A Configurational Contribution to the Heat Capacity of Gaseous $(HDO)_2$

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Z. Naturforsch. **46a**, 39–42 (1991); received July 18, 1990

Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday.

$(HDO)_2$ can form two isomeric species, HOD.OHD and DOH.OHD. The species are studied in terms of the Bopp-Jancsó-Heinzinger potential. The deuterium-bonded structure is stabilized in zero-point vibrational energy by about 0.77 kJ mol^{-1} over the hydrogen-bonded one. In gas-phase the exactly equal stability of both structures would however be reached at a temperature of 638 K. The thermodynamic functions of HOD.OHD and DOH.OHD are different and, moreover, they essentially differ from the (overall) functions belonging to the equilibrium mixture of both structures (which is understood as one pseudospecies). For the heat capacity at constant pressure it is shown that a maximum of the difference between the pseudospecies' overall value and the HOD.OHD value appears at a temperature of about 39 K, amounting to some 4.6 J K^{-1} mol^{-1}.

Introduction

The water dimer is a subject of continuous interest of both theory [1] and experiment [2]. Attention has also been paid to the water-dimer isotopomers; for example in order to enhance the amount of observed information [3–6] or to investigate differences [7] between H- and D-bonded water dimers. In the latter case a preference of D-bonded species was found as a special case of the D-bond preference [8–10] in the systems of HOD.B and DOH.B (the Buckingham-Liu rule [8]). Hence, the dimer[3] HOD.OHD is lower [7] in energy than its isomer DOH.OHD. This isomerism does not exist in the light and heavy water dimers $(H_2O)_2$ and $(D_2O)_2$ and there is thus an interesting question as to what kind of changes such a configurational multiplicity can bring to thermodynamics. In this report the question is investigated for gas-phase conditions with special regard to the heat capacity at constant pressure terms.

The Computations

In this study, $(HDO)_2$ was described with the powerful BJH potential [11, 12], namely its version employing the quartic spectroscopic force field [13] of a free (gas-phase) water molecule. Within the Born-Oppenheimer approximation the structural features as well as the change in potential energy ΔE due to dimerization are exactly the same for both isotopomers (and for any other isotopomer as well; for the uniform set of parameters, presented for the $(H_2O)_2$ species, see [14]). In fact, up to and including the force-constant matrix construction the computational treatment for the two isotopomers is identical with that already applied [14] to $(H_2O)_2$. The first principal difference comes at the level of the harmonic vibrational frequencies and, subsequently, in the ground-state energy changes (standard enthalpy changes at zero temperature) $\Delta H^0_{0,i}$ upon dimerizations:

$$2\ \mathrm{HDO(g)} = (\mathrm{HDO})_2(i;\ \mathrm{g}) \qquad (1)$$

where i stands for 1 (HOD.OHD) or 2 (DOH.OHD). Table 1 surveys the ΔE and $\Delta H^0_{0,i}$ BJH terms. Clearly, in view of the different vibrational frequencies, thermodynamic functions belonging to HOD.OHD(g) and DOH.OHD(g) (treated as individual species) must be different.

Let us consider the motions within the HOD.OHD and the DOH.OHD species to be independent in spite of the obviously low potential energy barrier(s) separating them (for an evaluation of three interconversion

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[3] Throughout the report, the well known C_s symmetry structure of the water dimer [3, 6] is used; thus, in the notation HOD.OHD, HOD is the donor and OHD the acceptor part of the dimer (hydrogen atoms of the latter part, if non-labelled, are symmetrically equivalent).

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Table 1. Survey of the $(HDO)_2$ formation energetics (in kJ mol^{-1}) evaluated in the BJH potential.

Process	Potential energy ΔE	Ground-state energy $\Delta H^0_{0,i}$
$2\,HDO(g) = HOD.OHD(g)$	−23.54	−17.47
$2\,HDO(g) = DOH.OHD(g)$	−23.54	−16.70

paths, see [15]. Then the species can be treated as two chemical individuals (cf. [16]), and the thermodynamic characteristics of each of them can be evaluated in terms of their individual partition functions. In reality, however, the species cannot be separated[4] just because of the fast interconversions, so that they in fact represent one pseudospecies. Let us introduce the mole fractions w_i of the isomers $(HDO)_2(i)$. For the conditions of thermodynamic equilibrium between the isomers their mole fractions can be evaluated using the energetics from Table 1 and the BJH structural and vibrational parameters for construction of the rigid-rotor and harmonic-oscillator (RRHO) partition functions, supposing that the dimers behave like an ideal gas.

