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# Low Temperature Kinetics of the Reaction Between Methanol and the CN Radical

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## Roles of authors

Author	Role
Divita Gupta	Experimental measurements using EM II (see text). Theoretical calculations. Drafting and correction of article.
Sidaty Cheikh Sid Ely	Experimental measurements using EM I (see text).
Ilsa R. Cooke	Experimental measurements using EM II (see text). Drafting and correction of article.
Théo Guillaume	Laser setup for EM II
Omar Abdelkader Khedaoui	Design, 3D printing fabrication and testing of lowest T Laval nozzle used for EM II
Thomas S. Hearne	Construction and operation of Controlled Evaporator Mixer system for EM II
Brian M Hays	Laser alignment for EM II
Ian R. Sims	Scientific direction of project, participation in EM I measurements, correction of article.

## Abstract

Methanol (CH<sub>3</sub>OH) is considered by astronomers to be the simplest complex organic molecule (COM) and has been detected in various astrophysical environments, including protoplanetary disks, comets, and the interstellar medium (ISM). Studying the reactivity of methanol at low temperatures will aid our understanding of the formation of other complex, and potentially prebiotic molecules. A major destruction route for many neutral COMs, including methanol, is via their reactions with radicals such as CN, which is ubiquitous in space. Here, we study the kinetics of the reaction between methanol and the CN radical using the well-established CRESU technique (a French acronym standing for Reaction Kinetics in Uniform Supersonic Flow) combined with Pulsed Laser Photolysis – Laser-Induced Fluorescence (PLP-LIF). Electronic structure calculations were also performed to identify the exothermic channels through which this reaction can proceed. Our results for the rate coefficient, are represented by the modified Arrhenius equation,  $k(T) = 1.26 \times 10^{-11} (T / 300 \text{ K})^{-0.7} \exp(-5.4 \text{ K} / T)$  and display a negative temperature dependence over the temperature range 16.7—296 K, which is typical of what has been seen previously for other radical-neutral reactions that do not possess potential energy barriers. The rate coefficients obtained at room temperature strongly disagree with a previous kinetics study, which is currently available in the Kinetics Database for Astrochemistry (KIDA) and therefore used in some astrochemical models.

## 1. Introduction

The interstellar medium is host to a rich chemistry that produces a variety of species, including those with six or more atoms that have been named complex organic molecules (COMs).<sup>1</sup> While the abundance of many COMs in the gas-phase has been explained by their formation and desorption from icy dust grain surfaces,<sup>2-4</sup> COMs have also been detected in very cold ( $< 10$  K) environments where thermal desorption from ices is prohibited, suggesting a possible role of gas-phase formation routes at these low temperatures.<sup>5-7</sup>

For a long time, reactions between two neutral species had not been considered to play a major role at the low temperatures and densities of the interstellar medium (ISM). Over the past couple of decades, however, the importance of neutral-neutral reactions has become well established as many of these reactions are barrierless, involve an initial weakly bound complex or proceed through submerged barriers — meaning that many of these reactions continue at a sufficiently fast rate even at low temperatures.<sup>8-12</sup> Given the difficulty in performing gas-phase kinetics experiments and theoretical calculations at low temperatures, kinetics data for most of the reactions expected to take place in interstellar and planetary environments are missing. In the absence of low temperature data, many models either extrapolate from the room temperature rate coefficients or take the value as measured at room temperature over the whole temperature range, often down to 10 K.<sup>7,13</sup>

Methanol was first detected in Sagittarius A and B2<sup>14</sup> and has since been detected in various sources including galactic H II regions,<sup>15</sup> pre-stellar cores,<sup>16,17</sup> ISM clouds,<sup>18</sup> protostellar sources,<sup>19,20</sup> protoplanetary disks,<sup>21</sup> and comets.<sup>22,23</sup> The abundance of methanol is one of the highest amongst the COMs, as high as  $3 \times 10^{-5}$  with respect to  $H_2$  in some sources.<sup>1</sup> Explaining the abundance of methanol in these sources requires accurate kinetic measurements (either experimental or theoretical) of the various routes involved in both its formation and destruction.

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3 Rate coefficients for bimolecular reactions are often measured under pseudo-first order  
4 conditions, in which the concentration of one of the neutral species (usually a stable  
5 molecule) must be accurately known. Given the low saturated vapor pressure of most  
6 COMs below 200 K, kinetics studies of their reactivity at low temperature can be difficult.  
7 Gas cooling by collisions with cold walls in cryogenically cooled cells can only be used  
8 down to about 200 K, except for certain light species like CO where lower temperatures  
9 can be achieved, before condensation on the cell walls causes large uncertainties in the gas  
10 concentration.<sup>24,25</sup> Free jet expansions have been used extensively in spectroscopy to  
11 produce cold gas; however, the density and temperature vary strongly along the beam  
12 making them unsuitable for kinetics measurements. The CRESU<sup>a</sup> technique, an essentially  
13 wall-less cooling method, allows precise control over these parameters. It involves an  
14 expansion of gas from a high-pressure region to a low-pressure region through a particular  
15 type of convergent-divergent nozzle called a Laval nozzle. This expansion results in a beam  
16 of cold gas that is uniform in velocity, temperature, and density typically for several tens  
17 of centimeters. Rowe and co-workers<sup>26</sup> developed the use of CRESU flows to study gas-  
18 phase kinetics and this technique has since been used to characterize many ion-neutral  
19 reactions,<sup>27–31</sup> neutral-neutral reactions,<sup>8,12,32–36</sup> and collisional energy transfer processes.<sup>37–</sup>  
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<sup>40</sup> A detailed summary of the reactions studied using the CRESU technique was published recently.<sup>41</sup>

