN in  $v=1-4$  even though the energy content of  
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5 the vibrationally excited CN levels is quite sizable (e.g.  $\Delta v_{1-0}=24.4 \text{ kJ mol}^{-1}$ ,  $\Delta v_{2-0}=48.6 \text{ kJ mol}^{-1}$ ,  
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7  $\Delta v_{3-0}=72.4 \text{ kJ mol}^{-1}$ ); on the other side, there is a strong similarity with the results by Huang *et al.*  
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9 and it is known that the CN generated in their laser ablation beam source is produced mostly in the  
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11 ground  $v=0$  level. The lack of visible effects in the scattering functions due to the vibrational  
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13 excitation of CN is not surprising, as the vibrational excitation is expected to promote a reaction  
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15 when it affects a bond which is going to break during the reaction itself. Since the CN moiety is  
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17 actually incorporated in the HCCCN/HCCNC products, it is reasonable to expect that the  
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19 vibrational excitation of the reactant will be maintained essentially as vibrational excitation of the  
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21 molecular product. In other words it is not unexpected that the extra amount of energy available to  
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23 the system when the reaction involves CN in one of the excited vibrational levels is not converted  
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25 into product translational energy. Our interpretation is perfectly in line with that proposed by Smith  
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27 and coworkers [35,67] by analyzing the rate coefficients for the reaction  $\text{CN}+\text{C}_2\text{H}_2$  with CN in  $v=0$   
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29 and 2 at  $T=296 \text{ K}$ . The measured  $k$  was  $\sim 2.7 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  irrespectively of the CN  
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31 vibrational state, thus suggesting that vibrational excitation does not promote the reactivity. It is  
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33 interesting to note that also the  $\text{CN}+\text{C}_2\text{H}_6$  and  $\text{CN}+\text{CH}_4$  abstraction reactions were found to be  
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35 essentially vibrationally adiabatic [36, 37]. In their studies Macdonald and coworkers [36,37] varied  
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37 the initial vibrational population of the CN radical by using different precursor molecules for the  
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39 CN radical source. For both reactions it was found that the initial  $\text{CN}(v)$  excitation did not appear as  
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41 HCN excitation of the C-N,  $\text{HCN}(v_1,0,0)$ , or combination stretching vibrational levels,  
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43  $\text{HCN}(v_1,0,v_3)$ , in which the C-H stretching motion is also excited (the bending  $v_2$  could not be  
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45 analyzed in those studies). In fact, the  $\text{HCN}(v_1,0,v_3)$  vibrational levels were not significantly  
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47 populated by the reaction, and hence, if the reaction is adiabatic in terms of the CN vibrational  
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49 degree of freedom, then bending motion must also be excited along the C-N stretching motion in  
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51 the HCN product. Indeed, IR chemiluminescence studies by Copeland *et al.* [38] of HCN ( $v_1, v_2, v_3$ )  
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53 formed from CN reactions with a variety of alkanes (including methane and ethane) found that the  
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bend stretch combination levels of HCN were preferentially populated and not the pure HCN(0, 0,  $v_3$ ) stretching manifold.

The effect of the CN rotational excitation is more difficult to predict and quantify. It is known that the rotational excitation of a reactant molecule can affect the reaction mechanism when the system follows direct dynamics and the transition state geometry is different from the geometry of the van der Waals complex formed in the entrance channel because of long range forces, as in the case of the Cl+H<sub>2</sub>/D<sub>2</sub>/HD reactions [16,17,68]. Also, in the case of slightly endothermic reactions characterized by a potential energy barrier, such as O(<sup>3</sup>P)+HCl→OH+Cl, a marked increase in reaction cross section with HCl rotation was observed by Zare and coworkers [69,70]. The effect is much more subtle when an exothermic reaction proceeds through the formation of a bound intermediate and without an entrance barrier (associated to a transition state), such as the reaction of interest here. For instance, in the case of the reaction O(<sup>1</sup>D)+H<sub>2</sub>, the OH product rovibrational distributions have been seen to be slightly different when the reactant H<sub>2</sub> is in the ground or first excited rotational level [71]. Accurate quantum dynamical calculations for the barrierless reaction C(<sup>1</sup>D)+H<sub>2</sub> have shown small differences in the detailed shape of the CM angular distributions when the reacting H<sub>2</sub> is in the ground and first excited rotational levels and also the value of the integral cross sections is slightly affected by the H<sub>2</sub> rotational state [15,72].

A very interesting experimental finding concerning the effect of CN rotation on the CN+C<sub>2</sub>H<sub>2</sub> reaction comes from the determination of the rate coefficients for the reaction of CN in various rotational levels of the  $v=2$  state [35, 67]. In particular, the rate coefficients decrease from  $7.9 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  for  $N=0$  to  $0.8 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  for  $N=20$ , clearly indicating a minor capability of reacting for the higher rotational levels of CN in  $v=2$  [35]. As far as the reaction mechanism is concerned, we can conceive that a fast rotating CN radical can smear the preference for the C-side attack connected to the formation of the much more stable *cis/trans*-HCCHCN intermediates. This is because the long-range forces that would orient the CN radical with the electron-density rich C-side towards the  $\pi$  system of acetylene are contrasted by the fast CN

