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A computational evaluation of altitude profile of the equilibrium monomer–dimer H_2 mole fraction in the atmosphere of Jupiter [1]

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Abstract

Populations of the hydrogen molecule dimer in the atmosphere of Jupiter are evaluated from the dimerization equilibrium constant calculated either from the Lennard-Jones potential or from quantum-chemical treatments. The latter calculations are of an ab initio type with the second-order Møller–Plesset (MP2) treatments in the 6-311G and 6-311G** basis sets. The computed dimerization equilibrium constant is combined with observed height profiles of temperature and pressure in the Jupiter atmosphere in order to derive the dimeric mole fraction x_2 in the partial thermodynamic equilibrium with the monomer. In all the treatments considered, it is found that the mole fraction decreases with increasing height. Various approximations suggest that the dimeric mole fraction at the Jupiter 1 atm pressure level is between 0.04% and 0.94%.

INTRODUCTION

The presence of hydrogen dimers in the atmosphere of Jupiter has recently been the subject of considerable interest [1–4] in connection with the Voyager mission. However, hydrogen dimer states had already been observed in laboratory conditions [5] in 1964. Nevertheless, an evaluation of the dimer atmospheric populations has not yet been achieved. The evaluation basically represents a thermodynamic problem, assuming tem-

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perature and pressure profiles are available [6]; the problem has been studied for various species at different levels of sophistication [7–18]. The related dimerization equilibrium constants can, inter alia, be computed using data from quantum-chemical calculations. This paper is devoted to the computational thermodynamic problem for the hydrogen dimer in the atmosphere of Jupiter.

COMPUTATIONS

The dimerization equilibrium constant K_p in terms of the partial monomeric and dimeric pressures p_i

$$K_p = \frac{p_{(H_2)_2}}{p^2_{H_2}} \tag{1}$$

for the dimerization process

$$2H_2(g) = (H_2)_2(g) \tag{2}$$

is evaluated here from partition functions supplied with parameters from ab initio computations. The partition functions are of the usual rigid-rotor and harmonic-oscillator quality [19] (see below).

Hydrogen forms 88.8% of the atmosphere of Jupiter [20, 21]. Hence, for our purposes components other than H_2 and $(H_2)_2$ will be disregarded and only a partial thermodynamic equilibrium between the monomer and dimer will be treated. It is assumed that the equilibrium constant K_p has the same value in the presence or absence of the minor components (primarily He). The composition of the equilibrium monomer–dimer mixture is described by the mole fractions x_1 and $x_2 (x_1 + x_2 = 100\%)$. The total atmospheric pressure P was scaled down by the hydrogen fraction of 88.8% [20, 21]. For the dimer mole fraction

$$x_2 = \frac{2PK_p + 1 - (4PK_p + 1)^{1/2}}{2PK_p} \tag{3}$$

The pressure and temperature values for selected heights Z above the Jupiter 1 atm pressure level were taken from ref. 6 (range from 0 to 124 km).

For methodological purposes, an independent treatment of the dimeric populations suggested by Stogryn and Hirschfelder [22] based on the second viral coefficients (derived from the Lennard-Jones (LJ) potential) is also considered. They decomposed 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

$$x_2 = -b_0(B^*_b + B^*_m)n/V \tag{4}$$

where B^*_b and B^*_m are the reduced second virial coefficients, b_0 is a constant related to the LJ potential, and n/V denotes the molar concentration per unit volume.

The molecular orbital calculations were carried out using a GAUSSIAN program package [23]. The standard 6-311G and 6-311G** basis sets were employed in conjunction with the second-order Møller–Plesset (MP2) perturbation treatment. Geometry optimization and harmonic vibrational analysis were performed in both approximations, MP2/6-311G and MP2/6-311G**.

