Tunneling Enhancement of the Gas-Phase CH + CO$_2$ Reaction at Low Temperature

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Abstract
The rates of numerous activated reactions between neutral species increase at low temperatures through quantum mechanical tunneling of light hydrogen atoms. Although tunneling processes involving molecules or heavy atoms are well known in the condensed phase, analogous gas-phase processes have never been demonstrated experimentally. Here, we studied the activated CH + CO$_2$ → HCO + CO reaction in a supersonic flow reactor, measuring rate constants that increase rapidly below 100 K. Mechanistically, tunneling is shown to occur by CH insertion into the C-O bond, with rate calculations accurately reproducing the experimental values. To exclude the possibility of H-atom tunneling, CD was used in additional experiments and calculations. Surprisingly, the equivalent CD + CO$_2$ reaction accelerates at low temperature as zero point energy effects remove the barrier to product formation. In conclusion, heavy-particle tunneling effects might be responsible for the observed reactivity increase at lower temperatures for the CH + CO$_2$ reaction, while the equivalent effect for the CD + CO$_2$ reaction results instead from a submerged barrier with respect to reactants.
1 Introduction
Typically, a chemical reaction occurs spontaneously when the reagents have enough energy for product formation to occur. Endothermic reactions and reactions which possess activation barriers over the relevant potential energy surface (PES) generally display reaction rates that increase with temperature because the higher kinetic energy leads to a greater proportion of these reagents having the minimum energy necessary for a successful collision. For these systems, an adequate description of the rate constant \( k \) can be obtained around room temperature by applying the Arrhenius’ expression, \( k = A \exp(-E_a/RT) \), where \( A \) is the pre-exponential parameter and \( E_a \) is the activation energy (\( T \) and \( R \) refer to the temperature and ideal gas constant, respectively). Conversely, at low and very low temperatures, the rate constants for these processes are expected to become negligible since the reagents do not possess enough energy to reach the product side. While this statement is universally true for endothermic reactions, certain exothermic reactions characterized by energetic barriers have shown startling deviations from Arrhenius behaviour at low temperatures, with rate constants increasing by several orders of magnitude. This behaviour appears to be due to quantum mechanical tunneling (QMT) and has been confirmed through qualitative\(^1\) and quantitative\(^2\) studies of product formation. These findings are beginning to transform our view of low temperature environments such as interstellar clouds and planetary atmospheres as a wide range of activated reactions involving H/D-atom transfer that were previously neglected from models, particularly those involving OH radicals reacting with volatile organic compounds,\(^1,3\) are potentially relevant to the overall chemistry of these regions.

Although many gas-phase reactions deviate from Arrhenius behaviour at low temperature through weakly bound complexes\(^4\) or tunneling effects,\(^5,6\) the reactions presenting substantial QMT effects possess specific features. Notably, a strong van der Waals complex seems to be a prerequisite for efficient QMT. Indeed, as the temperature falls, the lifetime of the molecular complex is extended, leading to an increase in the attempt frequency and an enhanced probability for tunneling to occur.\(^7\) To date, large tunneling effects in gas-phase reactions have only been observed in systems where the mechanism involves the transfer of light atoms such as hydrogen or deuterium. Although less widespread, heavy particle tunneling effects have also been demonstrated at low temperature. In particular, carbon atom tunneling has been shown to be at the origin of several phenomena including bond shift effects in 1,3-cyclobutadiene solutions\(^8\) and the observed ring expansion\(^9\)
of matrix isolated 1-methylcyclobutylfluorocarbene. Even molecules themselves have been shown to undergo QMT with the well-known example of formaldehyde polymerization as demonstrated by Goldanskii in the 1970's.\textsuperscript{10,11}

Despite these earlier studies in condensed phases, there is no experimental evidence for any gas-phase reaction occurring through heavy particle tunneling yet. Reactions that could display such behavior are characterized by a strong van der Waals complex in the entrance valley, similarly to the gas-phase tunneling reactions described above, while the PES should also present a particularly low activation barrier to product formation. A recent theoretical study\textsuperscript{12} of the reaction between the methylidyne radical (CH) and carbon dioxide (CO\textsubscript{2}) suggests that this system could fulfil these requirements. The energy profile exhibited in Figure 1 indicates that the preferential pathway for the CH + CO\textsubscript{2} reaction follows the initial formation of a pre-reactive CH...CO\textsubscript{2} complex (stabilized by 8.8 kJ/mol with respect to reagents), which is converted to a stable intermediate molecular adduct (IM1) by means of a transition state structure (TSR1); a process presenting an activation energy of only 2.7 kJ/mol over the 300 – 700 K range. Through simulations of the species concentrations as a function of time, Vichietti et al.\textsuperscript{12} showed that the elementary CH + CO\textsubscript{2} → IM1 step is rate determining for the global reaction, CH + CO\textsubscript{2} → products, over a broad temperature range (200 - 3500 K). Earlier experimental kinetic studies by Berman et al.\textsuperscript{13} over the 297 - 676 K range support this theoretical hypothesis, finding an Arrhenius’ activation energy of 2.9 ± 0.5 kJ/mol.
Figure 1. Energy profile (electronic energies extrapolated to the basis set limit, $E_{CBS}$, plus vibrational zero-point corrections, ZPE) relative to the reagents along the preferential pathway encountered by Vichietti et al.\textsuperscript{12} for the CH + CO\textsubscript{2} $\rightarrow$ HCO + CO reaction, according to ROCCSD(T)/CBS//UCCSD/cc-pVDZ dual-level calculations (molecular structures were plotted with Molden 5.3).\textsuperscript{14} The inset in the top right is the energy profile of the CH(CD) + CO\textsubscript{2} $\rightarrow$ IM1 elementary step obtained here in more advanced DKH-CV-CCSD(T)/CBS calculations.

Mechanistically, the rate determining step of the CH + CO\textsubscript{2} reaction (Figure 1) involves the approach of the CH radical to one of the C=O bonds of CO\textsubscript{2} (TSR1),\textsuperscript{12} eventually forming the cyclic species (IM1). The C=O bond initially belonging to CO\textsubscript{2} then breaks, leading to the formation of an OC(H)-CO adduct (IM2) that is converted to another conformer (IM3) prior to product formation (HCO + CO). The essential point to retain here is that cleavage of the initial C-H bond is not predicted to occur, implying that eventual tunneling effects during C-H insertion might not be due to H-atom QMT.
To verify the possible influence of tunneling on this process, we report the results of a gas-phase kinetic study of the \( \text{CH} + \text{CO}_2 \) reaction below room temperature, where QMT effects are more likely to manifest. To further examine the role of QMT in the overall mechanism, rate constants for the \( \text{CD} + \text{CO}_2 \) reaction were also measured over the same range. Earlier kinetic measurements of these two processes have already shown that their reactivity is similar at room temperature.\textsuperscript{15} Measurements were performed using the CRESU technique (Cinétique de Réaction en Écoulement Supersonique Uniforme or reaction kinetics in a uniform supersonic flow)\textsuperscript{16} to generate the prerequisite low temperature gas flows. In addition to the experimental work, new rate constant calculations are also reported for the rate-determining step of the reactions under study, extending the preliminary work of Vichietti et al.\textsuperscript{12}