Radical-neutral reactions are thought to be an important destruction route for gas-phase methanol at low temperatures. The rate coefficients for the reactions of methanol with other radicals such as OH<sup>36</sup> and C(<sup>3</sup>P)<sup>42</sup> have been measured experimentally using the CRESU technique and were found to remain rapid at low temperatures relevant to the cold ISM. The CN radical has been found in many astronomical sources,<sup>43–46</sup> and CN chemistry has been shown to play an important role in Titan's atmosphere.<sup>47–49</sup> Thus, the reaction with CN radicals is a feasible destruction route for methanol in a range of low temperature

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<sup>a</sup> Cinétique de Réaction en Ecoulement Supersonique Uniforme: A French acronym standing for Reaction Kinetics in Uniform Supersonic Flow

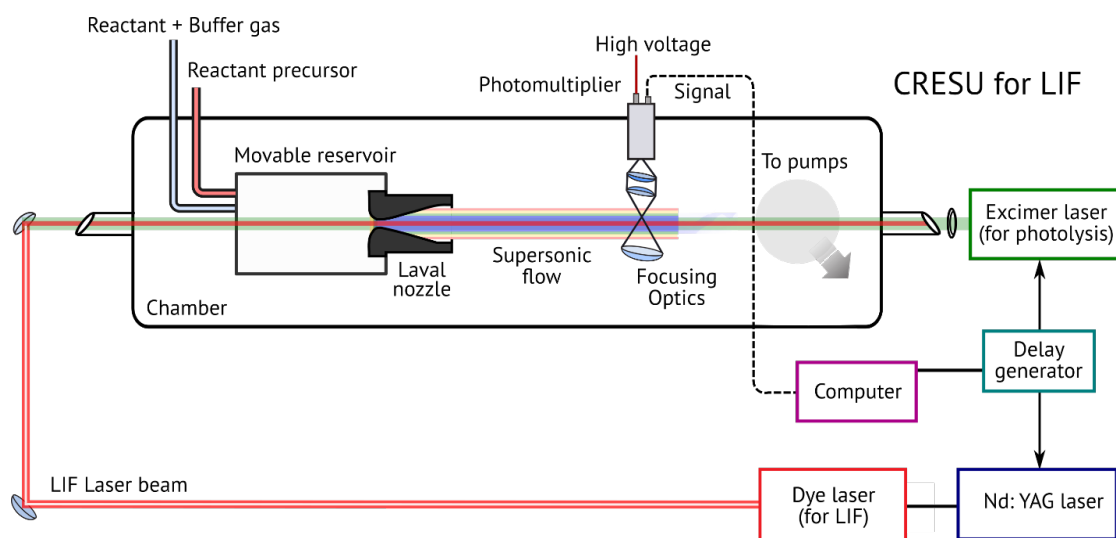
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3 environments. One of the expected products of this reaction, the methoxy radical ( $\text{CH}_3\text{O}$ ),  
4 has been detected in the cold source Barnard 1b<sup>50</sup> and there has been a significant  
5 discussion concerning its abundance compared to its isomer, hydroxymethyl radical  
6 ( $\text{CH}_2\text{OH}$ ), which has not been detected yet. In the low-temperature conditions of Barnard  
7 1b, non-thermal mechanisms must be invoked if methoxy formation is expected to occur  
8 on dust grains, as  $\text{CH}_3\text{O}$  and  $\text{CH}_2\text{OH}$  cannot thermally desorb from ice surfaces. However,  
9 ice-phase experiments on the photodissociation of methanol suggest the  $\text{CH}_2\text{OH}$  isomer is  
10 favored and therefore it has been suggested that the methoxy radical abundance could be  
11 explained by its formation in the gas-phase.<sup>51</sup> In particular, the reaction between methanol  
12 and the OH radical has been discussed as a source of  $\text{CH}_3\text{O}/\text{CH}_2\text{OH}$ , but the branching  
13 ratio into the two channels has not yet been fully characterized.<sup>12,36,51</sup>

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24 To the best of our knowledge, no previous experiments have been published for the reaction  
25 of CN radicals with methanol below room temperature. The earliest study at room  
26 temperature was conducted by Sayah and co-workers<sup>52</sup> who performed flow-tube  
27 experiments using photo-dissociation of  $\text{C}_2\text{N}_2$  at 193 nm as their source of CN radicals.  
28 They determined a rate coefficient of  $(1.2 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  which is different by an  
29 order of magnitude from a later study by Janssen and Hershberger,<sup>53</sup> who report a value of  
30  $(1.03 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  at room temperature. Janssen and Hershberger used photolysis  
31 of ICN at 266 nm to produce the CN radicals and studied the reaction using time-resolved  
32 infrared diode laser absorption spectroscopy, allowing them also to investigate the reaction  
33 products.