RESULTS AND DISCUSSION

As frequently happens with weak molecular complexes, the MP2/6-311G and MP2/6-311G** approximations lead to minimum-energy structures of different symmetry. In the lower MP2/6-311G approximation, the dimer is linear, while in the higher quality MP2/6-311G** approach, it possesses a non-linear T-shaped structure of C_{2v} point group of symmetry. In addition, the potential energy changes for the dimerization are somewhat different (Table 1). In fact, the energy minima are so shallow that they cannot accommodate even the computed harmonic vibrational ground state. This does not prevent vibrational motion but this motion must be treated in a proper anharmonic potential. In order to reflect the feature at the partition-function level, we neglected the harmonic vibrational contribution.

Table 2 presents the temperature dependence of the calculated equilibrium constants K_p. Within the considered temperature interval (50–300 K),

TABLE 1

Survey of the calculated potential energy change ΔE for the H_2 dimerization

Approach	$(H_2)_2$ symmetry	$\Delta E/(\mathrm{kJ\ mol^{-1}})$
MP2/6-311G	$D_{\infty h}$	−0.079
MP2/6-311G**	C_{2v}	−0.13

TABLE 2

Temperature dependence of the calculated dimerization equilibrium constant $K_p = p_{(H_2)_2}/p^2_{H_2}/(\mathrm{atm}^{-1})$

T/K	K_p	
	MP2/6-311G	MP2/6-311G**
50.0	0.16	0.21
100.0	0.025	0.042
150.0	0.0071	0.015
200.0	0.0028	0.0066
250.0	0.0014	0.0036
298.15	0.00076	0.0022
300.0	0.00074	0.0021

TABLE 3

The mole fraction x_2 (%) of $(H_2)_2$ in its equilibrium mixture with H_2 in the Jupiter atmosphere evaluated for several relative altitudes Z

Z/km	x_2		
	LJ	MP2/6-311G	MP2/6-311G**
0.0	0.04	0.44	0.94
16.4	0.03	0.38	0.76
31.5	0.02	0.27	0.50
44.3	0.01	0.16	0.29
56.7	0.005	0.06	0.11
72.1	0.001	0.02	0.03
88.3	0.0006	0.006	0.01
105.0	0.0003	0.003	0.005
124.0	0.00008	0.0008	0.002

there is a decrease of between two and three orders of magnitude. The MP2/6-311G** values are systematically somewhat higher.

The primary output of this study is reported in Table 3, which gives the calculated dimeric mole fractions x_2 for selected altitudes Z above the Jupiter 1 atm pressure level (Z varies between 0 and 124 km) for each of the three treatments considered. The dimeric populations found for lower atmospheric levels (between 0.04% and 0.94% for the lowest level considered) are certainly of an interest for spectroscopic observations.

Both quantum-chemical approaches yield higher values than the LJ potential, a feature also reported for the atmosphere of Venus [17]. However, the dependences exhibit a common qualitative feature — a decrease in the equilibrium dimeric fraction x_2 with increasing height Z. This result can be interpreted from the thermodynamic point-of-view as a temperature–pressure inter-compensation. The atmospheric temperature first decreases with altitude (which produces an increase in the related K_p value) and then increases. However, the atmospheric pressure systematically decreases with the height. The starting increase in the K_p values contributes to the dimeric stability; and the decrease in the pressure induces dissociation. The proportions of both dependences determine the Z dependency of the x_2 term in the lower atmospheric levels. At the higher altitudes, both the increasing temperature and the still decreasing pressure work together, so that the x_2 decrease is faster.

Although the temperatures considered are relatively low, there is still a problem with the quality of the partition functions applied. Their approximation is rough but only possible with respect to the amount of the computed information available. It is, however, clear that a more advanced approach should deal with a direct summation of levels from vibrational problems in a realistic, at least four-dimensional, anharmonic potential. While there is no information on anharmonicity corrections available from our quantum-chemical calculations, the LJ treatment involves a portion of these effects. It should, however, be noted that a recent study [24] of the argon dimer [25] populations under saturation conditions pointed out a qualitative agreement between diverse partition-function approximations including the harmonic treatment. Finally, the quantum-chemical part of the computations can also be carried out at a still higher level; this work is in progress.

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