For the molar enthalpy of the dimeric pseudospecies comprising the equilibrium mixture of the isomeric dimers the following relation holds:

$$H^0 = w_1 H_1^0 + w_2 H_2^0, \tag{2}$$

where the H_i^0 terms denote the molar enthalpies of the isomers. Let us carry out temperature differentiation of (2), keeping in mind that all terms on its right-hand side are temperature dependent. In this way the following expression for the molar heat capacity at constant pressure of the dimeric pseudospecies can be derived [18]:

$$C_p^0 = w_1 C_{p,1}^0 + w_2 C_{p,2}^0 + \frac{w_1 w_2 (\Delta H^0)^2}{RT^2}, \tag{3}$$

where $\Delta H^0 = H_2^0 - H_1^0$ denotes the isomerization enthalpy at temperature T. The C_p^0 term can be called overall (in contrast to partial terms $C_{p,i}^0$) or relaxation, in order to reflect the fact that all the terms involved in (2) relax after temperature change. In order to have a deeper insight in the behaviour of (3) it is convenient to introduce the term

$$\delta C_{p,1} = C_p^0 - C_{p,1}^0, \tag{4}$$

which can be called [18] (relaxation) isomerism or configurational contribution to the heat capacity related to the species 1 (it shows how much the heat capacity term is changed compared to an idealized situation when no isomer 2 is present). Finally, in order to evaluate the importance of the temperature changes of w_i, let us also consider the term

$$\delta C_{p,w,1} = w_2 (C_{p,2}^0 - C_{p,1}^0) \tag{5}$$

to which the relaxation isomerism contribution is reduced if the w_i terms are, in the above differentiation, treated as temperature independent. In order to reflect the constant nature of w_i in (5), its designation as isofractional configurational (or isomerism) contribution to the heat capacity can be suggested.

Results and Discussion

Figure 1 presents the temperature dependence of the w_i terms at low temperature. Clearly, only at extremely low temperatures does the HOD.OHD species prevail. At moderate and higher temperatures the populations of the isomeric dimers approach each other and their change with temperature becomes finally insignificant. In fact, at 638 K, $w_1 = w_2 = 50\%$ holds precisely (though, practically, an equal stability is reached sooner) while above this temperature the hydrogen bonded species becomes relatively more populated; however, the shift from the 50% level is again practically negligible.

Temperature dependences of the relaxational $\delta C_{p,1}$ and isofractional $\delta C_{p,w,1}$ configurational contribu-

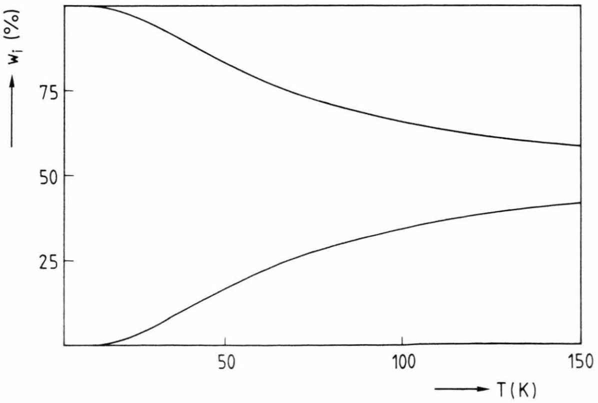

Fig. 1. Temperature dependence of the equilibrium mole fractions w_i of HOD.OHD (upper curve) and DOH.OHD at low temperatures, evaluated on the basis of the BJH potential.

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[4] At least not in gas phase; for matrix-isolation conditions, see [4], [17].

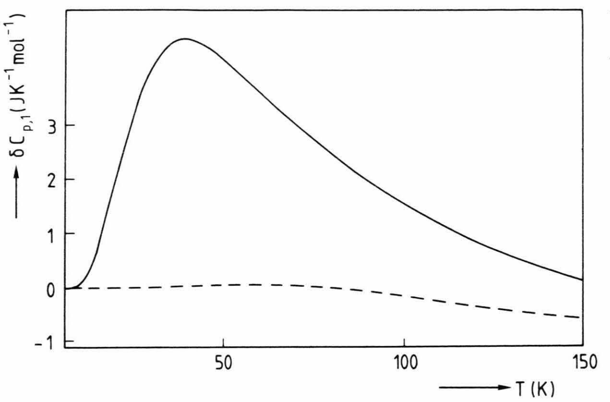

Fig. 2. Temperature dependence of the relaxation $\delta C_{p,1}$ (solid line) and isofractional $\delta C_{p,w,1}$ (dashed line) configurational contributions to the heat capacity of the pseudospecies $(HDO)_2$(g) (related to the HOD.OHD isotopomer as the reference structure), evaluated on the basis of the BJH potential.