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43 Here, the rate coefficients for the reaction of methanol with the CN radical over a wide  
44 temperature range of 16.7—296 K using the CRESU technique are presented. First the  
45 experimental and theoretical methodologies used in these measurements are detailed  
46 followed by the rate coefficients and their dependence on temperature, and a discussion of  
47 the implications of the results and their astrophysical importance is given. These  
48 measurements can be input into astrochemical models in order to assess the importance of  
49 the reaction as a destruction route for methanol at various temperatures.

## 2. Experimental Methodology

The kinetics of the reaction between the CN radical and methanol were measured using the Pulsed-Laser Photolysis-Laser Induced Fluorescence (PLP-LIF) technique. The low temperatures, down to 16.7 K, were achieved using the CRESU technique (a French acronym standing for Reaction Kinetics in Uniform Supersonic Flow), which has been described in detail in previous publications,<sup>37,41,54</sup> and will only be described in brief here. Figure 1 shows a schematic of the CRESU technique configured for the study of neutral-neutral reaction kinetics using PLP-LIF.<sup>41</sup> A dilute mixture (typically <1%) of the reactant and radical precursor in a buffer gas (He, Ar, or N<sub>2</sub>) expands isentropically from a high-pressure region (reservoir), into a low-pressure region (chamber) through a convergent-divergent Laval nozzle to generate a cold supersonic flow that is uniform in temperature and density. Given the high density of the molecules ( $10^{16}$ – $10^{17}$  cm<sup>-3</sup>) in the flow, collisions between the molecules ensure thermal equilibrium is maintained, typically for tens of centimeters. A wide range of temperatures can be reached by careful manipulation of the physical dimensions of the nozzle (in particular the throat diameter), the buffer gas used, and the flow conditions/pumping capacity, which varies the pressure in the reservoir and in the chamber. Characterizing the flow temperature is essential to study chemical kinetics and was performed using impact pressure measurements<sup>54</sup> for each nozzle prior to undertaking kinetics experiments.



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3 **Figure 1.** Schematic of the CRESU setup at Université de Rennes 1, used for the study of  
4 the kinetics of the reaction of methanol with the CN radical. The reactant gas mixture  
5 expands through a Laval nozzle from the high-pressure reservoir into the low-pressure  
6 chamber creating a uniform supersonic flow. An excimer laser is used for the generation  
7 of the CN radicals and a dye laser pumped by the third harmonic of a pulsed Nd:YAG laser  
8 is used for LIF and is aligned along the path of the flow and the excimer laser. A  
9 photomultiplier tube along with the corresponding optics is used to record the fluorescence  
10 signal. The laser timings and delays are controlled using a delay generator. Reprinted from  
11 Cooke & Sims, 2019.<sup>41</sup>  
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21 Two methods were used to perform the experiments, as the first set of measurements at  
22 room temperature deviated significantly from previous measurements made by Sayah and  
23 co-workers.<sup>52</sup> In the first method, hereon referred to as EM I, gas mixtures were made in a  
24 Teflon coated stainless steel container by careful control of the partial pressures of  
25 methanol vapor and the buffer gas. Different concentrations of methanol could be obtained  
26 by varying the pressure of the buffer gas. A solid sample of ICN was placed on a frit  
27 (porous glass) in a glass vessel and introduced into the chamber via a controlled flow of  
28 buffer gas (~200 sccm). The fourth harmonic output of a Nd:YAG laser (Spectra Physics  
29 GCR 190) at 266 nm was used to photo-dissociate ICN (Acros Organics, 98%) at a laser  
30 fluence in the reaction zone of ~35 mJ cm<sup>-2</sup>, producing CN radicals largely in the  $v=0$  level  
31 of the  $X^2\Sigma^+$  state. In the second method, referred to as EM II hereinafter, a Controlled  
32 Evaporation and Mixing system (CEM) was used to introduce methanol into the flow. A  
33 stainless steel vessel containing methanol was pressurized with nitrogen and a flow of  
34 liquid methanol was passed via a Coriolis liquid flow meter (Bronkhorst mini CORI-  
35 FLOW ML120V00) into an evaporator (Bronkhorst W-202A-222-K), and was mixed with  
36 a controlled flow of buffer gas via a thermal mass flow controller (Bronkhorst EL-FLOW  
37 Prestige). The CN radicals were generated by photodissociation of ICN (Acros Organics,  
38 98%) at 248 nm using a KrF excimer laser (Coherent LPXPro 210) at a laser fluence in the  
39 reaction zone of ~25 mJ cm<sup>-2</sup>. Photodissociation of ICN at this wavelength also produces  
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3 CN radicals primarily ( $\approx 93\%$ ) in the  $v = 0$  level of the  $X^2\Sigma^+$  state.<sup>55</sup> At both wavelengths,  
4 rapid rotational relaxation is assured by collisions with the cold, dense buffer gas.  
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8 In both the methods, the LIF/fluorescence signal was then recorded by excitation in the  
9 (0,0) band of the  $B^2\Sigma^+ \rightarrow X^2\Sigma^+$  electronic transition at 388.3 nm using a dye laser (Laser  
10 Analytical Systems, LDL 20505, operating with 0.2g/L mixture of Exciton Exalite 389 dye  
11 in 1,4-dioxane) pumped by the frequency-tripled output at 355 nm of a Nd:YAG laser  
12 (Continuum, Powerlite Precision II). A narrowband interference filter centered at 420 nm  
13 (Ealing Optics) was used with a photomultiplier tube (PMT, Thorn EMI 6723) to select the  
14 off-resonant fluorescence into the first vibrational level of the ground state via the (0,1)  
15 band. As the start of the reaction is marked by the initiation of ICN photolysis, delays in  
16 the range of zero to hundreds of  $\mu\text{s}$  between the excimer and the LIF laser pulses, both  
17 operating at 10 Hz, allowed us to record the time dependence of the CN radical depletion  
18 during the reaction.  
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29 The experiments were performed under pseudo-first order conditions with methanol in  
30 excess. The absorption cross-section of ICN has been reported as  $3 \times 10^{-19} \text{ cm}^2$  at 266 nm<sup>56</sup>  
31 and  $4.7 \times 10^{-19} \text{ cm}^2$  at 248 nm.<sup>57</sup> Given the density of ICN in the gas flow ( $\sim 10^{12} \text{ cm}^{-3}$ ), an  
32 estimated maximum CN ( $X^2\Sigma^+$ ) concentration of  $\sim 1 \times 10^{10} \text{ cm}^{-3}$  in either condition (EM I  
33 or EM II) was obtained at the laser fluences used, which is lower than the concentration of  
34 methanol used by a factor of at least 100.  
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41 The LIF signals were recorded by a gated integrator (Stanford Research Systems) at 200  
42 evenly-spaced time delays and were averaged typically 5-10 times. These were fit to single  
43 exponential decays, yielding pseudo-first order rate coefficients. Linear plots of these  
44 pseudo-first order rate coefficients versus the methanol concentration were then used to  
45 calculate the second-order rate coefficient. The procedure was repeated for multiple  
46 temperatures using different Laval nozzles. The experimental parameters and rate  
47 coefficients measured for each temperature are summarized in Table 1.  
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**Table 1.** <sup>a</sup>: Experiments performed using EM I