2 Theoretical Methods
The thermochemical properties were calculated by using the equilibrium structures of stable points (reactants, product, saddle point and pre-complex) found previously by Vichietti et al.\textsuperscript{12} for the rate-determining step of the global \( \text{CH} + \text{CO}_2 \rightarrow \text{products} \) reaction (the \( \text{CH} + \text{CO}_2 \rightarrow \text{IM1} \) elementary step illustrated in Figure 1), which were obtained with unrestricted coupled cluster theory allowing single and double excitations (UCCSD)\textsuperscript{17} in combination with the cc-pVDZ basis set.\textsuperscript{18} The same geometries are also considered for the \( \text{CD} + \text{CO}_2 \rightarrow \text{IM1} \) process. In addition, the previous study\textsuperscript{12} already demonstrated that the single-reference treatment devised here is reliable for these reactions. For example, the largest \( T_1 \) diagnostic value found for the structures investigated here was only 0.022 (for TSR1 and IM1), which is within the safe limits recommended in the literature for radicals, 0.045.\textsuperscript{19}

Single-point calculations were performed at these stationary point structures using the restricted coupled cluster theory allowing single, double and connected triple excitations, CCSD(T).\textsuperscript{20} Two more contributions were considered in this study to improve the description of thermochemical properties with respect to the previous work of Vichietti et al.:\textsuperscript{12} (i) scalar relativistic effects by means of the second-order Douglas-Kroll-Hess Hamiltonian (DKH);\textsuperscript{21-26} (ii) the contribution of core electron correlation (also known as core-valence correlation, CV). This combined method is labelled here as DKH-CV-CCSD(T). Therefore, appropriate basis sets for the DKH Hamiltonian including core-valence correlating functions\textsuperscript{27} of quadruple- and quintuple-zeta qualities were employed, cc-pCVXZ-DK (\( X = Q,5 \)),\textsuperscript{28,29} and the results were
extrapolated to the complete basis set (CBS) limit. These calculations were performed by using the Molpro 2015 package. It should be emphasized that the largest $T_1$ diagnostic value obtained in these DKH-CV-CCSD(T) calculations is only 0.020 (IM1). The thermochemical properties determined also considered the harmonic vibrational frequencies previously calculated with the UCCSD/cc-pVDZ approach scaled by a factor of 0.947 to take into account anharmonicity effects.

The high pressure limit thermal rate constants were obtained by transition state theory (TST) within the improved canonical variational theory (ICVT), which maximizes the free energy along the reactional path. The minimum energy path was built by using a dual-level methodology, employing the DKH-CV-CCSD(T)/CBS//UCCSD/cc-pVDZ approach as the high-level choice and the UCCSD/cc-pVDZ method as the low-level one. This procedure is usually referred to in the literature as variational transition state theory with interpolated single-point energies (VTST-ISPE). Tunneling effects were considered by the small curvature tunneling (SCT) method. The chemical kinetic calculations were carried out by using the Polyrate 2008 package and the Gaussrate 2009 interface between Gaussian 09 and Polyrate. The reaction rate calculations also considered the spin-orbit coupling of the CH radical by means of the same approach followed in Vichietti et al. The reaction was considered as a one-step process and the pre-complex was included in the calculation of rate constants, as implemented in the Polyrate package. The derived rate constants considering the DKH-CV-CCSD(T)/CBS electronic structure results are listed in Tables S1 and S2 of the Supporting Information. The thermochemical properties of the CH(CD) + CO$_2$ → IM1 elementary step are presented in Table S3.

3 Experimental Methods
The CRESU technique was used for the present study. As the method has been previously described, only the experimental details specific to the current investigation will be outlined here. Three Laval nozzles were employed during this study producing supersonic flows with temperatures of 177 K, 127 K, 75 K and 50 K (the same nozzle was used to generate flows at 177 K and 127 K using N$_2$ and Ar as carrier gases respectively). The characteristic properties of these flows (such as the temperature, velocity and density), are summarized in Table S4 alongside other relevant information.
These values were calculated from earlier measurements of the impact pressure as a function of distance from the nozzle using a Pitot tube and the stagnation pressure within the reservoir. To extend the kinetic measurements to higher temperature, measurements were also performed at room temperature (296 K) by removing the Laval nozzle. In this case, the flow velocity was significantly reduced, effectively using the reactor as a slow-flow flash photolysis apparatus.

CH(X^2Π_r) radicals were generated by two methods during this study. The first employed the multiphoton dissociation of CHBr_3 molecules at 266 nm with ~ 23 mJ of pulse energy. The photolysis laser was aligned along the supersonic flow, creating a column of CH radicals of uniform density. CHBr_3 was entrained in the flow by bubbling a small flow of carrier gas through liquid CHBr_3 held at a known pressure. An upper limit of 1 × 10^{13} \text{cm}^{-3} was estimated for the gas-phase concentration of CHBr_3 in the experiments from its saturated vapour pressure. The second employed the multiphoton dissociation of CBr_4 molecules at 266 nm, allowing C(^3D) atoms to be created in the supersonic flow. H_2 (or D_2) molecules were added to the supersonic flow in excess concentrations (greater than 4.2 × 10^{14} \text{cm}^{-3}), allowing CH (CD) radicals to be generated through the fast C(^3D) + H_2 (D_2) reaction. CBr_4 molecules were introduced into the flow by passing a small amount of Ar carrier gas over solid CBr_4 held at a known pressure. An upper limit of 2.5 × 10^{13} \text{cm}^{-3} was estimated for the gas-phase concentration of CBr_4 in these experiments. The C(^3P) atoms generated by CBr_4 photolysis are unreactive with H_2 (D_2) and CO_2, so these atoms do not interfere with the kinetics of the CH + CO_2 reaction. This method allowed us to overcome issues related to cluster formation at 50 K. Indeed, as a large molecule with a non-zero electric dipole moment of 0.99 Debye, CHBr_3 readily formed clusters with coreagent CO_2 at this temperature, limiting the exploitable range of CO_2 concentrations. In contrast, the use of non-polar CBr_4 molecules allowed somewhat larger CO_2 concentrations to be used, leading to a greater range of pseudo-first-order rate constants and a more reliable measurement of the second-order rate constant. To ensure that the rate constants obtained with this method were not affected by secondary reactions, experiments were also performed using CBr_4 at higher temperatures (127 K and 296 K) where the results could be compared directly with those obtained by experiments employing CHBr_3 as the CH source.
CH(χ2Π, ρ) radicals were followed by a chemiluminescence detection method during experiments. Here, molecular oxygen O2 was added to the reactor so that the CH + O2 → OH + CO reaction occurred, producing electronically excited OH(A2Σ+) (hereafter denoted OH*). The fluorescence emission from OH* was detected using a UV sensitive photomultiplier tube and an interference filter centered on the OH (A2Σ+ → X2Π) transition around 310 nm, in a similar manner earlier measurements of the CH + H2O reaction by Hickson et al.43 A constant O2 concentration used for any single series of measurements, with a maximum value of 2.3 × 10^{14} \text{ cm}^{-3}. For most experiments, including all those employing CHBr3 as the CH source, the O2 concentration was much lower. This detection method provided certain advantages over the laser induced fluorescence (LIF) method usually employed during this type of experiment. Firstly, by detecting OH*, the entire CH temporal profile was traced for each photolysis laser shot, drastically reducing the time required for signal acquisition. Secondly, the simultaneous acquisition of all datapoints after each laser shot significantly lowered the potential for signal drift as a function of experiment time, thereby improving the accuracy of the derived decays when compared to the LIF method. The time dependent chemiluminescence signals consisted of 500 time points acquired by a 500 MHz digital oscilloscope for a range of excess CO2 concentrations. The signal was averaged over 768 photolysis laser shots for each kinetic decay, while several kinetic decays were recorded for each value of the CO2 concentration. At least eight CO2 concentrations were used at each temperature. The chemiluminescence intensities were recorded at a fixed distance from the Laval nozzle. This distance corresponded to the maximum displacement from the nozzle where optimal flow conditions could be guaranteed, so that the decays could be exploited over as large a time period as possible. These values were determined during the supersonic flow characterization experiments described above.

