

# The reaction of carbon dioxide cations ( $\text{CO}_2^+$ ) with methane ( $\text{CD}_4$ )

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**Abstract:** The reactivity of  $\text{CO}_2^+$  with  $\text{CD}_4$  is investigated, using a guided ion beam apparatus coupled to VUV synchrotron radiation, by changing either the kinetic energy of  $\text{CO}_2^+$  or its vibrational excitation and measuring collision energy-dependent rate constants and branching ratios. Reactivity is found to depend on reagents' collision energy, but far less on  $\text{CO}_2^+$  vibrational excitation. Results are relevant in the chemistry of plasmas used for the conversion of  $\text{CO}_2$  in carbon-neutral fuels.

**Keywords:** plasma, ion-molecule reaction,  $\text{CO}_2$  dissociation, vibrational excitation, astrochemistry

## 1. Introduction

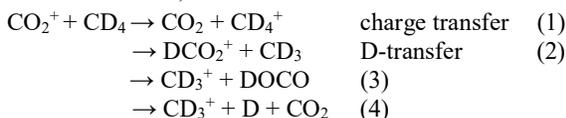
Non-thermal plasmas have been explored for their capability to activate very stable molecules and achieve a higher energy efficiency compared to purely thermal methods, when applied to processes such as dry reforming of methane, *i.e.* conversion of  $\text{CH}_4$  and  $\text{CO}_2$  into value-added chemicals [1-4]. To improve the performances of plasma-based processes, insight into the physicochemical mechanisms at play is desired. We have reinvestigated one of the key processes in methane dry reforming, the reaction of  $\text{CO}_2^+$  with  $\text{CH}_4$ , for which literature data on the branching ratios (BRs) are scattered. Since vibrationally excited levels of  $\text{CO}_2^+$  can be populated in plasmas, we have investigated the effect of  $\text{CO}_2^+$  vibrational excitation on reactivity.

## 2. Experiment

Experiments have been performed using a guided ion beam tandem mass spectrometer coupled with VUV radiation at the DESIRS beamline of the SOLEIL synchrotron radiation facility [5, 6]. Absolute reaction cross sections and BRs are derived as a function of the collision energy and the vibrational excitation of the parent ion. Full vibrational state-selection is achieved using TPEPICO (Threshold Photoelectron Photoion Coincidence) [7], but some measurements are performed with  $\text{CO}_2^+$  in a distribution of excitation that is varied by changing the energy of the ionizing photons.

## 3. Results and discussion

Absolute cross section values as a function of the collision energy ( $E_{CM}$ ) have been measured at two selected photon energies  $E_{phor}=13.78$  eV (no vibrational excitation of the  $\text{CO}_2^+$  cation) and 16.48 eV (some excitation to high vibrational levels). The main reaction channels are:



Thermochemistry indicates that channels (1) and (2) are exothermic by -1.17 and -1.26 eV respectively, while channels (3) and (4) are both endothermic by  $\sim 0.6$  eV. Product cross sections as a function of the reagent collision energy measured with no vibrational excitation of  $\text{CO}_2^+$  are shown in Fig. 1. Due to the highly efficient reaction of the major  $\text{CD}_4^+$  product with  $\text{CD}_4$ , a non-negligible amount of secondary  $\text{CD}_5^+$  product is observed, and absolute cross sections and BRs have been corrected for such contribution.

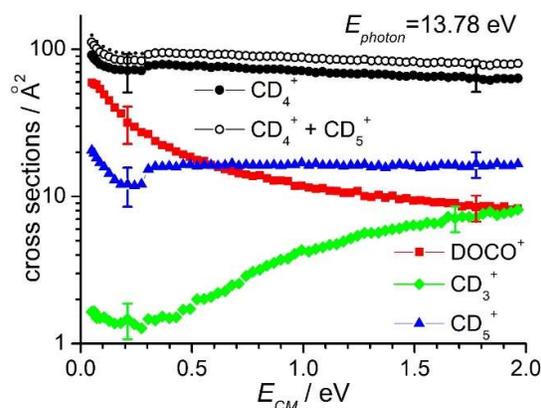


Fig. 1. Reactive cross sections for various products as a function of collision energy measured with no vibrational excitation of  $\text{CO}_2^+$