<sup>b</sup>: Experiments performed using EM II

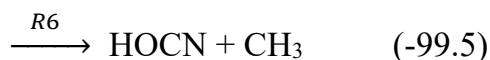
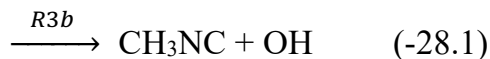
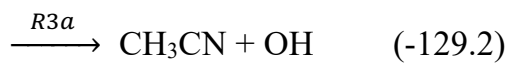
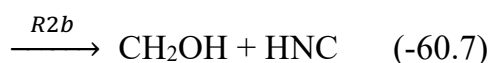
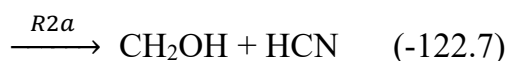
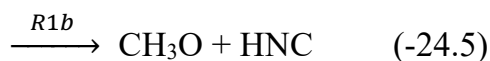
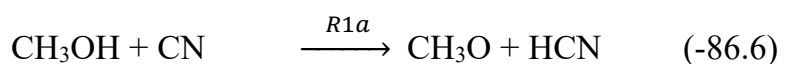
Rate coefficients for the reaction of the CN radical with methanol measured at different temperatures, with the associated experimental parameters. Quoted uncertainties are calculated using the standard error evaluated from the second order plot, multiplied by the appropriate Student's *t* factor for 95% confidence, and then combined with an estimated systematic error of 10%. Entries in bold are variance weighted mean values of rate coefficients at the same temperature, calculated using statistical uncertainties only, where the resulting uncertainty is then combined in quadrature with an estimated systematic error of 10%.

<i>T</i> (K)	Buffer gas	Total density (10 <sup>16</sup> cm <sup>-3</sup> )	Range of [CH <sub>3</sub> OH] (10 <sup>13</sup> cm <sup>-3</sup> )	No. of experimental points	Rate coefficient <i>k</i> (10 <sup>-11</sup> cm <sup>3</sup> s <sup>-1</sup> )
16.7	He <sup>b</sup>	4.89	0.90-6.50	9	7.4 ± 1.2
24	He <sup>a</sup>	18.30	0.00-8.94	8	5.82 ± 0.63
	He <sup>a</sup>	18.30	0.00-5.81	10	6.82 ± 0.77
					<b>6.1 ± 0.6</b>
36	He <sup>a</sup>	5.28	0.00-3.64	7	5.4 ± 0.6
52.8	Ar <sup>a</sup>	20.20	0.00-6.72	7	3.7 ± 0.5
71.5	N <sub>2</sub> <sup>a</sup>	5.79	0.00-6.22	9	3.2 ± 0.4
82.6	N <sub>2</sub> <sup>b</sup>	4.88	0.97-9.74	12	3.37 ± 0.84
	N <sub>2</sub> <sup>b</sup>	4.88	0.96-9.01	6	2.96 ± 1.30
					<b>3.3 ± 0.7</b>
97.4	Ar <sup>a</sup>	15.45	0.00-12.14	8	3.2 ± 0.4
141	Ar <sup>a</sup>	6.95	0.00-16.89	8	1.6 ± 0.2
168	Ar <sup>a</sup>	9.01	0.00-25.28	9	1.6 ± 0.2
296	N <sub>2</sub> <sup>a</sup>	15.15	1.07-20.92	8	1.49 ± 0.18

