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A computational evaluation of altitude profiles of the equilibrium monomeric–dimeric CO_2 fractions in the atmosphere of Venus

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Abstract

The equilibrium constant of the gas-phase carbon-dioxide dimerization is evaluated either from the Lennard-Jones potential or from two recent quantum-chemical calculations. The dimerization equilibrium constant is combined with observed height profiles of temperature and pressure in the atmosphere of Venus in order to derive the equilibrium dimeric mole fraction. In all the three treatments it is found that the mole fraction decreases with increasing height. The decrease is interpreted in terms of competition between temperature and pressure effects. The dimeric mole fraction should be at least 4% at the surface of Venus and, thus, is important in the planning of future observations.

INTRODUCTION

Evaluations of the populations of molecular complexes in the atmospheres of the Earth, planets or comets represent a subject of considerable interest in atmospheric and space research, especially in spectroscopic connections [1–11]. Carbon dioxide has been recognized as an important atmospheric component in view of the greenhouse effects. It is thus not surprising that its dimer, $(CO_2)_2$, has recently received ever-increasing attention [12–30], both experimental and theoretical. Among cosmic body atmospheres, that of Venus is particularly relevant regarding the carbon dioxide dimer because its atmosphere is mostly composed of CO_2 (96.5%) and is very dense [31].

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Recent quantum-chemical studies of $(CO_2)_2$ supplied new data on the dimer [21,30] which allowed a re-evaluation of the previous results based on the simple Lennard-Jones potential [32]. Stability reasoning can be combined with observed temperature and pressure atmospheric profiles [31], leading to an important characterization of the atmosphere–height dependency of the dimer concentration. The present report is devoted to this problem which is essentially one of chemical thermodynamics.

COMPUTATIONS

The dimerization equilibrium constant K_p (p_i denotes partial pressures of the monomer and dimer)

$$K_p = \frac{p_{(CO_2)_2}}{p^2_{CO_2}} \tag{1}$$

for the process

$$2CO_2(g) = (CO_2)_2(g) \tag{2}$$

is the most important input parameter in this study. It was evaluated in terms of partition functions in the usual rigid-rotor and harmonic-oscillator (RRHO) approximation [33].

According to the quantum-chemical calculations by Brigot et al. [21], there should actually be two different structures of the dimer, the parallel and the T-form, possessing C_{2h} and C_{2v} point groups of symmetry, respectively. In the more recent treatment by Eggenberger et al. [30], the T-shaped conformation was identified as a transition state for interconversion between two parallel structures, i.e. the T species does not contribute to the dimer concentration. The former result [21], however, requires a simultaneous consideration of both isomers. One can first evaluate the partial equilibrium constants [33] $K_p(C_{2h})$ and $K_p(C_{2v})$, and then construct the K_p term as a sum of the partial ones

$$K_p = K_p(C_{2h}) + K_p(C_{2v}) \tag{3}$$

The partial terms are evaluated in exactly the same way as if no isomerism is present.

For our purposes, components other than CO_2 and $(CO_2)_2$ in the atmosphere of Venus will be disregarded. In other words, it is assumed that the equilibrium constant K_p has the same value in the presence or absence of the minor components (primarily N_2 [31]). The composition of the equilibrium monomer–dimer mixture is described by the mole fractions x_1 and x_2 (here we shall use the convention $x_1 + x_2 = 100\%$). Under the above assumption, the ratio of both terms should not be influenced by the presence of minor components. The total atmospheric pressure P is composed of contributions from all the components. For our purposes the pressure was scaled down by the known [31] mixing ratio of carbon dioxide in the atmosphere of Venus (96.5%). Henceforth, the referred total pressure P denotes the scaled pressure and it is thus the sum of the partial pressures of the monomer and dimer only. The dimer mole fraction is given by

$$x_2 = \frac{2PK_p + 1 - (4PK_p + 1)^{1/2}}{2PK_p} \tag{4}$$

For a height Z above the surface of Venus, the related temperature and scaled pressure is interpolated from the observed values [31] (in the range from 0 to 65 km).

There is an older, independent treatment of the dimeric populations suggested by Stogryn and Hirschfelder [32], based on the second virial coefficients (derived from the Lennard-Jones potential in particular). They broke down the virial coefficients into three parts related to bound (b), metastable (m) and free molecules. The first two terms can be used for evaluation of the dimer concentrations. The mole fraction of dimers is given by

$$x_2 = -b_0(B_\mathrm{b}^* + B_\mathrm{m}^*)n/V \tag{5}$$

where B_b^* and B_m^* are the reduced second virial coefficients, b_0 is a constant related to the Lennard-Jones potential, and n/V denotes the molar concentration per unit volume. (For a detailed discussion of several computational aspects of this approach, see our earlier paper [11].)

RESULTS AND DISCUSSION

Table 1 presents results for two representative altitudes, $Z = 0$ and 50 km, for each of the three treatments considered. In going from the surface

TABLE 1

The mole fraction x_2 (%) of $(CO_2)_2$ in its equilibrium mixture with CO_2 in conditions [a] in the atmosphere of Venus evaluated for two selected heights Z from the Lennard-Jones (LJ) potential [32] and from quantum-chemical (QC) data [b]

Z (km)	Treatment	T (K) [a]	p (atm) [a]	x_2 (%)
0	LJ	733	87.6	4.20
	QC(1) [b]			13.1
	QC(2) [b]			22.9
50	LJ	344	0.9	0.33
	QC(1) [b]			0.18
	QC(2) [b]			0.67

[a] Temperature T and pressure p were interpolated from the observed data [31].

[b] The indices 1 and 2 refer to calculations in refs. 30 and 21, respectively.