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3 rotation. A resulting effect can be to enhance the HCCNC channel over the HCCCN one. Also, the  
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5 increased internal energy content of the addition intermediates *cis/trans*-HCCHCN and *cis/trans*-  
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7 HCCHNC with respect to the experiments by Huang *et al.* (due both to the increase of  $E_c$  and to the  
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9 internal excitation of the CN radical) can significantly shorten the intermediate lifetimes. This in  
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11 turn leads to a more pronounced bias for the forward scattering – as already commented on – and  
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13 might impede the conversion of *cis/trans*-HCCHNC to *cis/trans*-HCCHCN which was predicted by  
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15 RRKM calculations to be the most probable fate of the *cis/trans*-HCCHNC intermediates formed by  
16  
17 the CN addition on the N-side under the conditions of the experiments by Huang *et al.* In this  
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19 respect, we note that the relatively fast rise of the best-fit  $P(E'_T)$  can be taken as a hint that a second  
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21 contribution associated to the endothermic channel leading to HCCNC is open. In fact, because of  
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23 its endoergicity, the total available energy (for CN( $v=0$ ,  $N=0$ ) reaction) is only  $35 \text{ kJ mol}^{-1}$ , that is  
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25  $107 \text{ kJ mol}^{-1}$  less than for the HCCCN forming channel. Hence, if the product translational energy  
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27 distribution also peaks at about 30% of the total available energy, as in the case of the HCCCN  
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29 channel, the maximum would occur at the quite low translational energy of  $10 \text{ kJ mol}^{-1}$ , implying a  
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31 fast rise of the  $P(E'_T)$  distribution. As a matter of fact, during the best-fit procedure we have tried to  
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33 simulate the experimental results by using two different contributions, one associated to the  
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35 dominant HCCCN formation channel and one (accounting for roughly 10%, with an upper bound of  
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37 about 20%) associated to the HCCNC formation. Nonetheless, since a satisfying fit could be  
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39 obtained also when using a single set of CM functions, we have preferred not to report the double  
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41 channel fit.

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50 Notably, as discussed in the work of Macdonald and coworkers [36,37], particularly  
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52 interesting is the effect of the high CN rotation whereby a correlation between rotational motion in  
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54 the spectator diatom, CN, and the bending motion of the product HCN molecule could rationalize  
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56 the preference for the HCN product having bending excitation in the CN+C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> reactions. Also  
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58 in our case the high CN rotation could correlate with bending excitation of the HCCCN product.  
59  
60 However, the CN+C<sub>2</sub>H<sub>2</sub> reaction proceeds via an addition mechanism with formation of a stable



intermediate which then decomposes because of its high internal energy content, and therefore it is expected to follow a dynamics different than that of the  $\text{CN}+\text{C}_2\text{H}_6$  reaction, which is a direct abstraction reaction. Further experimental and theoretical effort will be needed to elucidate the extent of mode specificity in the  $\text{CN}+\text{C}_2\text{H}_2$  reaction.

In conclusion, the main characteristic of the scattering functions derived here are consistent with those derived by Huang *et al.* [43] at lower  $E_c$ . Since in their experiments the CN radical was produced mainly in the ground vibrational level, we can conclude that the CN vibrational excitation does not affect significantly the reactive scattering properties of the system, as expected because of the *spectator* nature of the CN bond. If there is an effect associated to the internal excitation of the CN radical, this is rather associated to the CN fast rotation which could partially enhance the minor HCCNC channel over the favoured HCCCN channel. Both observations are in line with the findings of previous kinetic experiments [35, 67].

**b)  $\text{CN} + \text{CH}_3\text{CCH}$**

Angular distribution and TOF spectra have been measured at the mass-to-charge ratio  $m/z=65$  ( $\text{C}_4\text{H}_3\text{N}^+$ ), at the electron energy of 60 eV, to explore the H-elimination channels (2a) and (2b) for the reaction of CN radicals with methylacetylene. In an attempt to verify the occurrence of methyl elimination (2c), reactive signal has been recorded at  $m/z=51$  ( $\text{C}_3\text{HN}^+$ ) and 50 ( $\text{C}_3\text{N}^+$ ). Unfortunately, carbon atoms are present in large amounts in the CN beams and that means that both reactions of C and CN occur at the same time. The main channel of the  $\text{C}+\text{CH}_3\text{CCH}$  reaction is the one leading to  $\text{C}_4\text{H}_3$  isomers which have the parent and an intense daughter peaks at  $m/z=51$  ( $\text{C}_4\text{H}_3^+$ ) and  $m/z=50$  ( $\text{C}_4\text{H}_2^+$ ), thus overlapping with the  $\text{CH}_3\text{N}$  and  $\text{C}_3\text{N}$  masses. Unfortunately, the signals recorded at  $m/z=51$  and  $m/z=50$  were essentially due to the  $\text{C}+\text{CH}_3\text{CCH}$  reaction and it was impossible to separate a contribution from the channel (2c) of the reaction  $\text{CN}+\text{CH}_3\text{CCH}$ . As a matter of fact, certainly because of the different fragmentation patterns of  $\text{CH}_3\text{N}$  and  $\text{C}_4\text{H}_3$ , a small difference in the  $m/z=51$  and  $m/z=50$  distributions was visible thus suggesting that the contribution