All gases (Linde: Ar 99.999%, CO2 99.998%; Air Liquide: N2 99.999%, H2 99.999%, D2 99.8%, CH4 99.9995%) were flowed directly from cylinders with no further purification. The carrier gas and precursor flows were regulated by digital mass flow controllers which were calibrated using the pressure rise at constant volume method for the specific gas used.

4 Results and Discussion
The pseudo-first-order approximation was applied for all the experiments performed here, with a large excess concentration of CO$_2$ with respect to the CH(CD) concentration. Under these conditions, the CH(CD) radical signal (as traced by OH*(OD*) chemiluminescent emission) followed a simple exponential decay profile. Examples of the CH decay profiles recorded at 127 K are shown in Figure 2.

![Figure 2](image)

**Figure 2** CH(OH*) chemiluminescence signal as a function of time recorded at 127 K using the C(^1D) +H$_2$ reaction as the source of CH radicals. [H$_2$] = 7.9 x 10$^{14}$ cm$^{-3}$, [O$_2$] = 9.9 x 10$^{13}$ cm$^{-3}$. (Red open squares) with [CO$_2$] = 6.1 x 10$^{15}$ cm$^{-3}$ (black solid squares) measured signal in the absence of CO$_2$. Solid lines represent exponential fits to the individual datasets.

Here, the signal intensities are plotted on a logarithmic scale for clarity. Upon addition of excess CO$_2$ to the reactor, a clear enhancement is observed in the loss rate of CH or CD radicals, thereby allowing pseudo-first-order rate constants to be derived over a range of CO$_2$ concentrations. Exponential fits to these and other decays allowed the pseudo-first-order rate constants, $k_{1st} = k_{CH+CHBr_3}[CHBr_3] + k_{CH+O_2}[O_2] + k_{CH+CO_2}[CO_2] + k_L$, to be derived for experiments employing CHBr$_3$ as the CH precursor. Here $k_{CH+CHBr_3}$, $k_{CH+O_2}$ and $k_{CH+CO_2}$ are the second-order rate constants for the reaction of CH with CHBr$_3$, O$_2$ and CO$_2$. 

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respectively and $k_L$ is an term representing additional first-order CH losses such as diffusion and reaction with impurities. For experiments employing CBr$_4$ as the CH(CD) precursor, the expression becomes

$$k_{1st} = k_{CH(CD)+CBr_4}[CBr_4] + k_{CH+H_2+M}[Ar] + k_{CH(CD)+O_2}[O_2] + k_{CH(CD)+CO_2}[CO_2] + k_L.$$  

In the absence of CO$_2$, CH(CD) radicals are lost by reaction with the precursor molecule (CHBr$_3$ or CBr$_4$), with O$_2$ (allowing CH(CD) radicals to be followed through OH chemiluminescence) and by diffusion/reaction with impurities. Additionally, in the case of experiments with CBr$_4$ and H$_2$ we also need to consider the CH + H$_2$ termolecular association reaction. As the precursor (CHBr$_3$ or CBr$_4$) concentration, [O$_2$] and [H$_2$] are constant for any single series of experiments, the observed decay rate increase when CO$_2$ is added to the flow originates solely from the additional contribution of the CH(CD) + CO$_2$ reaction. Second-order rate constants, $k'_{CH(CD)+CO_2}$, were thus extracted through weighted linear least-squares fits of $k_{1st}$ as a function of [CO$_2$] for data obtained at a specified temperature. Examples of such fits for both the CH + CO$_2$ and CD + CO$_2$ reactions are shown in Figure 3.
Figure 3. Derived pseudo-first-order rate constants $k_{1st}$ as a function of $[\text{CO}_2]$ for a range of temperatures. (Upper panel) The CH + CO\textsubscript{2} reaction (red solid circles) 296 K data with CHBr\textsubscript{3}; (green open circles) 127 K data with CHBr\textsubscript{3}; (green solid circles) 127 K data with CBr\textsubscript{4} and $[\text{H}_2] = 7.9 \times 10^{14}$ cm\textsuperscript{-3}; (magenta solid circles) 75 K data with CHBr\textsubscript{3}; (blue solid circles) 50 K data with CBr\textsubscript{4} and $[\text{H}_2] = 4.2 \times 10^{14}$ cm\textsuperscript{-3}. (Lower panel) The CD + CO\textsubscript{2} reaction (red solid circles) 296 K data with CBr\textsubscript{4} and $[\text{D}_2] = 1.5 \times 10^{15}$ cm\textsuperscript{-3}; (red open circles) 296 K data with CBr\textsubscript{4} and $[\text{D}_2] = 7.5 \times 10^{14}$ cm\textsuperscript{-3}; (blue solid circles) 50 K data with CBr\textsubscript{4} and $[\text{D}_2] = 4.2 \times 10^{14}$ cm\textsuperscript{-3}.

As it was only possible to measure rate constants at 50 K using CBr\textsubscript{4} and H\textsubscript{2}(D\textsubscript{2}) as the CH(CD) radical source (the formation of clusters between CO\textsubscript{2} and CHBr\textsubscript{3} severely limited the
useful range of [CO_2] when CHBr_3 was used as the CH source at this temperature), test experiments were performed at 127 K and 296 K to check that the two methods yielded similar results.

At 127 K, using CHBr_3 as the CH source, a value of $(1.28 \pm 0.13) \times 10^{-12}$ cm$^3$ s$^{-1}$ was obtained for the second-order rate constant which was close to the value obtained by the method using CBr_4 and H_2 of $(1.09 \pm 0.12) \times 10^{-12}$ cm$^3$ s$^{-1}$. At 296 K, the measured rate constant values using CHBr_3 to produce CH were $(1.19 \pm 0.12) \times 10^{-12}$ cm$^3$ s$^{-1}$ and $(1.35 \pm 0.14) \times 10^{-12}$ cm$^3$ s$^{-1}$ respectively for Ar and N_2 as the carrier gases respectively. The method using CBr_4 and H_2 to produce CH radicals gave a slightly higher value of $(1.71 \pm 0.17) \times 10^{-12}$ cm$^3$ s$^{-1}$ (all measurements with CBr_4 and H_2 as the CH source were performed with Ar as the carrier gas due to the rapid quenching of C(^1D) atoms by N_2). Similarly, two experiments were performed at 296 K for the CD + CO_2 reaction employing different D_2 concentrations, allowing us to check for possible interferences from secondary reactions. Rate constant values of $(2.23 \pm 0.23) \times 10^{-12}$ cm$^3$ s$^{-1}$ and $(2.07 \pm 0.21) \times 10^{-12}$ cm$^3$ s$^{-1}$ were derived using [D_2] = $1.49 \times 10^{15}$ cm$^{-3}$ and $7.46 \times 10^{14}$ cm$^{-3}$ respectively.