BRs at  $E_{phor}=13.78$  eV (see Table 1) show reaction (1) to be the dominant channel at all the explored collision energies. This result is at odds with existing literature values for the BR of reaction (1) and (2) that ranges from 1:0, to 0.5:0.5, to 0.28:0.72 and finally to 0:1 [8-13].

The TPEPICO method allowed to prepare  $\text{CO}_2^+$  ions in the (0,0,0) ground state and in two vibrationally excited states: (0,1,0) with one quantum of bending vibration and ((1,0,0) + (0,0,1)) corresponding to a combination of the symmetric

and antisymmetric stretching vibration. State-selected results for the reactive cross sections are shown in Fig. 2 for a collision energy  $E_{CM} = 0.17 \pm 0.02$  eV (the large uncertainties are due to the low S/N ratio in the coincidence mode).

Table 1. BRs at two different  $E_{CM}$  measured at  $E_{phot} = 13.78$  eV

	BRs ( $E_{CM}=0.1$ eV)	BRs ( $E_{CM}=1.9$ eV)
$CD_4^+$	$0.66 \pm 0.06$	$0.83 \pm 0.07$
$DOCO^+$	$0.33 \pm 0.03$	$0.09 \pm 0.009$
$CD_3^+$	$(8.9 \pm 0.9) \times 10^{-3}$	$0.08 \pm 0.01$

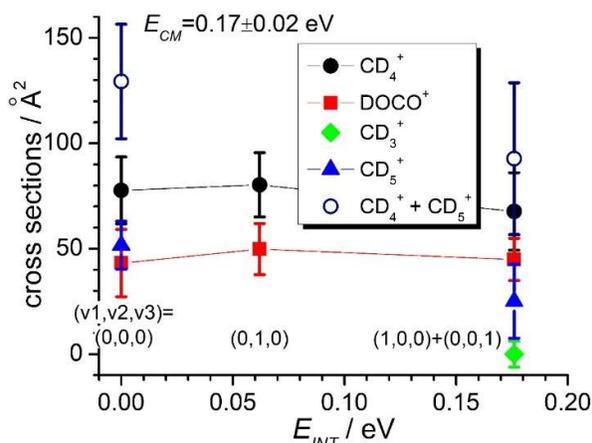


Fig. 2. Reactive cross sections for various products as a function of the vibrational excitation of  $CO_2^+$  ( $E_{INT}$ ).

#### 4. Conclusions and implication for plasma chemistry

In summary, our results show that:

- i) the main reaction products are  $CD_4^+$ ,  $DOCO^+$  and  $CD_3^+$
- ii) reactivity is found to depend on the reagent collision energy: cross sections for the endothermic channel leading to  $CD_3^+$  increase with collision energy, while those for D-transfer (2) are at a maximum at the lowest energies achievable in our set-up
- iii) cross sections change very little with increasing vibrational excitation of  $CO_2^+$

To put our results into the context of plasma chemistry used for the conversion of  $CO_2$  in carbon-neutral fuels [1, 3], both the  $CH_4^+$  and  $HOCO^+$  products of the reaction of  $CO_2^+$  with  $CH_4$ , i.e. reactions (1) and (2) eventually lead to the production of  $CH_5^+$  and  $CH_3$ , as shown in the following scheme:



Thus the energy initially used to ionize  $CO_2$  is transferred to  $CH_4$  to form  $CH_4^+$ ,  $CH_5^+$  and  $CH_3$ . Only processes (2) and (6) lead to  $HOCO^+$  that, in addition to react with  $CH_4$ , giving back  $CO_2$ , can also recombine with electrons to yields  $CO$  plus  $OH$ .

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