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3 to the observed signal from the channel (2c) was not negligible. Further experiments, focusing on  
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5 the distributions of the other daughter ions from  $C_4H_3$  at masses different from those originating  
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7 from HCCCN, can possibly allow us to disentangle the contribution from channel (2c). The  
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9 detection of the HCN or HNC products scattered by the  $CH_2CCH$  co-product is particularly difficult  
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11 because of the very unfriendly kinematics and was not attempted. Nevertheless, as already pointed  
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13 out in the introduction, these channels are supposed to be minor by analogy with the  
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15  $CN+CH_3CHCH_2$  reaction [44].  
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20 Figure 9 shows the product laboratory angular distribution detected at  $m/z=65$  together with  
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22 the relevant velocity vector (“Newton”) diagram. The error bars (representing  $\pm 1$  standard  
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24 deviation) are also reported when they exceed the size of the dots indicating the intensity averaged  
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26 over the different scans. In the Newton diagram of figure 9 are also shown the Newton circles  
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28 relative to the two possible isomers cyanomethylacetylene  $CH_3CCCN$  (channel 2a, dashed lines)  
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30 and cyanoallene  $CH_2CCHCN$  (channel 2b, dotted lines) in the assumption that all the available  
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32 energy is converted into product translational energy. The Newton circle associated to HCCCN  
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34 scattered by  $CH_3$  (channel 2c) is also shown. In figure 10 are shown the TOF spectra measured at  
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36 selected angles. The LAB angular distribution is relatively narrow, with a sharp peak in the  
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38 proximity of the center-of-mass angle ( $\Theta_{CM}=28.7^\circ$ ). The solid lines in figures 9 and 10 represent the  
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40 curves calculated with the best-fit CM functions depicted in figure 11. The grey areas in figure 11  
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42 delimit the range of CM functions which still afford an acceptable fit of the data. The best-fit CM  
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44 angular distribution (figure 11, top) exhibits a significant intensity in the whole angular range, with  
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46 some preference for sideways scattering with a peak around  $100^\circ$ . An isotropic  $T(\theta)$  still affords an  
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48 acceptable fit of the experimental distributions as shown by the upper limit of the  $T(\theta)$  error bars.  
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50 The best-fit  $P(E'_T)$  (figure 11, bottom) is characterized by a peak around  $30 \text{ kJ mol}^{-1}$ . The fit of both  
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52 angular and TOF distributions was very sensitive to the rise and the peak position, while it was less  
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54 sensitive to the tail of the  $P(E'_T)$ , as clearly visible from the shape of the grey area. The average  
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56 product translational energy is about  $43 \text{ kJ mol}^{-1}$  corresponding to a fraction of the total available  
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3 energy of about 0.30 when considering the reaction of CN in its ground rovibrational level ( $\nu=0$ ,  
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5  $N=0$ ) leading to the more stable isomer  $\text{CH}_3\text{CCCN}$ .  
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8 The present experimental results are consistent with those obtained by Balucani *et al.* [49] in  
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10 pulsed CMB experiments at the lower collision energies of 13.4, 24.7 and 34.9  $\text{kJ mol}^{-1}$ . At those  
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12 lower  $E_{\text{c}}$ s, the CM angular distributions are essentially isotropic, with a very small preference for  
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14 forward scattering at the highest  $E_{\text{c}}$  investigated and some propensity for sideways scattering in the  
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16 other cases. As already commented on, an isotropic CM  $T(\theta)$  can still furnish a good fit of the  
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18 present experimental distributions and, therefore, even though there is a more marked propensity for  
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20 sideways scattering, the present experimental results overlap with the previous ones within the  
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22 experimental uncertainties. Interestingly, since both the channels (2a) and (2b) contribute similarly  
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24 to the reactive signal, as seen in CMB experiments using isotopically labelled  $\text{CD}_3\text{CCH}$  [48], and  
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26 since the decomposing transition state leading to cyanoallene has the right properties to explain  
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28 sideways scattering (because there is a change from  $sp^3$  to  $sp^2$  hybridization of the carbon atom  
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30 involved in the C-H bond fission), a more pronounced preference for the sideways scattering can be  
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32 taken as an evidence that in our experiments there is an increase of cyanoallene production.  
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38 The best-fit  $P(E'_{\text{T}})$  is very similar to those determined by Balucani *et al.*: in those cases as  
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40 well, the peak position is around 30-40  $\text{kJ mol}^{-1}$  and correspond to an average fraction of energy  
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42 released as product translational energy of 0.30. Also for this system, therefore, the strong  
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44 similarities in the  $P(E'_{\text{T}})$  characteristics of the two sets of experiments point to a negligible role of  
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46 the CN vibrational excitation in determining the product energy release and this reaction can also be  
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48 considered vibrationally adiabatic.  
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53 As for the reaction mechanism, the rotation of the CN radical can favour the N-side attack to  
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55 the  $\pi$  orbitals of methylacetylene in this case as well, possibly leading to the isonitrile isomers.  
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57 Unfortunately, in addition to the reaction enthalpies there is not much theoretical information on the  
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59 channels (2d) and (2e), especially as far as possible exit barriers or easy pathways for the  
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conversion between nitriles and isonitriles intermediates are concerned. In all cases, there are no

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apparent signs of their formation, neither in our experiments nor in the experiments of Balucani *et al.* [49] at similar  $E_c$ s. As for other possible effects of the CN rotational excitation, a comparison of our results with those by Balucani *et al.* at the very similar  $E_c$  of  $34.9 \text{ kJ mol}^{-1}$  might indicate that the CN high  $N$  levels could enhance the sideways scattering, either by inducing a larger yield of the cyanoallene product or by affecting the total angular momentum associated to the reactive collision. In the case of the present experiments, in fact, a very low correlation between  $L$  and  $L'$  is expected because of the significant contribution of the reactant rotational angular momentum. How this should produce more sideways scattering is, however, unclear.

## 5. Conclusions

In CMB experiments, when using supersonic molecular radical beams produced by means of a discharge source or produced during the expansion by a chemical reaction, care has to be taken with the characterisation of the internal rovibrational or electronic levels of the molecular radicals. In our laboratory we have pursued LIF characterization to determine the rovibrational distributions of the transient species  $C_2$  and CN, produced in continuous supersonic beams by means of a separate RF discharge source which is identical to the one used in reactive scattering experiments. Because of the characteristics of the discharge beam source – which aims at limiting the radical recombination – the produced radicals undergo a limited number of relaxing collisions during the supersonic expansion and their rotational and, especially, vibrational distributions are not efficiently relaxed, leaving both diatomic species in excited levels.

Quite interestingly, both the reactions of  $C_2$  and CN with simple unsaturated hydrocarbons appear to be unaffected by the vibrational excitation of  $C_2$  and CN. This is not surprising, at least for the case of the reactions  $CN+C_2H_2$  and  $CN+CH_3CCH$  and  ${}^3C_2+C_2H_2$ , because both CN and  ${}^3C_2$  are not directly involved in the bond rearrangements leading from the reactant to the product species and they act as *spectator*. It is somewhat more surprising in the case of the  ${}^1C_2+C_2H_2$  reaction [22,73,74], because, according to the *ab initio* calculations of the relevant singlet potential

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3 energy surface [73,74], the two carbon atoms of the  $^1\text{C}_2$  reactant split during the rearrangements of  
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5 the initial addition intermediate that lead to the formation of  $\text{C}_4\text{H}+\text{H}$  products. In all cases, the  
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7 investigated systems appear to be vibrationally adiabatic. Less clear is the role of the rotational  
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9 excitation of CN and  $\text{C}_2$ . In the case of the CN radical, we might expect that a fast rotating CN will  
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11 smear the preference for the C-side attack to the unsaturated bond of the hydrocarbon, thus  
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13 increasing the yield of the less favourable channels leading to isonitrile isomers. The present  
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15 experimental results add further insights into the role of CN rotational and vibrational excitation  
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17 which are in line with those based on kinetic experiments [35] for the reaction  $\text{CN}(v, N) + \text{C}_2\text{H}_2$  and  
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19 [on time-resolved IR absorption studies \[36, 37\] for the reactions  \$\text{CN}\(v, N\) + \text{C}\_2\text{H}\_6\$  and  \$\text{CH}\_4\$ .](#)