Effects of the CH+O_2 tracer reaction and other secondary reactions

The photolysis of CHBr_3 at 266 nm could lead to the formation of some excited state CH(a^4Σ) radicals in our experiments which could interfere with the kinetics of the CH(X^2Π_r) + CO_2 reaction. It has been estimated that the photolysis of CHBr_3 at 248 nm produces five times more ground state CH(X^2Π_r) radicals than electronically excited CH(a^4Σ) ones, although the relative yield of CH(a^4Σ) radicals is likely to be even lower at 266 nm. Indeed OH* is also produced by the CH(a^4Σ) + O_2 reaction with a room temperature rate constant of $2.6 \times 10^{-11}$ cm$^3$ s$^{-1}$. Previous work by Hou and Bayes has shown that CH(a^4Σ) radicals react slowly with CO_2, with a room temperature rate constant of less than $3 \times 10^{-13}$ cm$^3$ s$^{-1}$. The intercepts of second-order plots such as those shown in Figure 3 represent the sum of several contributions as described above. In order to evaluate our understanding of the overall chemistry occurring in the reactor, we can consider the measurements performed for the CH + CO_2 reaction at 50 K, where the derived intercept value is approximately 15000 s$^{-1}$. As the chemiluminescent OH* emission of the CH(X^2Π_r) + O_2 reaction was used to follow CH(X^2Π_r) radicals, a small fraction of CH radicals is consumed by this process. The temperature dependent rate
constants for the CH + O₂ reaction have been measured previously allowing us to estimate a pseudo-first-order loss rate for CH of ~ 6000 s⁻¹ at 50 K. Additionally, using the rate constants for the CH + H₂ termolecular association reaction derived by Brownsword et al. leads to an estimate of the pseudo-first-order loss rate for CH of ~ 400 s⁻¹ by this process at 50 K. If we assume a large rate constant for the reaction of CH radicals with the precursor molecules CHBr₃ or CBr₄ (corresponding to reaction occurring for essentially every collision), we can estimate a contribution for this process to the CH pseudo-first-order loss rate of a few thousand s⁻¹ at 50 K. Finally, diffusional losses also amount to a few thousand s⁻¹ at this temperature based on earlier work. As the sum of these contributions is close to the measured intercept value, it does not appear that any major reactive processes are unaccounted for.

In previous work on the CH + H₂O reaction, Hickson et al. examined the influence of the O₂ concentration on the derived rate constants for this reaction. Test experiments were performed at 296 K with different fixed O₂ concentrations, each over a range of coreagent concentrations. These measurements yielded second-order plots with the same slopes, indicating that the tracer reaction products did not interfere with the CH kinetics.

**Product versus complex formation in the CH + CO₂ reaction**

To check that the recorded CH decays in the presence of CO₂ resulted in real product formation (rather than just simply complex formation with a long enough lifetime for it to remove CH from the flow on the timescale of the experiment), additional experiments were performed at 127 K. As can be seen from Figure 1, the products of the CH + CO₂ reaction are considered to be HCO + CO, while a significant fraction of the exothermic energy released by the reaction is expected to be carried away by the HCO fragment. Under these conditions, the HCO radical could further dissociate to H + CO. Here we detected the formation of atomic hydrogen by laser induced fluorescence at 121.567 nm in a similar manner to our previous work on the C + H₂O reaction. These experiments employed CHBr₃ photolysis at 266 nm as the source of CH radicals. In order to calibrate the H-atom production efficiency of the CH + CO₂ reaction to obtain quantitative information, the H-atom yield was compared with that of a reference process, namely the CH + CH₄ reaction which forms C₂H₄ + H as the exclusive products. Figure 4 shows the results of one of the six experiments that were performed.
Figure 4. H-atom temporal profiles as a function of time recorded at 127 K. (Red solid circles) H-atom signal from the \( \text{CH} + \text{CO}_2 \) reaction with \([\text{CO}_2] = 6.2 \times 10^{15} \text{ cm}^{-3}\). (Blue solid squares) H-atom signal from the \( \text{CH} + \text{CH}_4 \) reaction with \([\text{CH}_4] = 4.1 \times 10^{13} \text{ cm}^{-3}\). (Green solid triangles) H-atom signal recorded in the absence of \( \text{CH}_4 \) and \( \text{CO}_2 \), corresponding to nascent H-atoms produced by \( \text{CHBr}_3 \) photolysis. The green solid line represents a single exponential fit to the data.

Figure 4 clearly shows that the photolysis of \( \text{CHBr}_3 \) at 266 nm also results in the direct production of H-atoms, which decay slowly through diffusion from the observation region (green datapoints). This signal can therefore be considered as the baseline level for subsequent H-atom yield measurements. Here, \( \text{CO}_2 \) and \( \text{CH}_4 \) concentrations were carefully chosen to provide identical first-order production rates (~8000 s\(^{-1}\)) for H-atoms (so that H-atom diffusional losses were identical), based on the measured rate constants for these processes. When \( \text{CO}_2 \) is added to the flow a clear production of H-atoms is observed (red datapoints), over and above the baseline level, followed by a slow decay of these atoms. When \( \text{CH}_4 \) is added to the reactor (in the absence of \( \text{CO}_2 \)), a similar H-atom biexponential type profile is obtained (blue datapoints) to the one recorded for the \( \text{CH} + \text{CO}_2 \) reaction with yields...
that are clearly very similar in magnitude to those of the target reaction. To obtain quantitative yields from these data would require a subtraction of the nascent H-atom signal intensity from the signal obtained from the target and reference reactions. Unfortunately, this analysis resulted in large errors, so that quantitative yields could not be extracted. Nevertheless, the large observed H-atom yields from the CH + CO$_2$ reaction allow us to draw a couple of important qualitative conclusions: (1) the HCO product of the CH + CO$_2$ reaction dissociates almost entirely to H + CO in the present experiments (2) complex formation represents only a very small fraction of the overall end product of the CH + CO$_2$ reaction, with the majority of successful collisions resulting in real product formation.

