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Study of CO_2 Absorption and Negative Ion Formation during Direct Ionization of CO_2 with a Cs⁺ Beam

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OVERVIEW

We studied the CO_2 absorption process; and the negative ions and neutral products of the direct ionization of CO_2. The ionization method was the conventional bombardment at a Ti surface with a Cs⁺ beam to generate C⁻. Two different type of beam targets were used to absorb the CO_2. In the absorption study, pulses of CO_2 were injected. The amount of C⁻ detected represented the amount of absorbed CO_2. The data of absorbed CO_2 *vs* CO_2 pressure was interpreted with the Jovanovic-Freundlich isotherm model. In the other hand, most of the detected negative ions were O⁻, CO⁻ and C⁻. The O⁻/C⁻ proportion was 6/1. The detected neutrals were CO_2, CO, O, O_2, H_2O, OH. All the data indicates that the direct ionization of CO_2 is a multi step process.

INTRODUCTION

SIMS ionization has been used in AMS to directly create C⁻ from injections of CO_2 when the gas is brought in contact with a metal surface (ca titanium) and the Cs⁺ beam. The ionization process is still not well understood. From the SIMS theories, this negative ionization can be hypothesizes as: CO_2 (gas) → CO_2 (absorbed) + high energy → C⁻ + O⁻ + other negative ions + neutrals. Direct ionization of CO_2 is important because the graphitization process is tedious and time consuming. Also there is a need of directly analyze gaseous samples in order to couple the AMS with other gas producing analytical instruments like gas chromatograph.
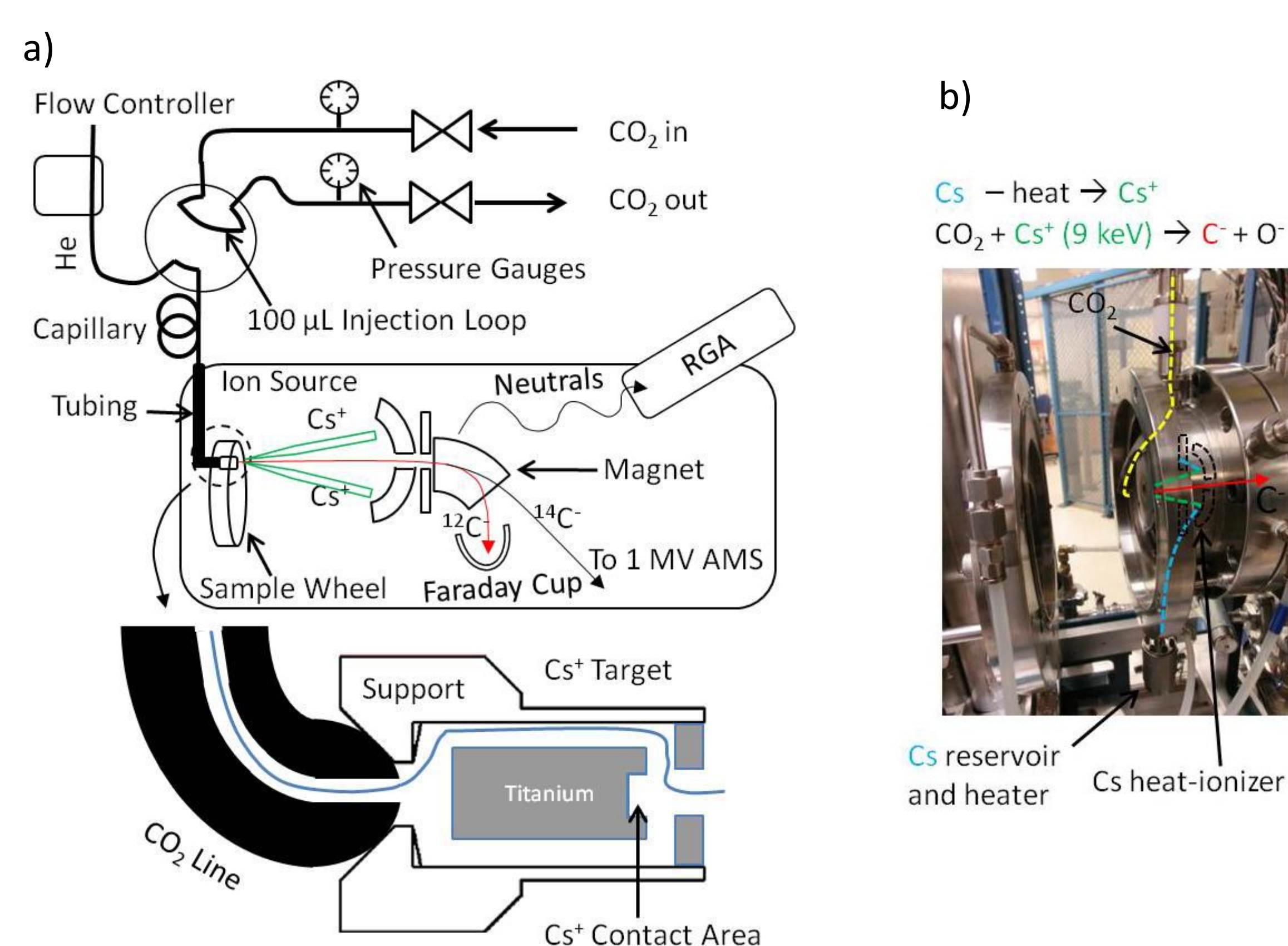
METHOD