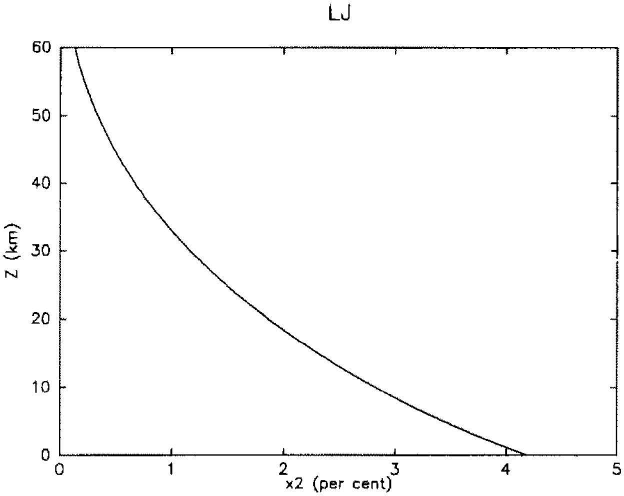

Fig. 1. The height profile of the equilibrium dimeric mole fraction x_2 in the atmosphere of Venus evaluated in the Lennard-Jones treatment (see Table 1).

to 50 km in height, the dimeric mole fraction x_2 decreases by one order of magnitude. Both quantum-chemical approaches yield higher values than the Lennard-Jones potential. The quantum-chemical data set exhibiting dimeric isomerism [21] yields higher x_2 terms compared to the newer calculations [30].

Figures 1–3 present the calculated height profiles of the x_2 term from the Lennard-Jones potential, and from quantum-chemical calculations [30] and [21], respectively. The figures exhibit a common qualitative feature—a

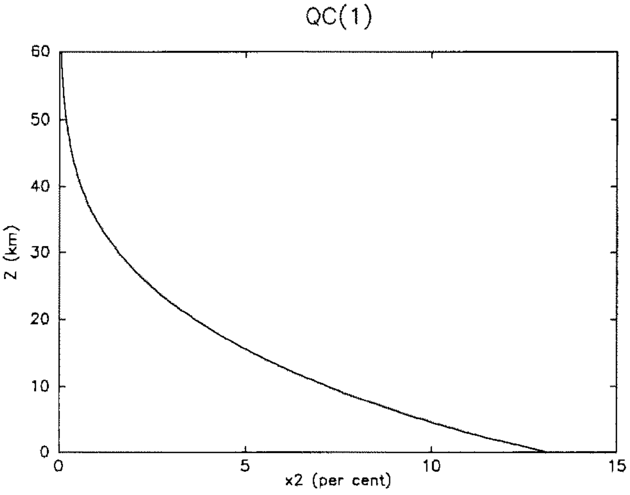

Fig. 2. The height profile of the equilibrium dimeric mole fraction x_2 in the atmosphere of Venus evaluated using quantum-chemical data [30] (see Table 1).

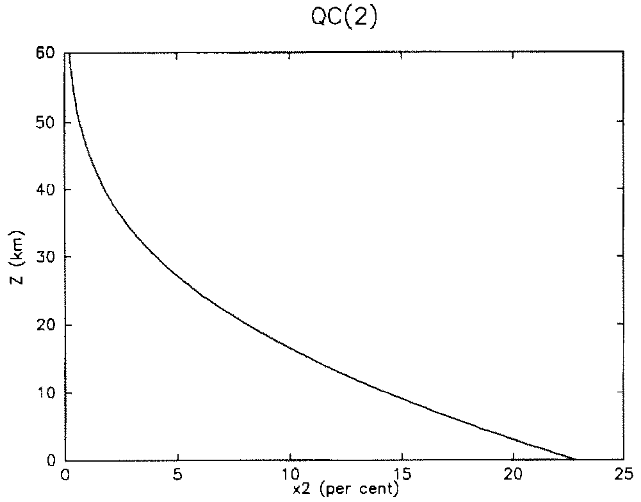

Fig. 3. The height profile of the equilibrium dimeric mole fraction x_2 in the atmosphere of Venus evaluated using quantum-chemical data [21] (see Table 1).

decrease of the equilibrium dimeric fraction x_2 with increasing height Z. This result represents the key conclusion of this study. It can be interpreted from the thermodynamic point of view as follows. Atmospheric temperature decreases with altitude which brings an increase in the related K_p value. However, the atmospheric pressure also decreases with height. Thus, there are two opposing effects: the increase in K_p values contributes to the dimeric stability, and the decrease in pressure induces dissociation. The proportions of both dependences ultimately determine the x_2 relation to Z. Nevertheless, one can speculate on a hypothetical atmosphere in which the convenient temperature and pressure profiles would lead to a qualitatively different picture, e.g. with an x_2 extremum.

Temperatures in the atmosphere of Venus are relatively high, so that the applicability of the RRHO treatment may be questioned. There is no information on anharmonicity corrections available from the quantum-chemical calculations: computational demands still prevent such calculations at present. However, the anharmonic character of the Lennard-Jones potential is somehow reflected in the latter treatment. It may seem probable that the RRHO approach can overestimate the K_p values, though the degree of overestimation is unclear. The overestimation should be related to the infinite nature of the summation in the harmonic vibrational partition function [34]. The differences between both quantum-chemical treatments reflect the still great uncertainties in the estimation of the CO_2–CO_2 interaction potential. In particular, the two-minimum nature of the potential remains a somewhat open question.

Our treatment, nevertheless, indicates that one should expect unusually high populations of carbon dioxide dimers in the atmosphere of Venus (apparently the highest in our Solar system). Such a significant degree of association should have substantial consequences for both spectroscopic and thermophysical properties.

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