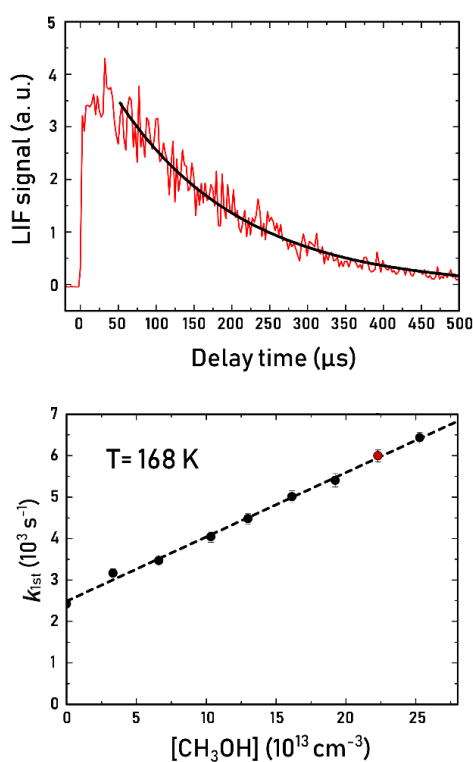
	N <sub>2</sub> <sup>a</sup>	14.30	0.00-27.46	9	1.45 ± 0.18
	N <sub>2</sub> <sup>a</sup>	32.00	0.00-41.46	9	1.48 ± 0.19
	N <sub>2</sub> <sup>b</sup>	9.02	10.51-52.57	5	1.72 ± 0.18
	N <sub>2</sub> <sup>b</sup>	11.69	6.84-34.19	5	1.66 ± 0.52
					<b>1.6 ± 0.2</b>

### 3. Theoretical Methodology

Electronic structure calculations were performed to optimise the stationary points for the different channels of the reaction of the CN radical with methanol using Gaussian09.<sup>58</sup> Only exothermic channels were considered as viable reaction channels at such low temperatures and are shown here:



High accuracy single point energies were calculated using CCSD(T)<sup>59,60</sup>/aug-cc-pVTZ<sup>61,62</sup> for all the structures (reactants and products) following optimisation of their geometries at CCSD<sup>59,63–65</sup>/aug-cc-pVTZ. The difference between the single point energies of the products and reactants was used to calculate the changes in energy for all the reaction channels, and are provided in parenthesis next to each channel in kJ/mol. The parameters for the optimised structures are given in the supplementary information. The standard reaction enthalpy  $\Delta H_r^\circ(298.15\text{ K})$  for each channel was also calculated, as explained by Ochterski,<sup>66</sup> using the composite CBS-QB3<sup>67,68</sup> method.

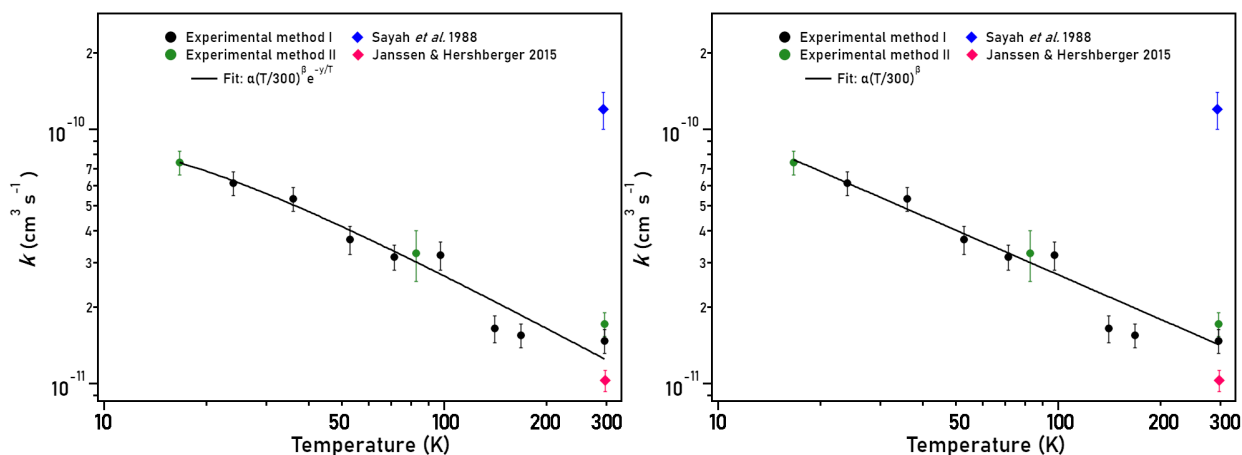


**Figure 2.** Typical kinetics plot obtained using PLP-LIF at a temperature of 168 K in continuous CRESU flow. The upper panel shows the LIF signal decay of CN ( $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ ) at a methanol density  $2.22 \times 10^{14}\text{ cm}^{-3}$  fitted to a single exponential decay function. The lower panel shows the second order plot where the pseudo-first order rate coefficients are plotted against the methanol concentration. The slopes of the second order plots yield the rate coefficients as shown in Table 1.

