**White Paper for *Frontiers of Plasma Science Panel***

| Date of Submission: | ***19 June 2015*** |
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Indicate the primary area this white paper addresses by placing "P" in right column.
Indicate secondary area or areas by placing "S" in right column

| | "P", "S" |
|---|---|
| • Plasma Atomic physics and the interface with chemistry and biology | P |
| • Turbulence and transport | |
| • Interactions of plasmas and waves | |
| • Plasma self-organization | |
| • Statistical mechanics of plasmas | |

Indicate type of presentation desired at Town Hall Meeting.

| | "X" |
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| Oral | X |
| Poster | |
| Either Oral or Poster | |
| Will not attend | |

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|---|---|
| Title: | Tailoring plasma vibrational excitation to enhance the energy efficiency of chemical conversions |
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**(Limit text to 3-pages including this form. Font Times Roman size 11.
1 page of references and 1 page of figures may also be included. *Submit in PDF format*.)**

- ***Describe the research frontier* and importance of the scientific challenge.**

The present white paper defines a scientific challenge in the understanding and control of (preferential) vibrational mode excitation in plasma. The purpose is enhancing the energy efficiency of chemical conversions by plasma activation of the reaction, in essence by lowering the energy barrier of molecular dissociation via vibrational excitation. Our recent findings illustrate how electron energy distribution functions become non-favorable for preferential vibrational excitation due to dissociative recombination [1]. We propose low ionization potential additives to mitigate the effect as well as free electron laser experiments to investigate the details of vibrational excitation in molecular dissociation.

The strong non-equilibrium conditions provided by the plasma phase offer the opportunity to beat traditional thermal process energy efficiencies via preferential excitation of molecular vibrational modes. The principal ideas have been described by Fridman [2] on basis of experimental work, in particular on plasma dissociation of $CO_2$ in which dissociation efficiencies of up to 90% were observed. Figure 1 summarizes the main results in the $CO_2$ context (reproduced from [2]) together with recent work in our own lab, illustrating both the promising high energy efficiencies as well as a trade-off between conversion and efficiency.

The explanation for the high efficiencies is based upon stepwise excitation of the asymmetric stretch mode of the $CO_2$ molecule up to the point of dissociation, as illustrated in the potential energy

diagram in panel (a) of figure 2. In this scheme of ladder excitation, the lower vibrational levels are over-populated by electron excitation. Subsequent collisions between excited CO2 molecules drive an effective diffusion in vibrational energy space, up the ladder. This causes, after term crossing, ideally efficient dissociation. Contrary is the dissociative excitation illustrated in panel (b), which involves a significant energy barrier and thus an inherently significant amount of heat to be released. Of course, also a mix of these two cases may be of importance, as illustrated in panel (c): vibrationally activated dissociative excitation, which is shown here as highly efficient as well by virtue of a more favorable Franck Condon overlap of the first excited asymmetric stretch level.

A microwave plasma approach for $CO_2$ dissociation has been recognized as the most favorable in terms of energy efficiency [3]. It is generally assumed that this is due to a low reduced electric field and hence preferential vibrational excitation. However, evaluation of the electron energy distribution function whilst taking into account dissociative recombination indicates that vibrational excitation is no longer dominant at relevant power densities under reaction conditions typical for our experiments [1]. This is shown by the energy loss fractions calculated as a function of total power input that are plotted in figure 3. It demonstrates that electronic excitation takes over around $10^2$ W so that the effect of vibrational excitation in activating molecular dissociation becomes less important.

- ***Describe the approach to advancing the frontier and indicate if new research tools or capabilities are required.***

Our proposal to achieve an advancement of the frontier contains two elements:

(i) Improving the understanding of the role and dynamics of plasma excitation of vibrational modes in molecular dissociation. In particular, we envisage to significantly perturb intrinsic vibrational mode distributions with resonant light from a Free Electron Laser (FEL) and to subsequently monitor the induced dynamics in dissociation. We expect that this will yield information on the importance of vibrational enhanced dissociative excitation versus vibrational ladder climbing, the role of the vibrational modes other than the asymmetric stretch, as well as rate constants involved in these processes.

(ii) Mitigating the effect of dissociative recombination on the electron energy distribution function with low ionization energy additives. In particular alkali metals are envisaged. The much lower ionization potential of e.g. Na lowers the average electron energy to values perfectly matching vibrational excitation as well as effectively eliminates dissociative recombination and thus the above encountered strong input power dependence of the electron energy distribution function. This is demonstrated with the calculated energy loss fractions with 0.01% Na added to the discharge shown in the final figure on the right.

- ***Describe the impact of this research on plasma science and related disciplines and any potential for societal benefit.***

Various examples exist in the literature of the application of plasma for the conversion of gas inputs. Much of the work represents an establishment of concept, however, none have yet demonstrate economic feasibility. The here proposed work aims at opening a new window on understanding and controlling the reaction dynamics in the plasma via the electron energy distribution function. In case of success, it would enable exploiting plasma vibrational excitation to lower energy barriers in chemical conversions and thus significantly improving energy efficiency. Focussing on $CO_2$ as feedstock molecule, it would open a new window on $CO_2$ reuse in the form of liquid fuel synthesis (with renewable energy). Hence, it will contribute to the societal challenges of an integrated, flexible and secure energy supply, and to the development of the low carbon economy that is necessary to counteract climate change. In a broader context, we also expect benefits for nitrogen fixation reactions and thus ultimately for production of ammonia.