The measured rate constants are listed in Table 1 and are shown in Figure 5 alongside the present theoretical results and previous data from the literature.

| T / K  | [CO$_2$] / 10$^{14}$ cm$^{-3}$ | $k_{\text{CH+CO}_2}$ (CHBr$_3$) / 10$^{-12}$ cm$^3$ s$^{-1}$ | [CO$_2$] / 10$^{14}$ cm$^{-3}$ | $k_{\text{CH+CO}_2}$ (CBr$_4$) / 10$^{-12}$ cm$^3$ s$^{-1}$ | [CO$_2$] / 10$^{14}$ cm$^{-3}$ | $k_{\text{CD+CO}_2}$ (CBr$_4$) / 10$^{-12}$ cm$^3$ s$^{-1}$ |
|-------|-----------------------------|-----------------------------------|-----------------------------|-----------------------------------|-----------------------------|-----------------------------------|
| 296   | 0 - 85.7$^a$                | (1.1 ± 0.12)$^c$ 63$^d$           | 0 - 85.4                    | (1.71 ± 0.17)$^e$ 30             | 0 - 84.7                    | (2.23 ± 0.23)$^e$ 30             |
| 296   | 0 - 85.7$^b$                | (1.35 ± 0.14)$^c$ 27              |                             | 0 - 85.1                        | (2.07 ± 0.21)$^f$ 30         |
| 177   | 0 - 45.9                    | (1.15 ± 0.13)$^c$ 42              |                             |                                  |                             |                                    |
| 127   | 0 - 62.9                    | (1.28 ± 0.13)$^c$ 42              | 0 - 62.5                    | (1.09 ± 0.12)$^c$ 24             | 0 - 62.5                    | (1.09 ± 0.12)$^c$ 24             |
| 75    | 0 - 21.4                    | (2.25 ± 0.23)$^c$ 46              |                             |                                  |                             |                                    |
| 50    | 0 - 3.5                     | (4.02 ± 0.68)$^d$ 51              |                             |                                  |                             |                                    |

$^a$Experiments conducted with Ar as the carrier gas. $^b$Experiments conducted with N$_2$ as the carrier gas. $^c$Errors are cited at the level of a single standard deviation from the mean and comprise an additional 10% contribution from possible systematic errors. $^d$Figures in italics represent the number of individual experiments. $^e$[D$_2$] = 1.49 × 10$^{15}$ cm$^{-3}$. $^f$[D$_2$] = 7.46 × 10$^{14}$ cm$^{-3}$. 15
Figure 5. Temperature dependence of the rate constants for the CH (CD) + CO$_2$ reactions. The CH + CO$_2$ reaction. Experimental studies; (purple square) Butler et al.$^{50}$; (cyan diamonds) Berman et al.$^{13}$; (Blue circles) Mehlmann et al.$^{15}$; (red squares) this work - CHBr$_3$ as CH precursor; (orange circles) this work - CBr$_4$ and H$_2$ precursors. Theoretical studies; (blue line) Vichietti et al.$^{12}$; (red line) this work - ICVT/SCT calculations at the DKH-CV-CCSD(T)/CBS level. The CD + CO$_2$ reaction. Experimental studies; (gray diamond) Mehlmann et al.$^{15}$; (green triangle) this work - CBr$_4$ and H$_2$ as CH precursors. Theoretical studies; (green solid line) this work - ICVT/SCT calculations at the DKH-CV-CCSD(T)/CBS level.

It can be seen from Figure 5 that the measured room temperature rate constants of $(1.19-1.71) \times 10^{-12}$ cm$^3$ s$^{-1}$ for the CH + CO$_2$ reaction agree well with those obtained in previous work,$^{13, 15, 50}$ $(1.80-2.05) \times 10^{-12}$ cm$^3$ s$^{-1}$, thereby validating the two experimental methods employed here. The experimental reaction rates present small variations between 100 K and 300 K, between 1.1 and $1.3 \times 10^{-12}$ cm$^3$ s$^{-1}$. However, the CH + CO$_2$ reaction becomes much faster below 100 K and the rate constant reaches a value of $(4.02 \pm 0.68) \times 10^{-12}$ cm$^3$ s$^{-1}$ at 50 K.
Figure 5 also shows that, while the previous rate constant calculations of Vichietti et al.\textsuperscript{12} already capture the main features of the upturn at low temperatures, a factor of two discrepancy is observed between theory and experiment in the intermediate plateau region. However, as CV correlation and scalar relativistic effects are accounted for in the present electronic structure calculations, the respective ICVT/SCT rate constants provide much better agreement with the experimental results. Moreover, this study clearly demonstrates that the proposed tunneling mechanism involving CH insertion can adequately explain the experimental measurements since the quantum tunneling correction (SCT) is the primary factor responsible for the reaction rate increases as the temperature is lowered (see Table S1 and Fig. S1). In other words, the rate constants for the CH + CO\textsubscript{2} reaction obtained without quantum tunneling corrections would erroneously decrease as the temperature is lowered, while good agreement with experimental observations occurs only through the inclusion of such corrections. In addition, since the reaction coordinate for the rate-determining step involves the displacement of the whole CH fragment, this suggests the involvement of a heavy-particle tunneling mechanism.

As a rigorous test of our understanding of the reaction mechanism, we also performed kinetic measurements and calculations for the CD + CO\textsubscript{2} system. Indeed, if H-atom tunneling was responsible for the observed acceleration at low temperature in the CH + CO\textsubscript{2} reaction then we would expect that the rate increase should be less pronounced for the deuterated equivalent due to the lower tunneling probability of D versus H. Surprisingly, the calculated and measured rate constants shown in Figure 3 present the opposite behavior, both displaying large increases below room temperature with almost perfect agreement between theory and experiment. A closer look at the electronic structure calculations (see Figure 1 and Table S3 in the Supporting Information) tells us that this effect originates from zero point energy (ZPE) contributions. Hence, while the ZPE corrected adiabatic barrier height ($\Delta V_{a}^{G,\ddagger}$ in Table S3) of the rate-determining step is positive with respect to CH and CO\textsubscript{2} (1.3 kJ/mol), the larger reduced mass of the equivalent deuterated species lowers $\Delta V_{a}^{G,\ddagger}$ to such an extent that it falls below the reagent asymptote (-0.5 kJ/mol), becoming a reef structure rather than a real barrier (see also the top right inset in Figure 1). Although this finding has little effect on room temperature results of both reactional systems, as back dissociation of the CH...CO\textsubscript{2} and CD...CO\textsubscript{2} pre-reactive complexes dominates (both the present and previous experimental studies\textsuperscript{15} of the CD + CO\textsubscript{2} reaction derived reaction rates that were similar in magnitude to
the CH + CO₂ ones), the passage forward over this reef structure is favored instead at lower
temperature, leading to a large enhancement of the reaction rate. It is worth noting that
tunneling from states with energies that lie below the reactants on the minimum energy path
was not considered since the reaction was treated as a one-step process. Non-classical
reflection was not taken into account. However, we believe that these contributions should
be small. Moreover, some error cancellation is expected from both contributions. In
summary, the rate constant increases observed for the CD + CO₂ reaction as temperatures
are lowered are due to ZPE corrections, resulting in a submerged barrier with respect to
reactants. Consequently, the CD + CO₂ reaction is comparable to a number of other systems
presenting similar features over the PES leading from reagents to products, such as the CH +
H₂O reaction as well as the reactions of C(³P) with NH₃ and CH₃OH.