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22 We are now also pursuing a similar characterization with other radical species, such as, for  
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24 instance, OH and  $\text{CH}_3$  (the latter through the REMPI technique). We expect that this will help the  
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26 interpretation of the reactive scattering experiments, especially in those cases where the radical  
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28 excited bond(s) is (are) more directly involved in the bond rearrangements.  
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37  
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51  
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53  
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55  
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57  
58 Programme 2008/2009 between Perugia and Rennes.  
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60

## FIGURE CAPTIONS

Figure 1 Side-view of the laser induced fluorescence apparatus. C, L and G are capacitor, inductance and ground, respectively (see ref. 7). PMT: photomultiplier. (+) indicates the radical beam – laser beam interaction region.

Figure 2 Top-view of the crossed molecular beam apparatus with rotating mass spectrometric detector and time-of-flight chopper.

Figure 3  $C_2(a^3\Pi_u)$  laser induced fluorescence spectrum using the (0, 0) band of the ( $d^3\Pi_g - a^3\Pi_u$ ) Swan system with helium as carrier gas; panel (a): experimental spectrum; panel (b): the best-fit simulation (see text).  $C_2(X^1\Sigma_g^+)$  laser induced fluorescence spectrum using the (0, 0), (1, 1) and (2, 2) bands of the ( $D^1\Sigma_u^+ - X^1\Sigma_g^+$ ) Mulliken system with helium as carrier gas; panel (c): experimental spectrum; panel (d): the best-fit simulation (see text).

Figure 4  $CN(X^2\Sigma^+)$  laser induced fluorescence spectrum using the (0, 0), (1, 1), (2, 2) and (3, 3) bands of the ( $B^2\Sigma^+ - X^2\Sigma^+$ ) system with helium as carrier gas; panel (a): experimental spectrum; panel (b): the best fit simulation (see text); panels (c) and (d): enlargement of panels (a) and (b), respectively, showing clearly the overlap of the (0, 0) and (1, 1) bands and their corresponding band heads.

Figure 5 (a)  $CN(X^2\Sigma^+, v=0)$  rotational distribution. (b)  $CN(X^2\Sigma^+)$  vibrational distribution, corresponding to a vibrational temperature of 6500 K (see text).

Figure 6 Laboratory angular distributions recorded at  $m/z=51$  for the reaction  $CN+C_2H_2$  at  $E_c=48.1 \text{ kJ mol}^{-1}$ . Error bars, when visible outside the dots, represent  $\pm 1$  standard deviation from the

