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To “The role of greenhouse gases in radiative equilibrium – Thermodynamic evaluation” and “Zur Physikalischen Chemie des Treibhaus-Effekts” by H. Ullmann and M. Bülow (Rebuttal)

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Abstract: We reject the opinion of the commented paper that the climate change does not depend mainly on antropogenic CO₂ and other GHG.

Keywords: climate change; carbon dioxide; greenhouse gases; IR absorption; heat/radiation transmitter

Abstract: Wir weisen die Meinung in den kommentierten Arbeiten zurück, dass der Klimawechsel nicht hauptsächlich von antropogenem CO₂ und anderen Spurengasen abhängt.

Schlagwörter: Klimawechsel; Carbon Dioxid; Treibhausgase; IR absorption; Wärme/Strahlung Überträger

1 The greenhouse gases and the global warming of the Earth

130 years ago, Svente Arrhenius predicted that carbonic acid in the air would affect ground temperature [1]. Meanwhile, we have the IPCC reports [2]: in 2019, atmospheric CO₂ concentrations reached 410 parts per million (ppm), whilst CH₄ reached 1 866 parts per billion (ppb) and nitrous oxide (N₂O) reached 332 ppb. The CO₂ concentration was 278 ppm in 1765 [3], but it has now a record concentration of about 427 ppm in 2025. It is actually around 50% above pre-industrial level [2, 4]. The concentration of methane far exceeds 150%, and the increase in N₂O is 25% [2].

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The global surface temperature was around 1.1°C above 1850–1900 in 2011–2020 [2]. Numerous studies, using different statistical methods, propose an association between greenhouse gases (GHG) and temperature [5, 6, 7, 8, 9, 10, 11], to name a few. Over the course of millennia during the glacial cycles, temperature appears to have influenced CO_2 concentrations through biogeochemical feedbacks of the ocean and the land [12]. The discussion on the cause-and-effect relationship continues [8]. However, over the last 150 years, this relationship emerges to have been reversed. Bloating GHG emissions drive up the temperature.

The here commented papers [13, 14] utilise the heat-storage capacity of the GHG for a negative conclusion. The main flaw in refs.[13, 14] is that the differences in heat-storage capacity of the various atmospheric GHG cannot be used to rule out the possibility that they are causing of the warming anomaly of the Earth's atmosphere. GHG are in fact present only in trace amounts and cannot store any significant amounts of heat. This is correct. They account for a fraction of $\approx 0.1\%$ of the atmosphere. Such a tiny proportion of the air does indeed have a tiny heat-storage capacity.

However, these gases absorb additional infrared (IR) radiation at their respective normal mode frequencies, which would otherwise be emitted into space [15, 16]. The normal modes of gaseous molecules depend on the chemical bonds and the masses of the atoms, and therefore vary from molecule to molecule [17]. Consequently, different GHG filter out different frequency lines. The main components of the atmosphere, N_2 with 78.1%, O_2 with 20.1% and argon with 0.9% do not absorb IR frequencies, whereas GHG do. Ref.[13] is correct with: “The heat retention in the greenhouse Earth is caused by all gas components according to their molar heat capacities and concentrations in the atmosphere, i.e., mainly by nitrogen and oxygen.” What HU and MB fail to answer is the question: Where has the additional heat of the last 150 years come from? The incompetent approach of refs.[13, 14] is not improved by repetition, compare ref.[18] and other papers by these authors.

With IR, the situation is similar to that of visible sunlight: some of the light is scattered in the air, which is why we see a bright sky. However, the majority of the sunlight strikes the Earth's surface directly, which is why we see a clear, sharply defined disc of the Sun.

IR light is also scattered and absorbed along its way. Following the additional IR absorption by the GHG, the energetically excited molecules in question relax and, through intermolecular collisions, return to the Maxwell-Boltzmann distribution. The energy of vibrational-rotational states is quantized. As rotational lines are dense, rotational relaxation proceeds rapid. This phenomenon takes place within 10^{-14} to 10^{-11} seconds, whilst the release of excited vibra-

tional energy through collisions with other gases proceeds somewhat more slowly [19, 20]. This already takes place in long-range interactions involving a transition dipole, in contrast to short-range interactions, which are defined by the repulsive walls of the molecules. It implies a larger collision cross section [21]. In particular, the bending mode of CO_2 has a high vibrational specific heat [20]. Its relaxation increases the heat of the atmosphere. Some of the excitation energy is re-emitted. However, this radiation is not only directed into space, but also into the atmosphere or even back towards the Earth. As a result, it also intensifies the greenhouse effect.

The cited works on a statistical correlation between the rise in GHG and temperature [5, 6, 7, 8, 9, 10, 11] do not constitute direct evidence. They do not explain the physical process. It is, however, a fact that additional IR radiation is absorbed by the newly introduced anthropogenic GHG. The absorbed energy accumulates in the atmosphere. On the other hand, a less efficient pathway is radiative decay of the excited molecules. IR emission typically occurs at higher temperatures, see for example refs.[22, 23]. Emission proceeds much more slowly than collisional relaxation. There is no equality between absorption and emission; otherwise, absorption spectroscopy of gases would not be possible [24].