5 Astrochemical Interest
The reactions of CH and CD with CO₂ could also be interesting from an astrochemical
perspective since related models predict that this species should be present at high relative
abundance levels (10⁻⁷ with respect to H₂), although gas-phase CO₂ has never been detected
in the interstellar medium due to the absence of a permanent electric dipole moment. As the
main source of protonated carbon dioxide (HOCO⁺) is thought to be the H₃⁺ + CO₂ reaction, the predicted CO₂ abundance has been indirectly confirmed through observations of HOCO⁺.

Given the predicted rate of the CH + CO₂ reaction of 1.1 × 10⁻¹¹ cm³ s⁻¹ at 10 K, this reaction is
likely to play only a minor role in the loss of interstellar CH, although it could be an important
source of interstellar HCO (formyl) radicals. Furthermore, the large measured difference in
the reactivity between CH or CD with CO₂ at low temperatures may represent an important
mechanism for deuterium enrichment of formyl radicals in the gas-phase interstellar medium.
Indeed, the present calculations predict rate constants of 4.2 × 10⁻¹² cm³ s⁻¹ and 9.5 × 10⁻¹¹
cm³ s⁻¹ for the CH + CO₂ and CD + CO₂ reactions, respectively, at 25 K; resulting in a difference
of more than a factor of twenty in reactivity which could lead to a significantly enhanced gas-
phase DCO/HCO ratio.

This work could also have implications for the chemistry of interstellar ices where CO₂ is
thought to be present at high levels with respect to water ice (10-50%). In these
environments, an HCOCO adduct is generated by the addition of a physisorbed CH radical to
solid CO₂, providing a potential mechanism for glycol CHOCHO formation through H addition.
(which are mobile at 10 K) to HCOCO. Another potential route for HCOCO formation is through the formation of an initial complex between atomic carbon and CO$_2$ ice (C…CO$_2$)$_5$, as C does not react with CO$_2$ directly. Instead, a hydrogen atom scans the surface until it encounters the C…CO$_2$ complex, reacting to produce CH…CO$_2$ before going on to form HCOCO. However, considering the very low binding energy of HCO-CO$_2$, the main products of the CH + CO$_2$ reaction are likely to be HCO + CO or H + CO + CO as the available excess energy to be redistributed to the ice phonon modes is probably too great to effectively stabilize HCOCO. This process could instead represent an important mechanism for the reconversion of CO$_2$ to CO on interstellar ices.

6 Conclusions
Here we present the results of a joint experimental and theoretical study of the CH(CD) + CO$_2$ reaction at low temperature. On the experimental side, the Laval nozzle (CRESU) method was employed, coupled with pulsed laser photolysis production of CH(CD), with these radicals being detected by chemiluminescence. On the theoretical side, thermal rate constants were obtained by transition state theory within the improved canonical variational theory including quantum tunneling corrections. These calculations were based on the thermochemical properties for stationary point structures of the CH(CD) + CO$_2$ system obtained with a high-level electronic correlation methodology including scalar relativistic and core-valence correlation effects. The rate of the CH + CO$_2$ reaction is seen to accelerate below 100 K, with good agreement between experiment and theory. Supplementary experiments detecting atomic hydrogen formed from product HCO dissociation clearly show that real product formation is the major outcome of this process. Mechanistically, the reaction is shown to occur by means of quantum mechanical tunneling of the CH radical through the activation barrier. To exclude possible contributions from H atom tunneling effects, measurements and calculations were also performed for the CD + CO$_2$ reaction. This deuterated process was seen to react much more rapidly at low temperature as zero point energy effects eliminate the barrier to product formation. The possible astrochemical implications of these reactions are discussed.

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Supporting information for

Tunneling Enhancement of the Gas-Phase CH + CO₂ Reaction at Low Temperature

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This PDF files includes:

Tables S1-S4 and Figure S1.
**Supplementary Tables**

**Table S1** Forward rate constants (in cm³/particle⁻¹s⁻¹) for the CH + CO₂ → IM1 elementary step calculated at the ICVT and ICVT/SCT levels for different temperatures (in K) and by using different approaches to build the reactional path.