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3 mean. The circles in the Newton diagram delimit the maximum velocity that the HCCCN (dashed)  
4 and HCCNC (dotted) products from channel (1a) and (1d), respectively, can attain if all the  
5 available energy is channelled into product translational energy. The solid line is the total  $N(\Theta)$   
6 calculated when using the best-fit CM angular and translational energy distributions of figure 8.  
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15 Figure 7 Time-of-flight distributions of the products (open circles) detected at  $m/z=51$  for the  
16 reaction  $\text{CN}+\text{C}_2\text{H}_2$  at  $E_c=48.1 \text{ kJ mol}^{-1}$  at the indicated LAB angles. Solid lines represent the TOF  
17 distributions calculated from the best-fit CM functions reported in figure 8.  
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24 Figure 8 Best-fit CM product (*top*) angular and (*bottom*) translational energy distributions for  
25 the reaction  $\text{CN}+\text{C}_2\text{H}_2$  at  $E_c=48.1 \text{ kJ mol}^{-1}$ . The arrows in the bottom panel indicate the total energy  
26 available to the products for different vibrational levels of reacting CN.  
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34 Figure 9 Laboratory angular distributions recorded at  $m/z=65$  for the reaction  $\text{CN}+\text{CH}_3\text{CCH}$  at  
35  $E_c=38.4 \text{ kJ mol}^{-1}$ . Error bars, when visible outside the dots, represent  $\pm 1$  standard deviation from the  
36 mean. The circles in the Newton diagram delimit the maximum velocity that the  $\text{CH}_3\text{CCCN}$   
37 (dashed),  $\text{CH}_2\text{CCHCN}$  (dotted) and HCCCN (dash-dotted) products from channel (2a), (2b) and  
38 (2c), respectively, can attain if all the available energy is channelled into product translational  
39 energy. The solid line is the total  $N(\Theta)$  calculated when using the best-fit CM angular and  
40 translational energy distributions of figure 11.  
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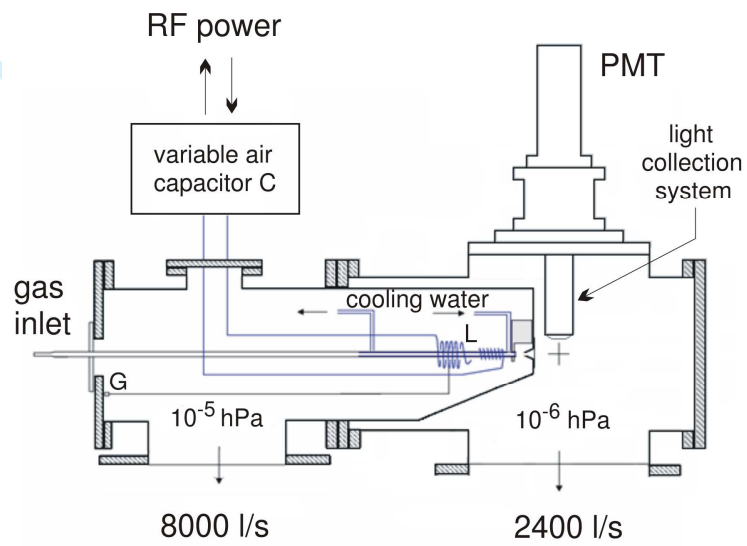
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53 Figure 10 Time-of-flight distributions of products (open circles) detected at  $m/z=65$  for the  
54 reaction  $\text{CN}+\text{CH}_3\text{CCH}$  at  $E_c=38.4 \text{ kJ mol}^{-1}$  for the indicated LAB angles. Solid lines represent the  
55 TOF distributions calculated from the best-fit CM functions reported in figure 11.  
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3 Figure 11 Best-fit CM product (*top*) angular and (*bottom*) translational energy distributions  
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5 for the reaction  $\text{CN} + \text{CH}_3\text{CCH}$  at  $E_c = 38.4 \text{ kJ mol}^{-1}$ . The arrows in the bottom panel indicate the total  
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7 energy available to the products for different vibrational levels of reacting CN.  
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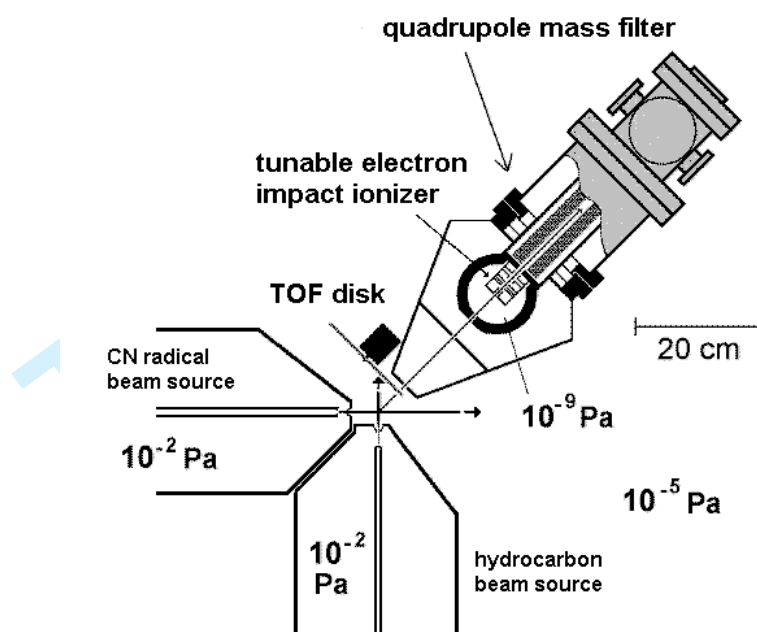
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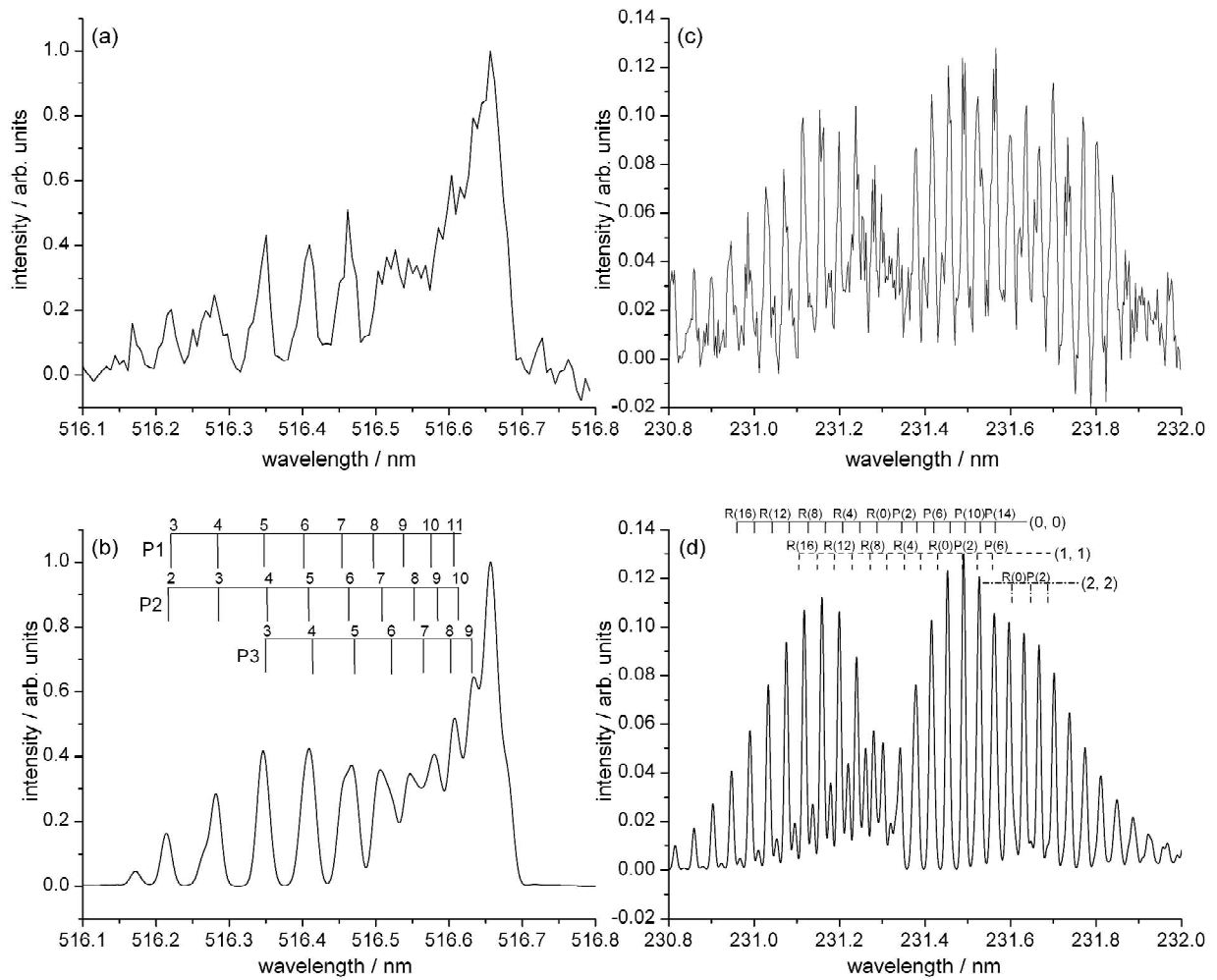
Figure 1