## References (Maximum 1 page)

[1] G.J. van Rooij et al., Faraday Discussions, 2015, DOI: 10.1039/C5FD00045A.
[2] A.A. Fridman, Plasma Chemistry, Cambridge University Press, New York, 2008.
[3] V. D. Rusanov et al., Sov. Phys.-Usp., 1981, 24, 447.

## Figures (maximum 1 page)

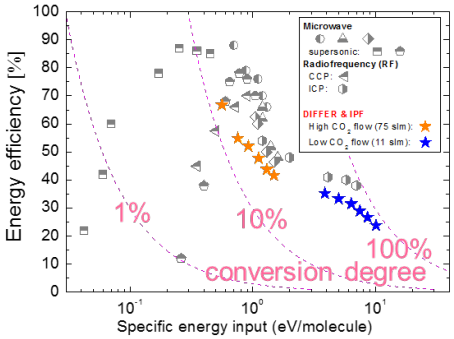


Fig. 1: Measured energy efficiencies for the plasma assisted reduction of $CO_2$ as a function of the specific energy($E_v$) input after [2]. The orange data points were measured in a collaboration between our institute and the Stuttgart University (Bongers et al.). The lines of constant conversion illustrate that a trade-off exists between efficiency and conversion.

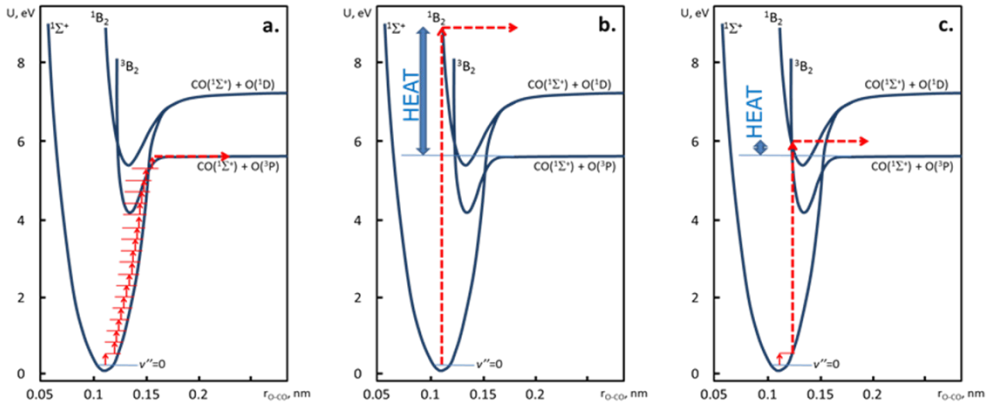


Fig. 2: Potential energy diagrams (as a function of one O-CO bond length) that illustrate the molecular physics behind three variants of $CO_2$ dissociation.

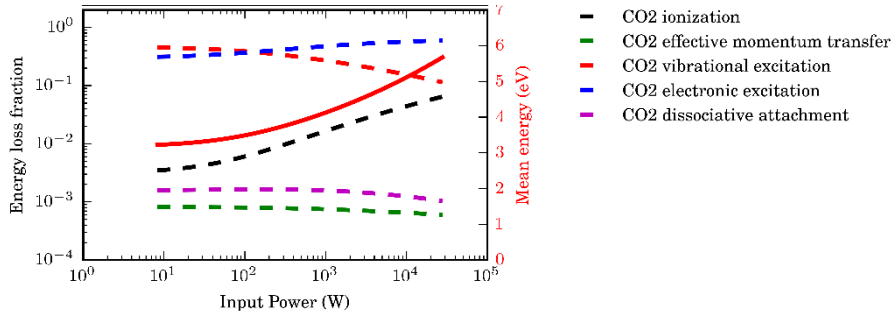


Fig. 3: Energy loss fractions for the various processes at play in a $CO_2$ microwave discharge.

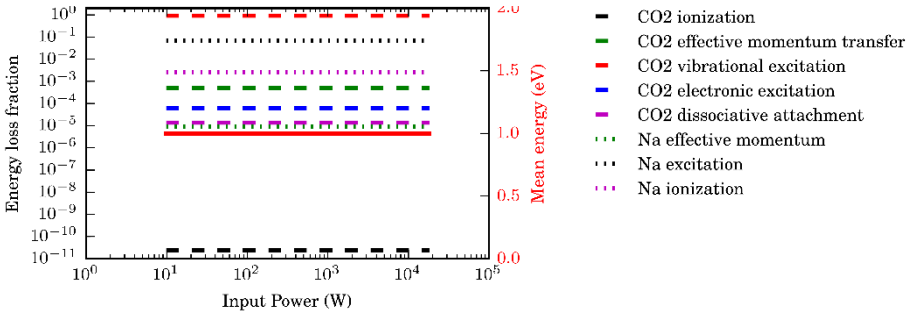


Fig. 4: Energy loss fractions for the various processes at play in a $CO_2$ microwave discharge with 0.01% Na added.