It should be noted that GHG absorb not only the far more significant re-emitted IR from the warmed Earth's surface, but also the incoming solar IR radiation, converting some of it into heat. GHG therefore have a dual effect, which is described somewhat misleadingly in the refuted papers [13, 14].

2 Influence of H_2O

Beside the GHG, gaseous water – which accounts for $\sim 70\%$ of the IR absorption in the bands $>15\mu\text{m}$ and around $6.3\mu\text{m}$ – and the reflection of radiation by clouds and aerosols play a significant role, with aerosols causing a cooling effect [2]. It is known that clouds of water droplets are not yet basically understood, neither their formation nor their precise role in the climate [25, 26, 27, 28]. However, there is a flow equilibrium; excess water in the atmosphere rains back to Earth.

Important are the other gases: CO_2 represents the next large proportion of the absorbers, and it absorbs in other regions: at $15\mu\text{m}$ (in the bending mode) and at $4.3\mu\text{m}$ (in the asymmetric stretching), and in further low intensive bands at $10\mu\text{m}$ [16]. A molecule of anthropogenic CO_2 emitted today remains in the air for 4 to 5 years [29], and the CO_2 concentration accumulates slowly. [2]. Other dangerous GHG are methane, CH_4 , nitrous oxide, N_2O , and fluorinated

synthetic gases, which can remain in the atmosphere for millennia. In contrast, the chemical destruction of CH_4 in the air results in additional CO_2 .

Besides the main bands of absorption one finds an ozone, O_3 , band at $9.6 \mu\text{m}$ [16] which affects the stratosphere. The upper layers of the atmosphere are very cold and contain no water. Note that the bands of the various molecules differ in most cases. More relevant and precise data can be found in the IPCC report [2] and in earlier reports – which, although cited by the authors HU and MB, are misinterpreted by them.

3 Radiation Equilibrium

The paper [14] discusses the energy balances of the global Earth system. It points out the small ratio between human energy production and the energy radiated by the Sun. Again, whilst this is correct, it is not the core problem. To be more precise, it hides the problem: human energy production produces additional GHG. These gases interfere with the ‘natural’ radiation exchange processes. They cause an intensification of the natural greenhouse effect (see above). At the current CO_2 concentration in the atmosphere, a main band of CO_2 at $15 \mu\text{m}$ exhibits a saturation effect, which is discussed in refs. [13, 14]. However, at both the current concentration and at higher concentrations, there are other bands (see above) that continue to absorb [16]. And a GHG molecule that has relaxed its absorbed energy by collision with another air molecule can again be re-excited by a further IR radiation. It means that higher man-made CO_2 concentrations still lead to a higher warming [30]. The fact is missing in refs. [13, 14].

Numerous non-linear cycles and chaotic processes take place in the atmosphere. The Earth is a complex, non-linear system [8] with a certain flow equilibrium over a given period of time [26]. However, the human-induced greenhouse gases disrupt this equilibrium and shift it to a different level [31]. This is not understood in refs. [13, 14], where the authors explain that, on the contrary, a number of questions remain unresolved and are probably not accessible experimentally.

4 CO_2 Capture

Paper [14] also examines the methods of Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU). Following on from [32], it is cor-

rectly pointed out that these methods require significantly more energy than is generated by the combustion of fossil coal and gas [33], especially because CCS or CCU entail an enormous entropy increase. We additionally remark that the ‘orchestrated lies’ of politics, media, and industry – compare ref. [34] – regarding these methods, obscure the second major problem: nature’s response to the climate change, the extinction of many species and the loss of biodiversity. A far more important part of the work of mankind should therefor be directed towards improving renatured ecosystems [35] and ecological farming [36]. Of course, there are natural sinks for CO₂ emissions on land and in the ocean, but they have absorbed a near-constant proportion [2, 37], and there is carbon response of vegetation and soil to the global warming [5]. Atmospheric CO₂ reacts with other molecules. A fraction can combine with rainwater to form carbonic acid [38], which can be dissolved in the oceans and stored there [12], or which can form rocks such as limestone, over the course of millennia [31]. However, these processes occur too slowly for this Earth [39, 40].

5 Summary

The average temperature of the Earth’s atmosphere has risen over the past 150 years and continues to rise. According to the prevailing view, this warming is due to the greenhouse effect, which is caused by ‘greenhouse gases’, primarily CO₂ and other polyatomic molecules. These convert infrared radiation into heat.

Helmut Ullmann and Martin Bülow deny the mainstream opinion. They insinuate another reason, one that has nothing to do with the GHG. We rebut the works [13, 14, 18]. They contain false statements about the influence of GHG on the anthropogenic climate change, in contrast to the known climate science [33, 34, 41, 42, 43] – to name a few references. HU and MB do not accept the established knowledge of about 200 years of climate science [15]. Contrary, we find in refs. [13, 14, 18] many questionable statements without citations.

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