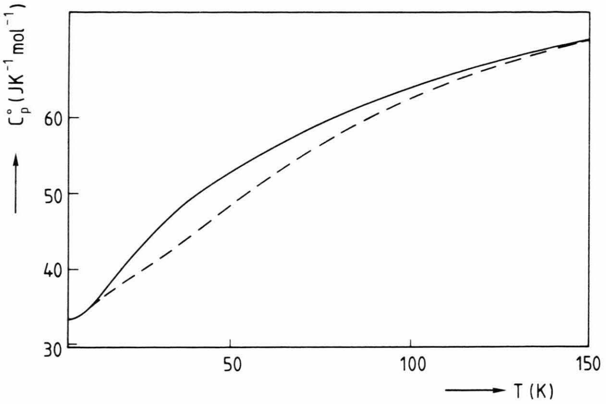

Fig. 3. Temperature dependence of the standard heat capacity $C^0_{p,1}$ of HOD.OHD(g) (dashed line) and of the overall term C^0_p belonging to the $(HDO)_2$(g) pseudospecies (solid line) evaluated on the basis of the BJH potential.

Table 2. Characterization of the $(HDO)_2$ equilibrium mixture at the temperature of the $\delta C_{p,1}$ maximum ($T = 38.9$ K), based on the BJH potential.

Quantity [a]	Value
Mole fraction w_1 (%)	89.6
Mole fraction w_2 (%)	10.4
Standard heat capacity at constant pressure $C^0_{p,1}$ (J K^{-1}mol^{-1})	44.5
Standard heat capacity at constant pressure $C^0_{p,2}$ (J K^{-1}mol^{-1})	45.1
Isofractional isomerism contribution $\delta C_{p,w,1}$ (J K^{-1}mol^{-1})	0.06
Relaxation isomerism contribution $\delta C_{p,1}$ (J K^{-1}mol^{-1})	4.64
Overall heat capacity of the mixture C^0_p (J K^{-1}mol^{-1})	49.2

[a] The indices 1 and 2 refer to HOD.OHD and DOH.OHD, respectively.

tions in the low temperature region are given in Figure 2. The isofractional term is not too much different from zero, its change of sign is of some interest. The behaviour of the terms at higher temperatures is not particularly interesting as both terms (owing to the vanishing temperature dependency of w_i mentioned in connection with Fig. 1) effectively approach one term, which is again close to zero (though not necessarily positive). However, the course of the relaxation term at low temperatures is really interesting. There is a clear, rather sharp maximum on the curve located at 38.9 K with a height of some 4.64 J K^{-1}mol^{-1}. Table 2 presents additional information on the temperature maximum. The values in the maximum region should not be particularly influenced by the RRHO quality of the partition functions involved just because of the low temperature. In fact, the configurational interplay is mostly based on the differences in vibrational frequencies (though there is also a difference in moments of inertia). There is no specific relationship between the frequencies of both isomeric isotopomers – on going from structure 1 (its frequencies read: 38, 112, 135, 185, 280, 392, 1453, 1468, 2709, 2806, 3865, and 3889 cm^{-1}) to 2 (33, 107, 135, 182, 283, 532, 1456, 1507, 2806, 2824, 3730, and 3865 cm^{-1}), some frequencies are increased some decreased. This feature is important for a larger variability of the interplay in the isomeric system. In particular, the above mentioned change in sign of the isofractional term $\delta C_{p,w,1}$ is related to these alternations in frequencies between the both isotopomers.

The enhancement of the heat capacity term of the $(HDO)_2$(g) system by the configurational interplay is surprisingly strong in the low temperature region (the isomerism contribution represents about 10% of the total heat capacity, cf. Table 2). However, the relaxation term (so far treated here) is actually a computational intermediate, not a directly observable quantity. Therefore, Fig. 3 presens the temperature dependence of the overall heat capacity term C^0_p together with the partial term $C^0_{p,1}$. It is evident from the plots that the temperature maximum in the relaxation configurational contribution is not conserved in the overall term but it is instead overlapped by a relatively fast temperature increase of the $C^0_{p,1}$ term.

The overall standard heat capacity of the water dimer C_p^0 itself would moreover not easily be obtained experimentally. Typically, an effective term composed of contributions from monomers, dimers and possibly other clusters can be measured (however, so far not for the very low temperature region suggested in this study as pertinent for a manifestation of the configurational contributions). The latter term is, of course, not only temperature but also pressure dependent. It would be useful to study the phenomenon in a simulation treatment, as for some temperature and pressure regions there might appear a maximum in heat capacity not present with H_2O or D_2O. An application of molecular dynamics in such rather unusual connections could also be of some interest from the point of view of the method itself.

Acknowledgement

The study was carried out within the scope of the Alexander von Humboldt fellowship scheme, the support being gratefully acknowledged.

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