## 4. Results

A typical LIF decay trace and second order plot obtained at temperature 168 K are shown in Figure 2. LIF measurements were also taken at negative time delays to establish a pre-trigger baseline, as seen in Figure 2. The fit is only made after 10-50  $\mu\text{s}$  so as to allow enough time for rotational relaxation of CN and for the photomultiplier tube to recover from the excimer laser scatter. The non-zero intercept in the second order plot, shown in the lower panel of Figure 2, is due to the loss of CN by diffusion out of the probed beam area and by reaction with the precursor and/or impurities in the buffer gas. As the laser alignment and other external factors may change over periods of days, the intercepts of different second-order plots are not necessarily constant. Therefore, we derive the second-order rate coefficient for each temperature from the readings taken on a given day rather than taking all of the  $k_{1st}$  values at that temperature.

The weighted means of these multiple readings are then calculated for each temperature are shown in Table 1 along with their uncertainties, calculated using 95% confidence limits of the standard error from the two-sided Student's  $t$ -distribution. The experimentally measured rate coefficients over the temperature range  $T = 16.7\text{--}296\text{ K}$  are well fit by the modified Arrhenius equation  $k(T) = 1.26 \times 10^{-11} (T/300\text{ K})^{-0.7} \exp(-5.4\text{ K}/T)\text{ cm}^3\text{ s}^{-1}$  and are shown in Figure 3 along with the rate coefficients measured at room temperature from two previous studies.



**Figure 3.** Rate coefficients for the reaction of the CN radical with methanol displayed on a log-log scale as a function of temperature. The filled black circles are the experiments performed with the CRESU setup using EM I and the filled green circles are the experiments using EM II. The blue diamond represents the work of Sayah *et al.* and the magenta diamond represents the work of Janssen and Hershberger. **a.** The modified Arrhenius fit:  $\alpha(T/300 \text{ K})^\beta e^{-\gamma/T}$  with the fitting parameters ( $\pm 95\%$  confidence limits):  $\alpha = (1.26 \pm 0.43) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ,  $\beta = (-0.72 \pm 0.33)$  and  $\gamma = (5.4 \pm 12)$ . **b.** Modified Arrhenius fit with  $\gamma=0$ :  $\alpha(T/300)^\beta$  with the fitting parameters:  $\alpha = (1.42 \pm 0.31) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  and  $\beta = (-0.58 \pm 0.09)$ .

The upper limit for the concentration of methanol is an important experimental constraint imposed due to the formation of methanol dimers, which could interfere with the experimental measurement. The range of methanol densities used to calculate the second-order rate coefficient for each temperature, as mentioned in Table 1, were based on the tests where first-order rate coefficients were measured against a large range of methanol density, and a careful observation of when the first order plot deviates from its linear behavior, which would indicate the loss of pseudo-first order conditions due to formation of dimers. The methanol concentration at which this deviation starts to occur is dependent on the nature of the buffer gas and its temperature and density, occurring at lower values for low temperatures and high densities.

The reaction enthalpies  $\Delta H_r^\circ(298.15 \text{ K})$  were obtained at CBS-QB3, which is a composite method used widely<sup>69-71</sup> to obtain accurate energies of molecules and radicals. The values obtained were compared with enthalpy values calculated using the active thermochemical table (ATcT)<sup>72-74</sup> and are shown in Table 2. ATcT has been developed by Ruscic and co-workers and is based on statistical analysis to produce a self-consistent thermochemical network. The reaction enthalpies for the various channels follow the same trend across the different methods, with channel R3a being the most exothermic, followed by R2a, R6, and R1a.

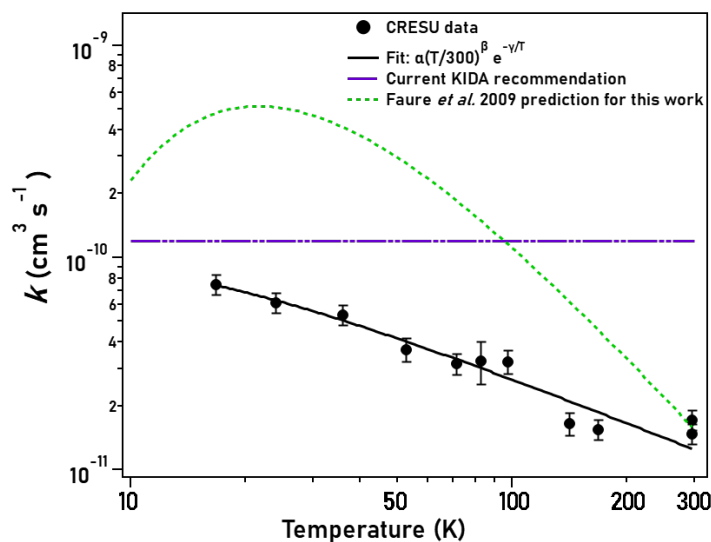
**Table 2.** Reaction enthalpies  $\Delta H_r^\circ(298.15 \text{ K})$ , in kJ/mol, calculated for each channel using CBS-QB3 compared with the enthalpy values calculated from the values provided in the Active Thermochemical Table ver. 1.22 e.<sup>74</sup> The reaction enthalpies for R4 and R5 could not be calculated as the species  $\text{CH}_3\text{OCN}$  and  $\text{NCCH}_2\text{OH}$  are missing from the thermochemical network of ATcT ver. 1.22 e