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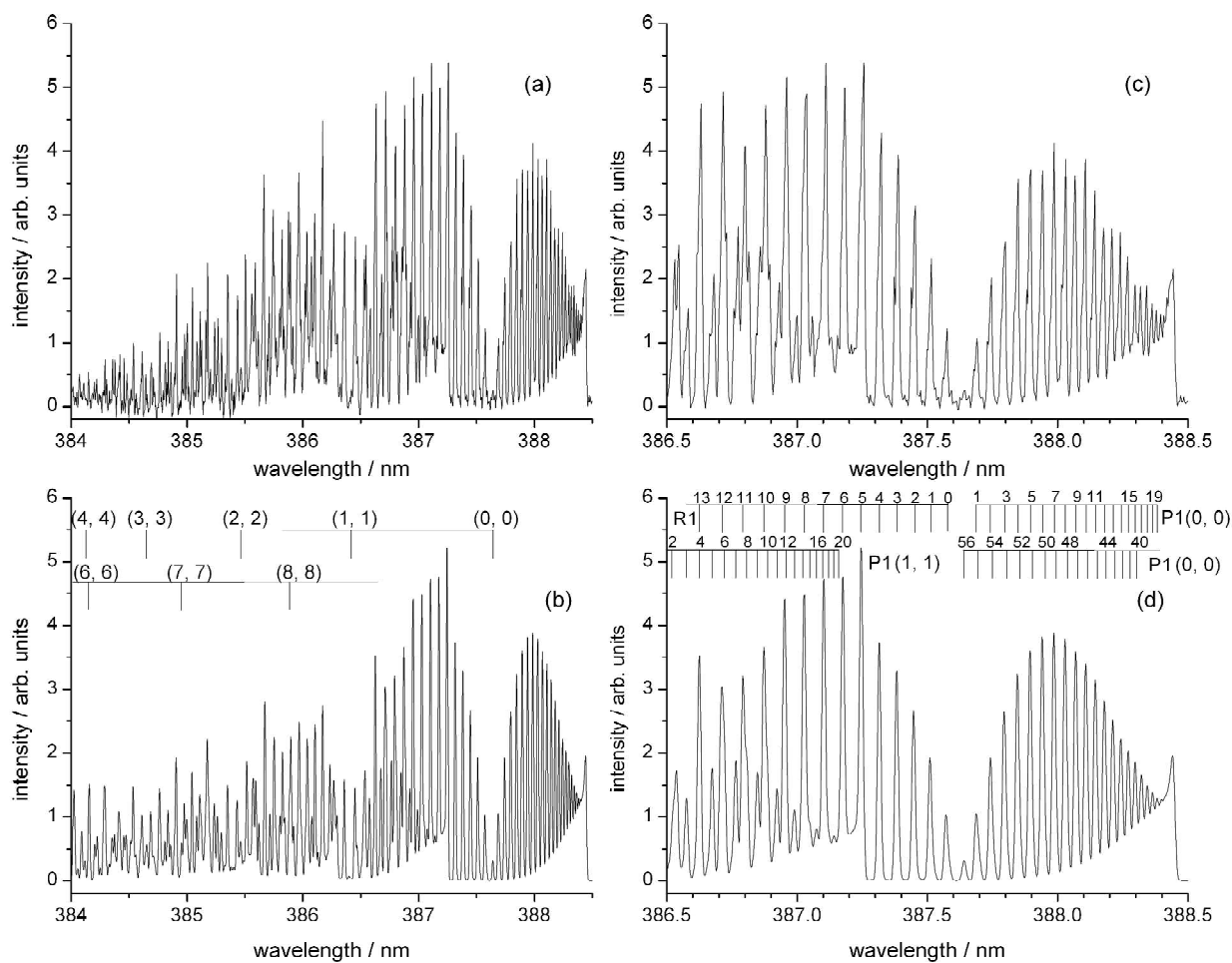
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Figure 2



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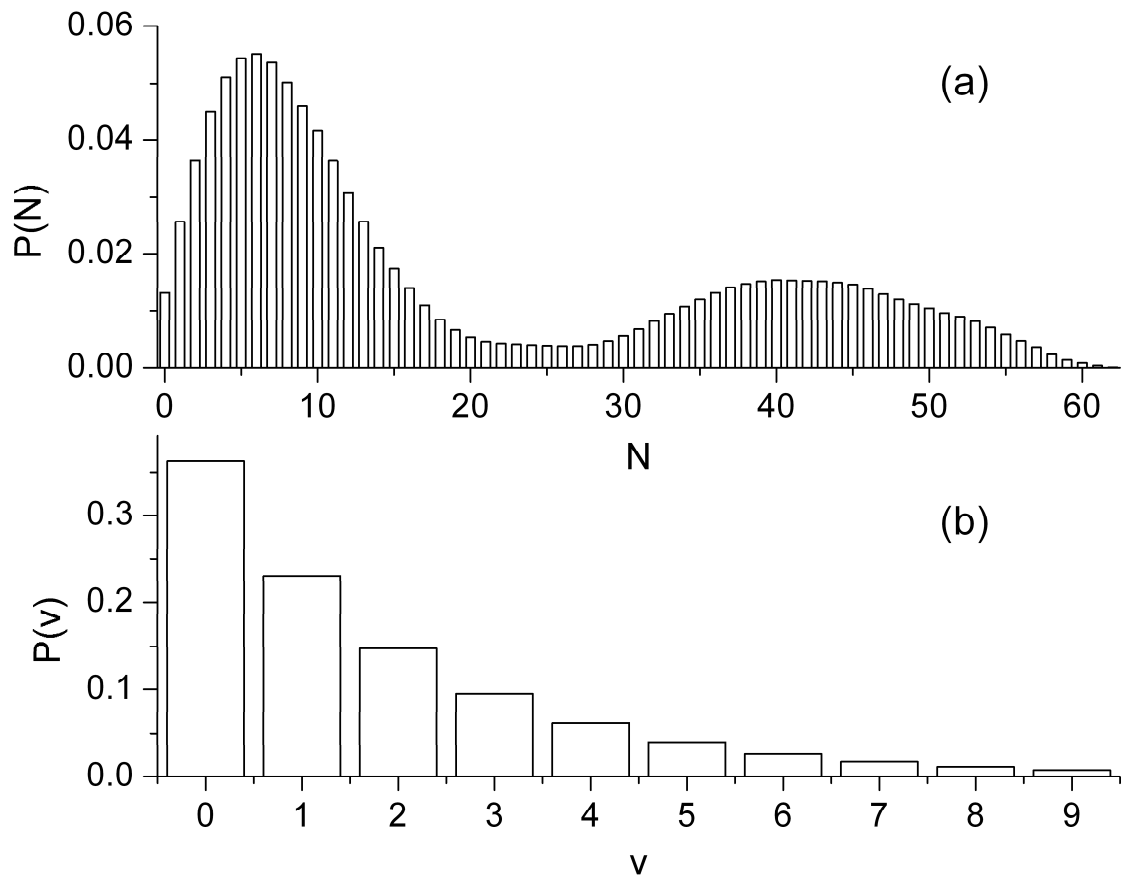
Figure 3