Fig. 1. Scheme of the CO_2 injection system. a) A tank containing pressurized CO_2 (Instrument grade 99.99% purity) was connected to an electrically actuated GC injection valve with a 100 mL sample loop. The pressure inside the sample loop was measured with 2 pressure transducers connected at both ends. These pressures, during the filling step, were kept within a relative difference of 4%. The CO_2 flow was controlled with two micro control valves. The CO_2 pressure was converted into grams of carbon based on ideal gas calculations. The He carrier flow, coming from a pressurized tank (Ultra high purity), was controlled with flow meters. The injection system and the ion source were connected with a fused silica capillary (3 m long, 0.25 mm id, 0.35 mm od) which was connected to a high-vacuum gas feedthrough (stainless steel tubing 30 cm long, 0.5 mm id, 1.6 mm od). Illustration of the (b) Picture of the system.
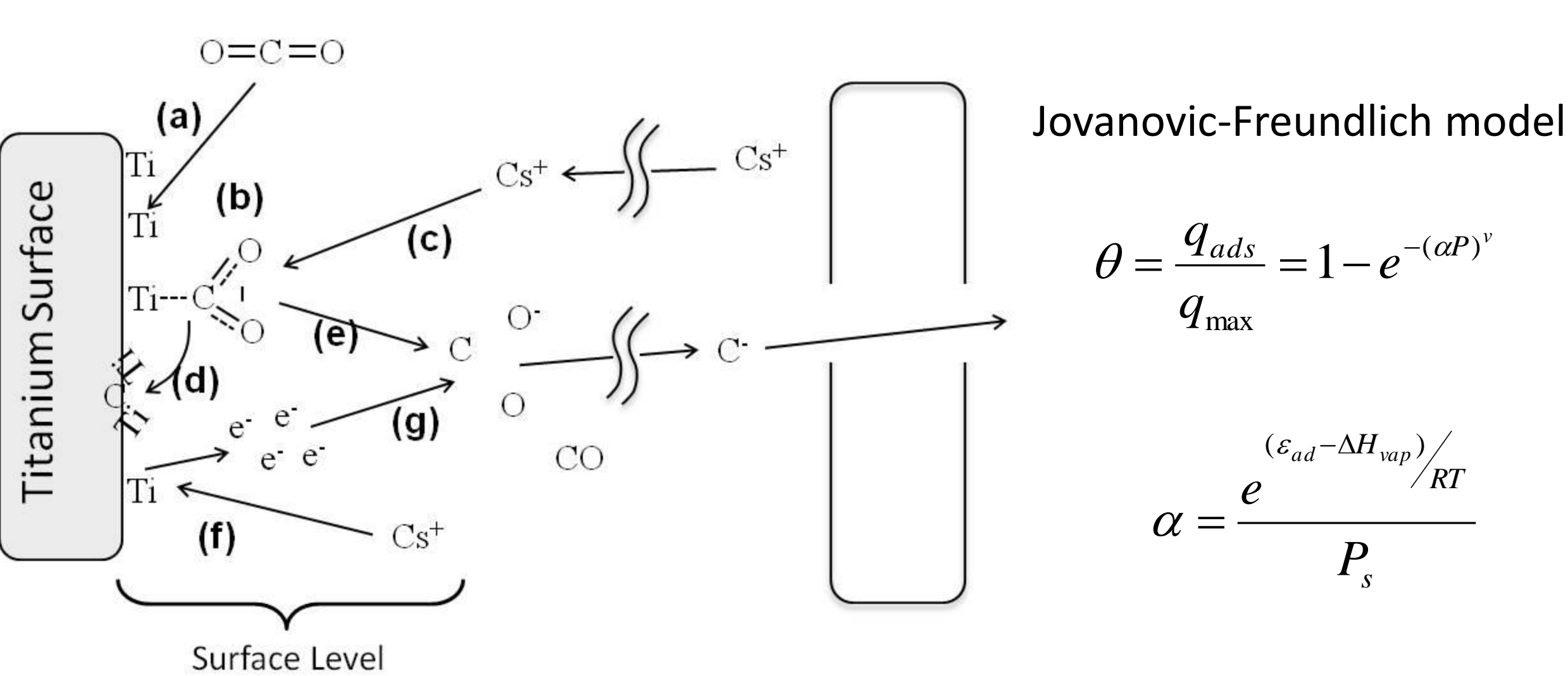