	<b>R1a</b>	<b>R1b</b>	<b>R2a</b>	<b>R2b</b>	<b>R3a</b>	<b>R3b</b>	<b>R4</b>	<b>R5</b>	<b>R6</b>
<b>CBS-QB3</b>	-90.9	-31.2	-126.0	-66.3	-127.6	-28.1	-23.2	-76.6	-111.0
<b>ATcT (1.22e)</b>	-99.3	-36.2	-137.5	-74.4	-138.4	-35.2	-	-	-118.4

## 5. Discussion

Figure 3 shows the experimentally obtained values of the rate coefficient from this work as a function of temperature, compared with the two previous studies measured at room temperature. The CRESU results have been fit to the modified Arrhenius equation (Kooij fit) in Figure 3a, and show a dependence  $k(T) = 1.26 \times 10^{-11} (T / 300 \text{ K})^{-0.7} \exp(-5.4 \text{ K} / T) \text{ cm}^3 \text{ s}^{-1}$ . The CRESU data was also fit using the  $\alpha(T/300 \text{ K})^\beta$  expression, which is shown in Figure 3b, and follows the curve  $k(T) = 1.42 \times 10^{-11} (T / 300 \text{ K})^{-0.6} \text{ cm}^3 \text{ s}^{-1}$ . The work by Sayah *et al.*<sup>52</sup> at room temperature yielded a value of  $1.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , which was different from the value obtained here using EM I by an order of magnitude. Following this, a secondary method for CN radical generation and for creating methanol/buffer gas mixtures (EM II) was used to confirm the measurements made using EM I (particularly those at room temperature) and to reduce the likelihood of systematic errors. A room temperature rate coefficient was measured using EM II that agrees within error to that obtained using EM I. The current results are further supported by the work of Janssen and Hershberger<sup>53</sup> who obtained a rate coefficient of  $1.03 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  at room temperature, which is in good agreement with the value reported here of  $(1.6 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . It is unclear why the value measured by Sayah *et al.* is faster than these three essentially independent measurements by an order of magnitude.

The difference between the ionization potential of methanol and the electron affinity of CN radical is 6.98 eV, which is less than the 8.75 eV semi-empirical limit proposed by Ian Smith and colleagues<sup>75</sup> for the existence of a non-submerged barrier to reaction. This suggests the reaction between the CN radical and methanol will be rapid even at low temperatures, with a rate coefficient greater than  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at 10 K, consistent with what was observed in this study.



**Figure 4.** The CRESU experimental data (black filled circles) fit with a modified Arrhenius equation (black solid line),  $k(T) = 1.26 \times 10^{-11} (T / 300 \text{ K})^{-0.7} \exp(-5.5 \text{ K} / T) \text{ cm}^3 \text{ s}^{-1}$ , and the prediction,  $k(T) = 1.80 \times 10^{-11} (T / 300 \text{ K})^{-2.1} \exp(-44.6 \text{ K} / T) \text{ cm}^3 \text{ s}^{-1}$ , based on the room temperature value from this work using capture theory model from Faure *et al.*<sup>76</sup> (green dashed line). The current KIDA recommendation for this reaction is shown in purple.

Faure *et al.*<sup>76</sup> provided a semiempirical model which combines room temperature kinetics data with a long-range capture method to predict rate coefficients for neutral-neutral reactions at low temperature. For reactions with rate coefficients greater than  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$  at room temperature, a fit ( $k(T) = \alpha(T/300 \text{ K})^\beta e^{-\gamma/T}$ ) is proposed to be valid at temperatures as low as 5 K. A plot obtained using the model is shown in Figure 4. The method, along with the parameters used are provided in Table S1 and Table S2 of Supplementary