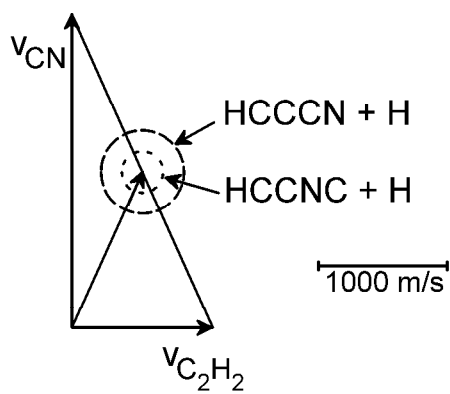
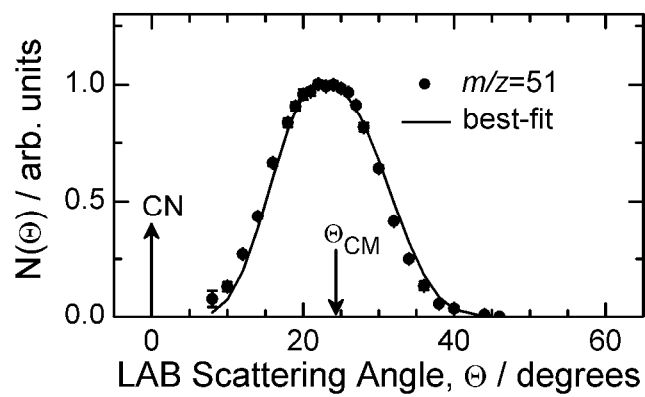
Leonori et al. **Figure 4**

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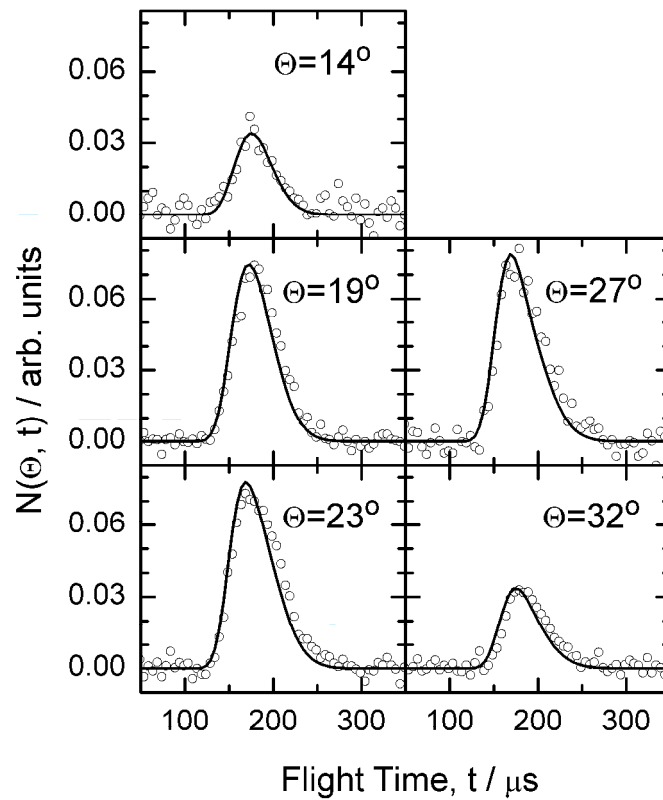


Leonori et al. **Figure 5**



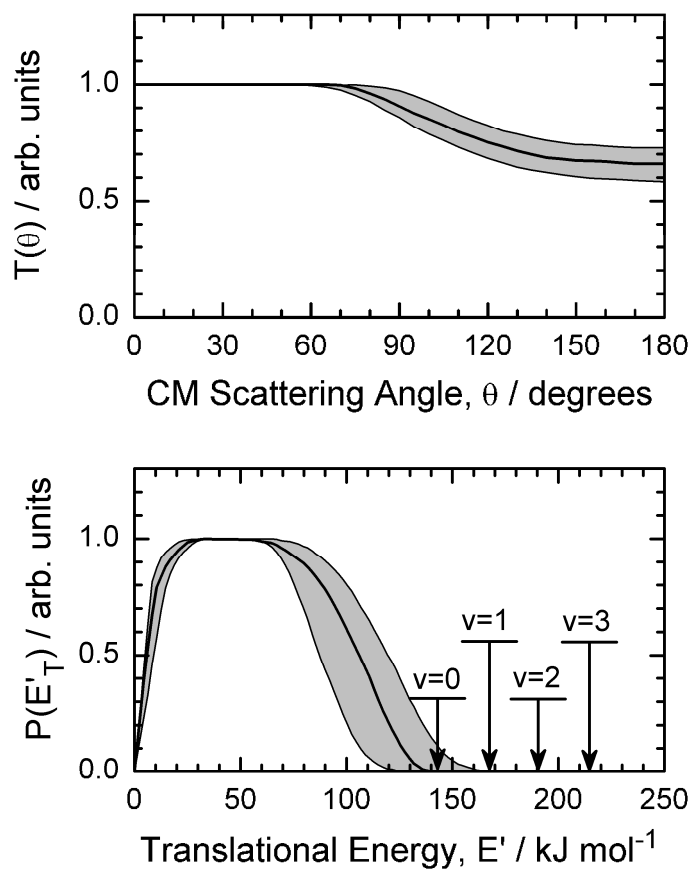
Leonori et al.