| T [K] | ICVT⁺ | ICVT/SCT⁺ | ICVT⁻ | ICVT/SCT⁻ | ICVT⁺ | ICVT/SCT⁻ |
|-------|-------|-----------|-------|-----------|-------|-----------|
| 25    | 1.57 × 10⁻¹² | 6.75 × 10⁻¹² | 9.54 × 10⁻¹⁴ | 4.88 × 10⁻¹² | 2.69 × 10⁻¹⁴ | 4.15 × 10⁻¹² |
| 50    | 2.12 × 10⁻¹² | 3.45 × 10⁻¹² | 5.22 × 10⁻¹³ | 2.43 × 10⁻¹² | 2.77 × 10⁻¹³ | 2.09 × 10⁻¹² |
| 75    | 2.08 × 10⁻¹² | 2.62 × 10⁻¹² | 8.18 × 10⁻¹³ | 1.85 × 10⁻¹² | 5.37 × 10⁻¹³ | 1.60 × 10⁻¹² |
| 100   | 2.02 × 10⁻¹² | 2.31 × 10⁻¹² | 1.00 × 10⁻¹² | 1.65 × 10⁻¹² | 7.30 × 10⁻¹³ | 1.44 × 10⁻¹² |
| 125   | 1.99 × 10⁻¹² | 2.17 × 10⁻¹² | 1.13 × 10⁻¹² | 1.58 × 10⁻¹² | 8.80 × 10⁻¹³ | 1.39 × 10⁻¹² |
| 150   | 1.98 × 10⁻¹² | 2.11 × 10⁻¹² | 1.24 × 10⁻¹² | 1.58 × 10⁻¹² | 1.01 × 10⁻¹² | 1.40 × 10⁻¹² |
| 175   | 2.00 × 10⁻¹² | 2.09 × 10⁻¹² | 1.34 × 10⁻¹² | 1.60 × 10⁻¹² | 1.12 × 10⁻¹² | 1.44 × 10⁻¹² |
| 200   | 2.04 × 10⁻¹² | 2.11 × 10⁻¹² | 1.44 × 10⁻¹² | 1.65 × 10⁻¹² | 1.23 × 10⁻¹² | 1.49 × 10⁻¹² |
| 225   | 2.10 × 10⁻¹² | 2.15 × 10⁻¹² | 1.54 × 10⁻¹² | 1.71 × 10⁻¹² | 1.33 × 10⁻¹² | 1.56 × 10⁻¹² |
| 250   | 2.16 × 10⁻¹² | 2.21 × 10⁻¹² | 1.63 × 10⁻¹² | 1.79 × 10⁻¹² | 1.44 × 10⁻¹² | 1.63 × 10⁻¹² |
| 275   | 2.24 × 10⁻¹² | 2.28 × 10⁻¹² | 1.73 × 10⁻¹² | 1.87 × 10⁻¹² | 1.55 × 10⁻¹² | 1.72 × 10⁻¹² |
| 300   | 2.32 × 10⁻¹² | 2.36 × 10⁻¹² | 1.84 × 10⁻¹² | 1.96 × 10⁻¹² | 1.66 × 10⁻¹² | 1.81 × 10⁻¹² |
| 325   | 2.42 × 10⁻¹² | 2.45 × 10⁻¹² | 1.95 × 10⁻¹² | 2.05 × 10⁻¹² | 1.77 × 10⁻¹² | 1.91 × 10⁻¹² |
| 350   | 2.52 × 10⁻¹² | 2.55 × 10⁻¹² | 2.06 × 10⁻¹² | 2.16 × 10⁻¹² | 1.88 × 10⁻¹² | 2.01 × 10⁻¹² |
| 375   | 2.61 × 10⁻¹² | 2.64 × 10⁻¹² | 2.17 × 10⁻¹² | 2.26 × 10⁻¹² | 1.99 × 10⁻¹² | 2.11 × 10⁻¹² |
| 400   | 2.71 × 10⁻¹² | 2.74 × 10⁻¹² | 2.28 × 10⁻¹² | 2.36 × 10⁻¹² | 2.10 × 10⁻¹² | 2.21 × 10⁻¹² |
| 500   | 3.18 × 10⁻¹² | 3.20 × 10⁻¹² | 2.77 × 10⁻¹² | 2.83 × 10⁻¹² | 2.60 × 10⁻¹² | 2.68 × 10⁻¹² |
| 700   | 4.38 × 10⁻¹² | 4.39 × 10⁻¹² | 3.96 × 10⁻¹² | 4.01 × 10⁻¹² | 3.79 × 10⁻¹² | 3.85 × 10⁻¹² |
| 1000  | 6.72 × 10⁻¹² | 6.73 × 10⁻¹² | 6.27 × 10⁻¹² | 6.30 × 10⁻¹² | 6.07 × 10⁻¹² | 6.12 × 10⁻¹² |
| 1500  | 1.20 × 10⁻¹¹ | 1.20 × 10⁻¹¹ | 1.14 × 10⁻¹¹ | 1.15 × 10⁻¹¹ | 1.12 × 10⁻¹¹ | 1.12 × 10⁻¹¹ |
| 2000  | 1.88 × 10⁻¹¹ | 1.88 × 10⁻¹¹ | 1.82 × 10⁻¹¹ | 1.82 × 10⁻¹¹ | 1.79 × 10⁻¹¹ | 1.79 × 10⁻¹¹ |
| 2500  | 2.73 × 10⁻¹¹ | 2.73 × 10⁻¹¹ | 2.65 × 10⁻¹¹ | 2.66 × 10⁻¹¹ | 2.62 × 10⁻¹¹ | 2.62 × 10⁻¹¹ |
| 3000  | 3.74 × 10⁻¹¹ | 3.74 × 10⁻¹¹ | 3.65 × 10⁻¹¹ | 3.65 × 10⁻¹¹ | 3.61 × 10⁻¹¹ | 3.62 × 10⁻¹¹ |
| 3500  | 4.90 × 10⁻¹¹ | 4.90 × 10⁻¹¹ | 4.81 × 10⁻¹¹ | 4.81 × 10⁻¹¹ | 4.76 × 10⁻¹¹ | 4.77 × 10⁻¹¹ |
| 4000  | 6.23 × 10⁻¹¹ | 6.23 × 10⁻¹¹ | 6.12 × 10⁻¹¹ | 6.12 × 10⁻¹¹ | 6.07 × 10⁻¹¹ | 6.07 × 10⁻¹¹ |

a The dual-level approach was employed using the electronic results of the CCSD(T)/CBS method.
b The dual-level approach was employed using the electronic results of the DKH-CCSD(T)/CBS method.
c The dual-level approach was employed using the electronic results of the DKH-CV-CCSD(T)/CBS method.
Table S2  Forward rate constants (in cm²/particle⁻¹s⁻¹) for the CD + CO₂ → IM1 elementary step calculated at the ICVT and ICVT/SCT levels for different temperatures (in K) and by using different approaches to build the reactional path.

| T [K] | ICVT⁺  | ICVT/SCT⁺ | ICVT⁻  | ICVT/SCT⁻ | ICVT⁺  | ICVT/SCT⁺ |
|-------|--------|-----------|--------|-----------|--------|-----------|
| 25    | 2.53 × 10⁻⁴ | 2.53 × 10⁰ | 3.37 × 10⁻¹⁰ | 3.37 × 10⁻¹² | 9.49 × 10⁻¹¹ | 9.49 × 10⁻¹¹ |
| 50    | 9.77 × 10⁻¹¹ | 9.77 × 10⁻¹¹ | 2.41 × 10⁻¹¹ | 2.41 × 10⁻¹¹ | 1.28 × 10⁻¹¹ | 1.28 × 10⁻¹¹ |
| 75    | 2.33 × 10⁻¹¹ | 2.33 × 10⁻¹¹ | 9.17 × 10⁻¹² | 9.17 × 10⁻¹² | 6.01 × 10⁻¹² | 6.01 × 10⁻¹² |
| 100   | 1.13 × 10⁻¹¹ | 1.13 × 10⁻¹¹ | 5.60 × 10⁻¹² | 5.60 × 10⁻¹² | 4.08 × 10⁻¹² | 4.08 × 10⁻¹² |
| 125   | 7.34 × 10⁻¹² | 7.34 × 10⁻¹² | 4.19 × 10⁻¹² | 4.19 × 10⁻¹² | 3.25 × 10⁻¹² | 3.25 × 10⁻¹² |
| 150   | 5.58 × 10⁻¹² | 5.58 × 10⁻¹² | 3.50 × 10⁻¹² | 3.50 × 10⁻¹² | 2.83 × 10⁻¹² | 2.83 × 10⁻¹² |
| 175   | 4.66 × 10⁻¹² | 4.66 × 10⁻¹² | 3.12 × 10⁻¹² | 3.12 × 10⁻¹² | 2.61 × 10⁻¹² | 2.61 × 10⁻¹² |
| 200   | 4.13 × 10⁻¹² | 4.13 × 10⁻¹² | 2.91 × 10⁻¹² | 2.91 × 10⁻¹² | 2.48 × 10⁻¹² | 2.48 × 10⁻¹² |
| 225   | 3.81 × 10⁻¹² | 3.81 × 10⁻¹² | 2.79 × 10⁻¹² | 2.79 × 10⁻¹² | 2.42 × 10⁻¹² | 2.42 × 10⁻¹² |
| 250   | 3.61 × 10⁻¹² | 3.61 × 10⁻¹² | 2.73 × 10⁻¹² | 2.73 × 10⁻¹² | 2.40 × 10⁻¹² | 2.40 × 10⁻¹² |
| 275   | 3.50 × 10⁻¹² | 3.50 × 10⁻¹² | 2.71 × 10⁻¹² | 2.71 × 10⁻¹² | 2.42 × 10⁻¹² | 2.42 × 10⁻¹² |
| 300   | 3.44 × 10⁻¹² | 3.44 × 10⁻¹² | 2.73 × 10⁻¹² | 2.73 × 10⁻¹² | 2.45 × 10⁻¹² | 2.45 × 10⁻¹² |
| 325   | 3.43 × 10⁻¹² | 3.43 × 10⁻¹² | 2.76 × 10⁻¹² | 2.76 × 10⁻¹² | 2.51 × 10⁻¹² | 2.51 × 10⁻¹² |
| 350   | 3.44 × 10⁻¹² | 3.44 × 10⁻¹² | 2.82 × 10⁻¹² | 2.82 × 10⁻¹² | 2.58 × 10⁻¹² | 2.58 × 10⁻¹² |
| 375   | 3.48 × 10⁻¹² | 3.48 × 10⁻¹² | 2.89 × 10⁻¹² | 2.89 × 10⁻¹² | 2.66 × 10⁻¹² | 2.66 × 10⁻¹² |
| 400   | 3.54 × 10⁻¹² | 3.54 × 10⁻¹² | 2.97 × 10⁻¹² | 2.97 × 10⁻¹² | 2.75 × 10⁻¹² | 2.75 × 10⁻¹² |
| 500   | 3.92 × 10⁻¹² | 3.92 × 10⁻¹² | 3.41 × 10⁻¹² | 3.41 × 10⁻¹² | 3.20 × 10⁻¹² | 3.20 × 10⁻¹² |
| 700   | 5.09 × 10⁻¹² | 5.09 × 10⁻¹² | 4.61 × 10⁻¹² | 4.61 × 10⁻¹² | 4.40 × 10⁻¹² | 4.40 × 10⁻¹² |
| 1000  | 7.55 × 10⁻¹² | 7.55 × 10⁻¹² | 7.04 × 10⁻¹² | 7.04 × 10⁻¹² | 6.82 × 10⁻¹² | 6.82 × 10⁻¹² |
| 1500  | 1.32 × 10⁻¹¹ | 1.32 × 10⁻¹¹ | 1.26 × 10⁻¹¹ | 1.26 × 10⁻¹¹ | 1.23 × 10⁻¹¹ | 1.23 × 10⁻¹¹ |
| 2000  | 2.06 × 10⁻¹¹ | 2.06 × 10⁻¹¹ | 1.99 × 10⁻¹¹ | 1.99 × 10⁻¹¹ | 1.96 × 10⁻¹¹ | 1.96 × 10⁻¹¹ |
| 2500  | 2.98 × 10⁻¹¹ | 2.98 × 10⁻¹¹ | 2.89 × 10⁻¹¹ | 2.89 × 10⁻¹¹ | 2.86 × 10⁻¹¹ | 2.86 × 10⁻¹¹ |
| 3000  | 4.07 × 10⁻¹¹ | 4.07 × 10⁻¹¹ | 3.97 × 10⁻¹¹ | 3.97 × 10⁻¹¹ | 3.93 × 10⁻¹¹ | 3.93 × 10⁻¹¹ |
| 3500  | 5.33 × 10⁻¹¹ | 5.33 × 10⁻¹¹ | 5.23 × 10⁻¹¹ | 5.23 × 10⁻¹¹ | 5.18 × 10⁻¹¹ | 5.18 × 10⁻¹¹ |
| 4000  | 6.77 × 10⁻¹¹ | 6.77 × 10⁻¹¹ | 6.65 × 10⁻¹¹ | 6.65 × 10⁻¹¹ | 6.60 × 10⁻¹¹ | 6.60 × 10⁻¹¹ |

