**Reviewer recommendation:**

**Comments to the author:**

The authors report on Thomson and Raman scattering experiments on a microwave discharge at a constant pressure and pulsed power input for three different gases, namely N2, CO2 and CH4. The experimental results are new and very interesting for the modelling community. The authors additionally interpret their experiments via some modelling that allows defining some major trends between the different molecules with respect to the thermalization of vibrational levels with Tgas and gas heating processes. The experimental results are new and will be of interest for the modelling community. The supporting modelling results are quite simple and maybe questionable (see comment below) but not the main focus of the paper. There is however a large mismatch between the title of the paper as well as the announced conclusions in the abstract and the contents of the paper itself. This will require a quite large revision of the paper. Some points in the paper also require further clarifications. See comment below.

- The paper title announces that the focus of the paper will be on the opportunities offered by vibrational excitation for greenhouse gases and nitrogen utilization. In the introduction the usual argument that vibrational excitation may enhance energy efficiencies is put forward. In the paper such promises are however no further discussed. The measurements and calculations show that initially a large fraction of energy from microwaves goes into vibrational excitation. However how much of this fraction of energy is actually spent into dissociation of the molecules and not ultimately spent into gas heating? This is not quantified and no conclusions on those promises can be drawn.

- In the abstract the authors state that products of CO2 dissociation do not contribution significantly to gas heating. However on p.19 the authors state the opposite and that the VT relaxation by CO2 is a factor 2 too small compared to the observed gas heating rate. Based on the Raman scattering of O atoms that is not detected, they state that electron impact dissociation probably explain the extra fast heating. However, this means that the products of CO2 dissociation indeed contribute to heating and that VT relaxation may not be that be so significant. The discussion here is only based on an absence of Raman signal. What is the CO yield in the present conditions and energy efficiency for CO production?

- Still in the abstract the authors comment that the “window to profit from vibrational excitation is limiting for practical applications”, while the conclusions state only that non equilibrium aspects should be optimized. Is vibrational driven chemistry still promising or not? The reader expects, especially with the current title of the paper, to get an answer to this question, or at least some actual perspectives/roadmap for unlocking vibrational driven conversion of molecules. The paper does not bring any answer to this question (which I reckon is very difficult to answer although a negative answer to that question is most probable) but the title should then be changed as no actual answer is provided excepted that “it is difficult”. Also the authors do not comment on the supposed general importance of vibrational excitation that has been advanced by several group for explaining the relatively better performance of microwave plasmas compared to other plasma sources. They have themselves provided amble evidence that it is not the case and it would be good that they comment more on it (as it is the reported main topic of the present paper).

- Figure 6 predict excellent selectivity for excitation of CO2 vibrationally while the authors conclude that probably 50% of total gas heating (cf. page 19) comes from electronic impact dissociation. This is not consistent with a preferential vibrational excitation as shown in figure 6. Such discrepancy indicates that the hypotheses using Bolsig+ for calculating energy share in vibrational excitation are probably not valid. Please comment on it as well.

Additional comments:

Reference 41 does not seem to be the correct. The authors do not cite on the other hand the following paper from the same group where Thomson scattering on Ar/CO2 and importance of collisions of electron with CO2 vibrational modes was discussed: Hübner, et al. Plasma Process. Polym., 11: 482-488. doi:10.1002/ppap.201300190

Figure 3: some structure at 534 nm is clearly seen but its origin is not discussed. Can the authors comment on it?

Page 11: the authors comment on being unsuccessful for measuring electron parameters in N2 but they show TS results in N2 in figure 5. Please amend the text accordingly to state the limited range where measurements could actually be done.

Still page 11: the authors do not mention that they used mean electron energies measured by TS as basis for estimating the initial amount of electron energy spent for vibrational excitation. Please comment if this is the methodology actually followed and amend the text accordingly.

Page 13 second line: “that a most” --> “that most”

Page 15 paragraph 1: the authors say that N2 specific heat due to vibrational modes is small compared to CO2 and CH4 because of the larger number of modes for the latter. The subsequent conclusion that N2 has more energy stored into vibration comes therefore as a surprise. Can the authors give the actual numbers of vibrational energy storage for the different molecules as a function of Tvib?

Page 15 paragraph 4: the authors present as a hypothesis that N efficiently quench vibrational states of N2. This is however a well know mechanism for thermalization and gas heating in N2 discharges. The authors may want to rephrase a bit this paragraph to tune their discussion with already existing knowledge on the topic.

Page 17: I believe that the authors want to refer to figure 8 and not figure 9.

Page 17 paragraph 4: “if the gas were” --> “if the gas was”

On page 20, the authors say that CO was not detected by Raman scattering, however CO is in principle not a Raman active molecule and so it is a bit strange to use its lack of detection as a proof that CO2 dissociation is small. What is the actual ratio of Raman scattering cross section between CO2 and CO?