Figure 6



Leonori et al.

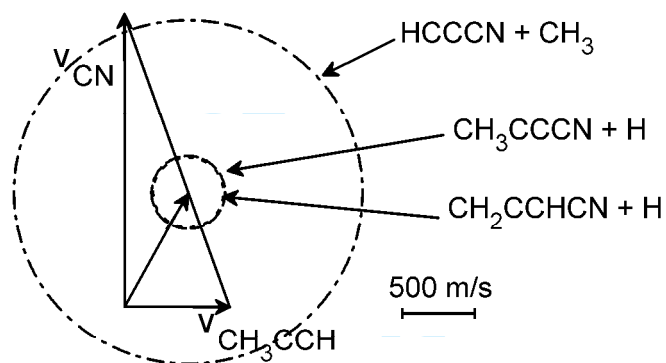
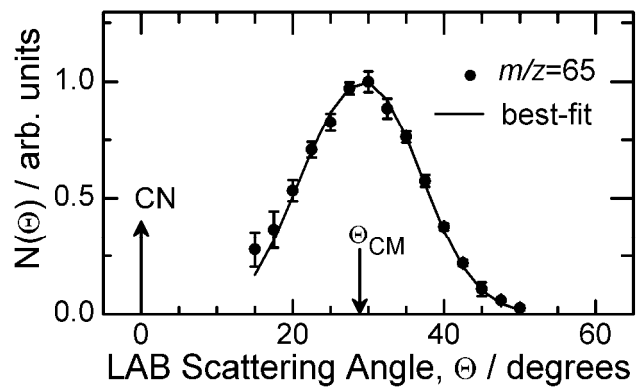
Figure 7



Leonori et al. **Figure 8**

Only

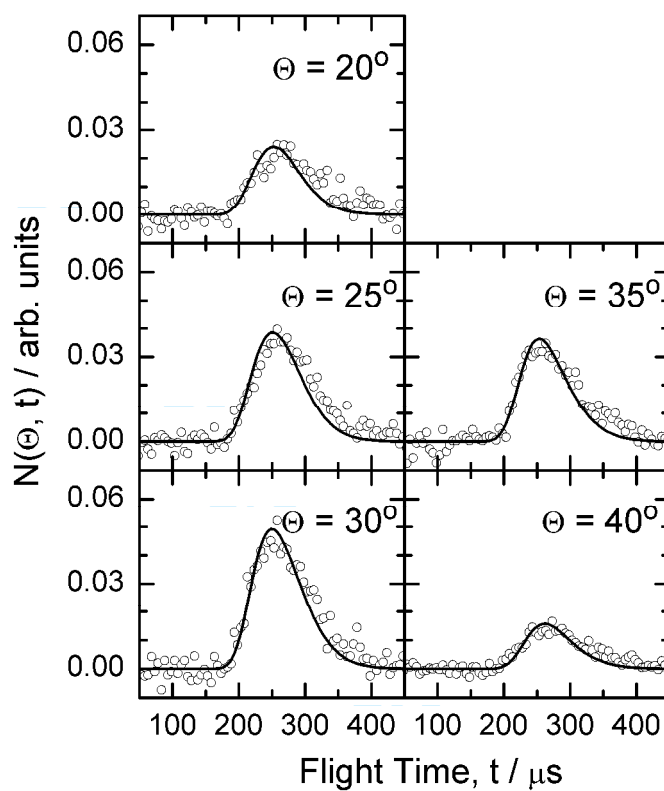




Leonori et al.

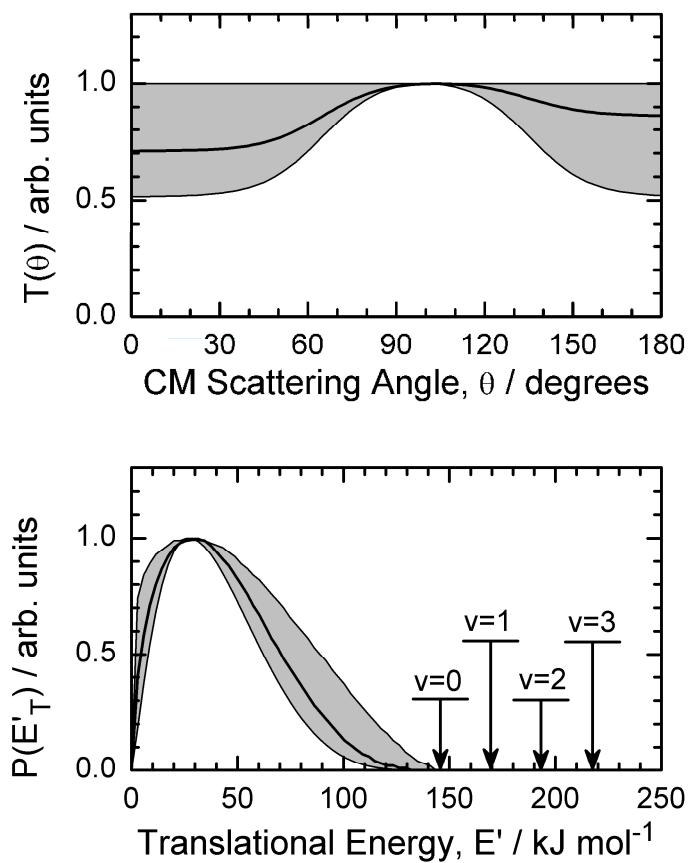
Figure 9

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Leonori et al.

Figure 10



Leonori et al.

Figure 11

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