Jovanovic-Freundlich model

$$\theta = \frac{q_{ads}}{q_{max}} = 1 - e^{-(\alpha P)^v}$$

$$\alpha = \frac{e^{(\varepsilon_{ad} - \Delta H_{vap})/RT}}{P_s}$$

Fig. 2 Possible pathways leading to the production of C- during Cs⁺ beam bombardment over CO_2. (a) CO_2 adsorption (b) Hypothetical transition state (Collins, A. *Transactions of the Faraday Society.* 1957, (53)).(c) Cs⁺ bombardment (d) Carbon burying (e) Fragmentation-Charge retention (f) Sputtered electrons (g) Electron Capture.
Absorption model: α is a factor that depends on the CO_2 adsorption rate over the vapor pressure. ε_{ad} absorption energy, ΔH_{vap} vapor enthalpy, P_s Pressure vapor, q_{ads} and q_{max} are the specific amount of absorbed molecules and the saturation capacity, θ is the fractional coverage, P is the CO_2 partial pressure and v is the homogeneity parameter.
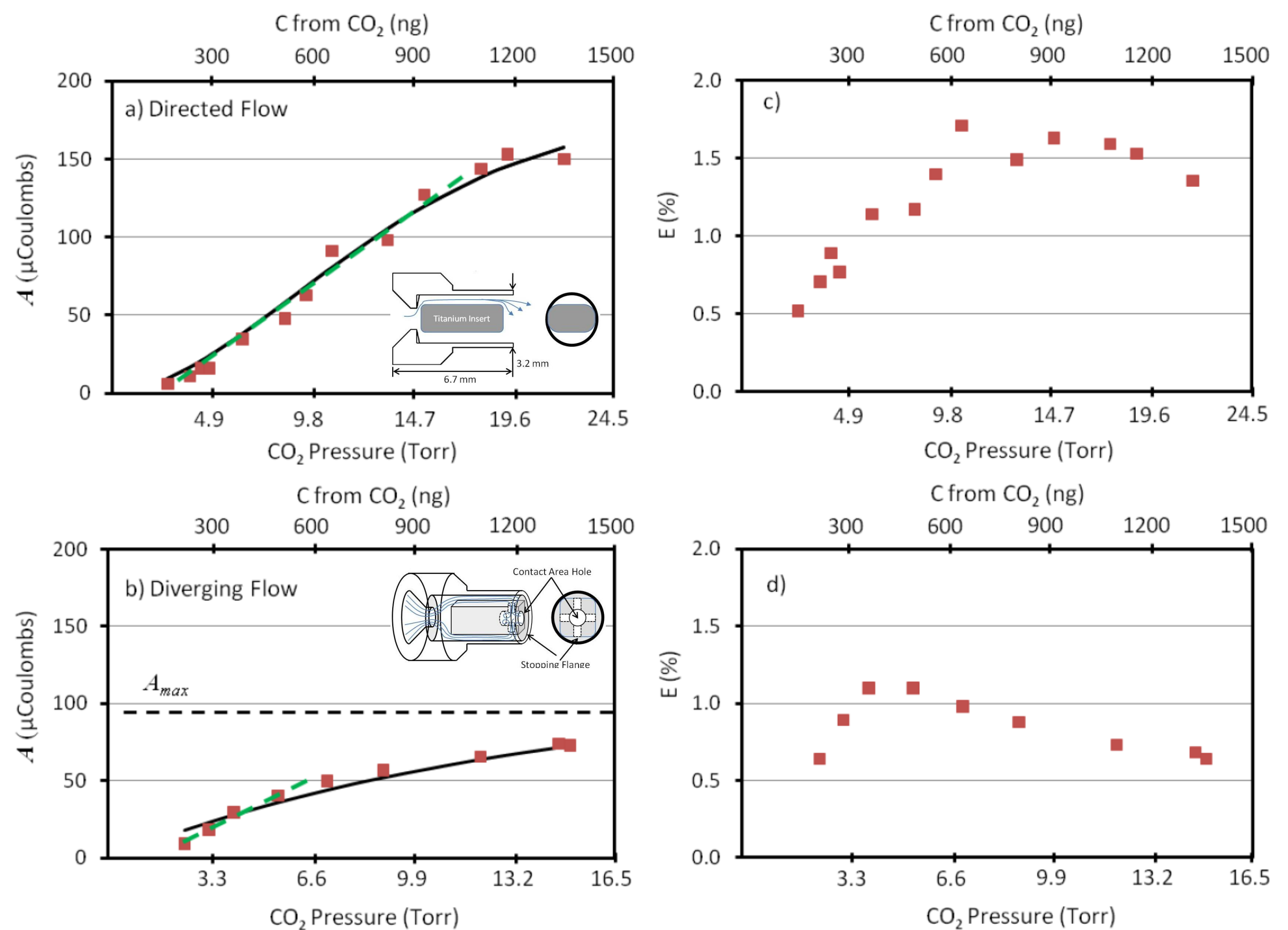