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3 information. This method, however, over-predicts the rate coefficient, suggesting that the  
4 reaction is not controlled by long-range attractive forces even at the lowest temperatures  
5 where measurements have been performed. It appears likely that submerged barriers are  
6 playing an important role in determining the low temperature reactivity.  
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11 The reaction enthalpies  $\Delta H_r^\circ(298.15 \text{ K})$  obtained using CBS-QB3 and ATcT, shown in  
12 Table 2, show a reasonable agreement. The reaction enthalpies for R4 and R5 could not be  
13 calculated from ATcT due to missing values for NCCH<sub>2</sub>OH and CH<sub>3</sub>OCN in the active  
14 thermochemical table. The reaction channels R1a, R2a, R3a and R6 are the most  
15 thermodynamically favored product channels of the studied reaction. Similar trends were  
16 also found from the reaction energies calculated using the difference between the single  
17 point CCSD(T)/aug-cc-pVTZ) energies of the reactants and products. The HNC channels  
18 for both R1 and R2 were found to have lower stabilization energies compared to the HCN  
19 analogues, which is expected as HCN is more stable than HNC. Preliminary calculations  
20 performed at B3LYP/aug-cc-pVTZ to identify the saddle points for the reaction channels,  
21 suggest that the channels R3a, R3b, and R4 have very high (zero-point corrected) barriers  
22 of 83.6 kJ mol<sup>-1</sup>, 134.7 kJ mol<sup>-1</sup> and 227.9 kJ mol<sup>-1</sup>, respectively, making them unlikely to  
23 take place in low temperature environments. These preliminary calculations were likely of  
24 an insufficiently high level to locate the submerged saddle points for the reaction channels  
25 R1 and R2, indicating the need for more accurate *ab-initio* methods.  
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40 To the best of authors' knowledge, this is the first set of kinetics data published for this  
41 reaction at low temperatures, which makes it useful for atmospheric and astrochemical  
42 models. The Kinetics Database for Astrochemistry, KIDA, (Homepage [http://kida.obs.u-](http://kida.obs.u-bordeaux1.fr/)  
43 [bordeaux1.fr/](http://kida.obs.u-bordeaux1.fr/) accessed July 2019),<sup>77,78</sup> currently uses the rate coefficient measured by  
44 Sayah *et al.* over the whole temperature range of 10-300 K, which is significantly different  
45 from what is observed experimentally both here and by Janssen and Hershberger.<sup>53</sup>  
46 Furthermore, the reaction is assumed to proceed in equal ratios via channels 1a (CH<sub>3</sub>O +  
47 HCN) and 2a (CH<sub>2</sub>OH + HCN). Janssen and Hershberger measured the CH<sub>2</sub>OH channel  
48 as the dominant reaction product at room temperature, with only 8% into the methoxy  
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3 channel, based on isotopic experiments. Models using the room temperature rate  
4 coefficient reported in KIDA, therefore, overpredict both the rate of CH<sub>3</sub>O formation and  
5 its yield relative to the CH<sub>2</sub>OH isomer. The product branching ratios for this reaction have  
6 not been measured below room temperature, so it is unknown whether the reaction will be  
7 a significant source of methoxy under dense cloud conditions.  
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13 A new technique combining Chirped-Pulse Fourier-Transform Microwave (CP-FTMW)  
14 spectroscopy with CRESU flows, named Chirped-Pulse in Uniform supersonic Flow  
15 (CPUF), has been used to measure the channel-specific rate coefficients at low  
16 temperature.<sup>79</sup> This technique can aid in understanding which reaction channels may be  
17 dominant at low temperatures. An E-band (~60-90 GHz) spectrometer has been developed  
18 in Rennes that will allow the investigation of the products formed in the reaction between  
19 the CN radical and methanol as some rotational lines corresponding to CH<sub>3</sub>O and CH<sub>2</sub>OH  
20 fall within this frequency range.  
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29 Other destruction routes for methanol with the OH radical<sup>36</sup> and the C(<sup>3</sup>P)<sup>42</sup> radical have  
30 been reported to have rate coefficients approaching 10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup> at 10 K. A similar rate  
31 coefficient for the reaction of CN with methanol further establishes the role of this reaction  
32 as a significant destruction route for methanol in cold interstellar clouds where both these  
33 species have been detected. The room temperature rate coefficient reported here is an order  
34 of magnitude lower than the current value in KIDA, suggesting that astrochemical  
35 networks involving warm gas temperatures (e.g., hot cores models) may overpredict the  
36 destruction of methanol. Use of the current KIDA-recommended rate coefficients may also  
37 lead to overprediction of the abundance of the methoxy radical, which is thought to be a  
38 precursor to more complex organic molecules like dimethyl ether and methyl formate.<sup>6</sup>  
39 Astrochemical models assuming the current KIDA rate coefficients (6.0 × 10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>  
40 into both the CH<sub>3</sub>O and CH<sub>2</sub>OH channels) should be updated to reflect these new laboratory  
41 data. Janssen and Herschberger's<sup>53</sup> room temperature branching ratios should be used at *T* <  
42 300 K until low temperature measurements have been made.  
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## 6. Conclusion and future outlook

The CRESU technique coupled with PLP-LIF has been employed to show that the reaction between the CN radical and methanol has a negative temperature dependence in the temperature range 16.7—296 K, well-characterized by the modified Arrhenius equation  $k(T) = 1.29 \times 10^{-11} (T / 300 \text{ K})^{-0.7} \exp(-5.5 \text{ K} / T)$ . The present measurements vary significantly from the room temperature value of Sayah *et. al.* which is currently the value recommended by the KIDA database for all temperatures between 10 and 300 K. While this experiment has yielded the overall rate coefficient for the reaction of the CN radical with methanol, the PLP-LIF technique is unable to provide product-specific rate coefficients or branching ratios. Electronic structure calculations revealed that the reaction channels involving CN substitution have high barriers, making them unlikely to occur at low temperatures. The H atom abstraction routes are likely to be the dominant reaction channels under cold ISM conditions, forming the isomers CH<sub>2</sub>OH and CH<sub>3</sub>O. More calculations are needed to locate the submerged saddle points for other channels for the reaction of the CN radical with methanol, followed by theoretical kinetics calculations. A new setup integrating chirped-pulse broadband microwave spectroscopy with continuous flow CRESU is being developed in Rennes and will allow the identification of the products and provide the branching ratios for the reaction channels at low temperatures.

## Supporting Information

The parameters and a description of the method suggested by Faure *et al.*<sup>76</sup> which extrapolates the room temperature rate coefficient to lower temperatures based on long-range capture model are provided in the supplementary information. The Cartesian coordinates of the optimized geometries for various suggested reaction channels are also provided.

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