a The dual-level approach was employed using the electronic results of the CCSD(T)/CBS method.
b The dual-level approach was employed using the electronic results of the DKH-CCSD(T)/CBS method.
c The dual-level approach was employed using the electronic results of the DKH-CV-CCSD(T)/CBS method.
Table S3  Thermochemical properties (in kJ/mol) for the CH(CD) + CO₂ → IM1 elementary step.\(^a\)

| Method                | \(\Delta E\) | \(\Delta H\) | \(V^\dagger\) | \(\Delta V_{a,G} G,^\dagger\) |
|----------------------|--------------|--------------|---------------|-----------------------------|
| CCSD(T)/CBS\(^b\)   | -171.1       | -153.8       | -6.4          | 0.4                         |
| DKH-CCSD(T)/CBS\(^c\) | -168.5       | -151.3       | -5.8          | 1.1                         |
| DKH-CV-CCSD(T)/CBS\(^d\) | -170.8       | -153.5       | -5.6          | 1.3                         |

| Method                | \(\Delta E\) | \(\Delta H\) | \(V^\dagger\) | \(\Delta V_{a,G} G,^\dagger\) |
|----------------------|--------------|--------------|---------------|-----------------------------|
| CCSD(T)/CBS\(^b\)   | -171.1       | -156.9       | -6.4          | -1.4                        |
| DKH-CCSD(T)/CBS\(^c\) | -168.5       | -154.4       | -5.8          | -0.8                        |
| DKH-CV-CCSD(T)/CBS\(^d\) | -170.8       | -156.6       | -5.6          | -0.5                        |

\(^a\) The equilibrium geometries considered for these calculations were previously calculated with the UCCSD/cc-pVDZ method.\(^10\) The properties presented are the classical barrier (\(V^\dagger\), electronic energy difference between the reactants and the saddle point), the adiabatic barrier height (\(\Delta V_{a,G} G,^\dagger\), defined as \(V^\dagger + \Delta ZPE^\dagger\)), the electronic energy of the reaction (\(\Delta E\)), the enthalpy of the reaction at 0 K (\(\Delta H = \Delta E + \Delta ZPE\)).

\(^b\) The CBS extrapolation was calculated by using cc-pVXZ (X=4 and 5) basis sets.

\(^c\) The CBS extrapolation was calculated by using cc-pVXZ-DK (X=4 and 5) basis sets.

\(^d\) The CBS extrapolation was calculated by using cc-pCVXZ-DK (X=4 and 5) basis sets.

Table S4  Continuous supersonic flow characteristics

| Mach number | 1.8 ± 0.02\(^a\) | 2.0 ± 0.03 | 3.0 ± 0.1 | 3.9 ± 0.1 |
|-------------|-------------------|------------|-----------|-----------|
| Carrier gas | N\(_2\)           | Ar         | Ar        | Ar        |
| Density (\(\times 10^{16}\) cm\(^-3\)) | 9.4            | 12.6       | 14.7      | 25.9      |
| Impact pressure (Pa) | 1093.2         | 1399.9     | 2039.8    | 3946.3    |
| Stagnation pressure (Pa) | 1373.2       | 1853.2     | 4653.0    | 15065.4   |
| Temperature (K) | 177 ± 2\(^a\)      | 127 ± 2    | 75 ± 2    | 50 ± 1    |
| Mean flow velocity (ms\(^-1\)) | 496 ± 4\(^a\)      | 419 ± 3    | 479 ± 3   | 505 ± 1   |

\(^a\) The errors on the Mach number, temperature and mean flow velocity, cited at the level of one standard deviation from the mean are calculated from separate measurements of the impact pressure using a Pitot tube as a function of distance from the Laval nozzle and the stagnation pressure within the reservoir.
**Supplementary Figures**

![Graph showing quantum tunneling effects (ICVT/SCT versus ICVT) on calculated rate constants of the CH + CO$_2$ reaction (see Table S1).](image)

**Figure S1.** Quantum tunneling effects (ICVT/SCT versus ICVT) on calculated rate constants of the CH + CO$_2$ reaction (see Table S1).