Fig. 3. Absorption model fitted to the data of C⁻ total integrated charge (**A**) and to the CO_2 average pressure (**P**). Linearity is represented with a green dashed line. **P** was obtained from simulations that corresponded to the amount of injected CO_2 in ng of carbon (**C**). (a) **A** *vs* **P** *vs* **C** (c) **E** *vs* **P** *vs* **C** for Directed-flow configuration with a large Ti surface area (1.8 mm²). (b) **A** *vs* **P** *vs* **C** (d) **E** *vs* **P** *vs* **C** for Diverging-flow configuration with Ti surface area of 1.9 mm². He flow 0.15 mL/min.

Table 1. Fitting Parameters for the Jovanovic-Freundlich and linear models

Target Configuration	Ti Area (mm²)	A_{max} [a](μC)	[b] r^2	v	α (x10⁻² Torr⁻¹)	ε_{ad} (eV)	τ (ns)	LDR range (ng)	LDR slope (μC/ng)
Directed Flow #1	1.8	180	0.93	1.75	6.9	0.26	39	150-1000	0.15
Diverging Flow	1.9	100	0.90	1.00	7.2	0.26	40	150-500	0.11
Directed Flow #2	0.49	80.0	0.91	1.75	7.0	0.26	39	150-800	0.088

[a] μCoulombs, [b] correlation coefficients for the adsorption model, LDR: linear dynamic range
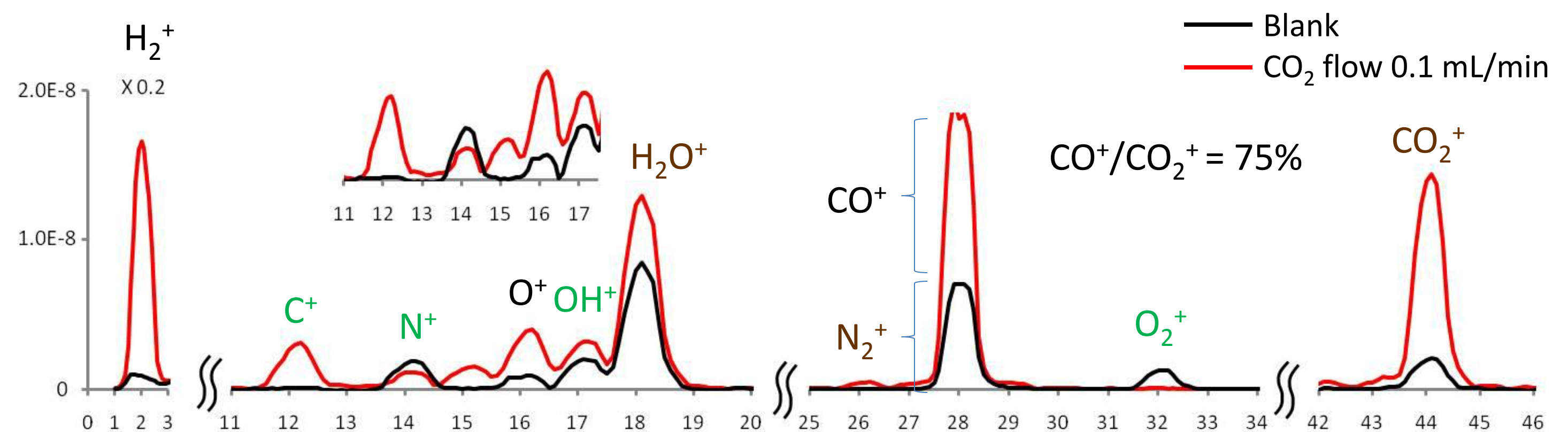

Fig. 4 Neutral particles detected by the Residual Gas Analyzer (RGA) in the positive mode. Green fragments ratios agree with EI ionization pattern of the RGA itself (webbook.nist.gov). The black fragments are produced by the Cs⁺ beam and the RGA. CO⁺/CO_2⁺ expected ratio for RGA fragmentation is 10%. The most abundant fragmentation neutral is CO. The spectra shows neutral water and H_2 from atmospheric water.
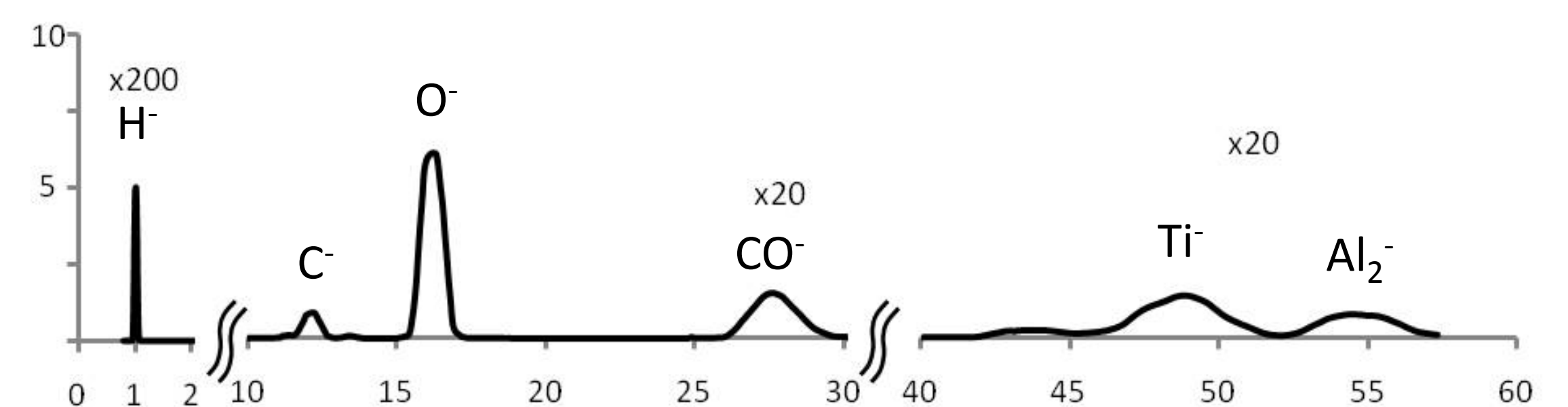

Fig. 5 Negative ions produced by the Cs⁺ beam bombardment over CO_2. Basically it is composed of O⁻ and C⁻. The area ratio O/C is 6.2. Ti and Al₂ anions come from the mounting metals. The peak assignment was based on the book Middleton, R. A *Negative-Ion Cookbook*. 1989.

CONCLUSIONS

The data suggests that the direct ionization of CO_2 requires an absorption step that depends on the absorption surface and the gas distribution (aerodynamics). Most of the created charge goes into O and C (electronegativity order). In addition, only a fraction of the CO_2 molecules fragment completely into C. A considerable amount becomes CO or stays as CO_2 neutral. These results explain the low ionization efficiency of the direct method relative to the ionization of graphite.