High-Temperature Heat Capacity of the Na₂ Molecule

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Abstract

The heat capacity of the Na₂ molecule is investigated in the 2000 K–6000 K temperature range. At these temperatures, the classical treatment is appropriate. The contributions from the ground state and all the excited states dissociating to the 3s + 3s and 3s + 3p limits are taken into account. The results are compared with other known data and are discussed under the influence of unbound rovibrational and electronic excited states.

Keywords Excited states · Heat capacity · High temperatures · Unbound states

1 Introduction

Difficulties in the calculation of thermophysical properties at high temperatures are widely known. The NIST-JANAF Table [1] have many inaccuracies, for example, due to neglecting electronic excited states as in the case of the BBr molecule [2]. Spectacular problems with the partition functions of some molecules obtained by the summation of rovibrational levels were reported by Babou et al. [3]

Heat capacity is a thermodynamic quantity which is very sensitive to all kinds of approximations (because of the second derivative in its relation with the partition function), making it a challenge to obtain reliable results. The other quantities can often be reliably calculated even if serious approximations, such as neglecting the rovibrational coupling, are used. It is particularly easy to calculate entropy [2,4–6].

The unbound states (both metastable and scattering) also significantly influence thermodynamic quantities; the heat capacity is again the most sensitive. The recent tendency is to use all the unbound states in thermodynamic calculations [7–9]. Fortunately, in the case of the classical approach, it is the simplest option available but at high temperatures one also needs to know the purely repulsive PECs (potential energy curves) to describe all the interactions between the atoms.

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This article presents the heat capacity of the Na_2 molecule in the temperature range of 2000–6000 K. This molecule was chosen because the results for this weakly bound molecule are vulnerable to various factors and approximations and because the results known so far do not agree.

Formulas (and calculations) of the internal partition functions and the internal heat capacities are in atomic units and the resulting heat capacities are given in $\text{J} \cdot (\text{molK})^{-1}$. All the calculations were performed with a Wolfram Mathematica computing system.

The rest of the article is organized as follows: Sect. 2 presents the methods for the classical calculation of heat capacity and the PECs used in those calculations. Section 3 contains the results and the discussion, and finally Sect. 4 contains the concluding remarks.

2 Method

2.1 Calculation of Heat Capacity

Heat capacity is expressed as the second derivative of the molecular partition function:

$$C_p = \beta^2 \frac{d^2 \ln Q_{int}}{d\beta^2} + \frac{5}{2}R, \quad (1)$$

where Q_{int} is the internal partition function of the molecule, $(5/2)R$ is the contribution to the heat capacity resulting from the translational motion, and $\beta = 1/(k_B T)$ is the inverse temperature.

The internal partition function for a given PEC (V) is calculated with the bound states approach [10]

$$Q_{rovib}^B = \frac{1}{\pi} \left(\frac{2\mu}{\beta} \right)^{3/2} \int_{\sigma}^{\infty} \exp(-\beta V) \gamma(3/2, -\beta V) r^2 dr, \quad (2)$$

where σ is given by the condition $V(\sigma) = 0$, γ is the incomplete gamma function, and μ is the reduced mass of the molecule; the approach with all unbound states [2,7]

$$Q_{rovib}^U = \frac{1}{2\sqrt{\pi}} \left(\frac{2\mu}{\beta} \right)^{3/2} \int_0^{\infty} [\exp(-\beta V) - 1] r^2 dr, \quad (3)$$

and finally with the approach excluding the negative contribution to the partition function [11]

$$Q_{rovib}^{NE} = \frac{1}{2\sqrt{\pi}} \left(\frac{2\mu}{\beta} \right)^{3/2} \int_{\sigma}^{\infty} [\exp(-\beta V) - 1] r^2 dr. \quad (4)$$

2.2 The PECs of the Na₂ Molecule

In the present calculations all states with the 3s+3s and 3s+3p dissociation limits were taken into account in an exact or approximate manner. The two states with the limit 3s+3s are $X^1\Sigma_g^+$ and $1^3\Sigma_u^+$. The excited states with the 3s+3p limit are $^3\Pi_u$, $^1\Sigma_u^+$, $^3\Sigma_g^+$, $^1\Pi_u$, $^1\Sigma_g^+$, $^1\Pi_g$, $^3\Pi_g$, $2^3\Sigma_u^+$ [12]. There are also higher lying excited states but at the temperatures considered here they can be neglected.

As discussed later the accuracy of the PECs at low and high inter-atomic distances is crucial so it is important to use *ab initio* PECs fitted to actually calculated energies as in Zhang et al. [13], not ones which are based only on spectroscopic constants (which describes best the vicinity of the PEC minimum and are often empirical) as in Biolsi [9] and Song et al. [4].

In the present study, the analytical PECs fitted to the *ab initio* energies were used.

For the ground $X^1\Sigma_g^+$ state the PEC from Zhang et al. [13] (CBS) was used. This publication also reports the first excited state ($1^3\Sigma_u^+$) but it has the wrong short-range limit ($-\infty$ instead of ∞).

All the excited states were approximated with the use of the Konowalow data [14] fitted to the expression:

$$V_K = \frac{a_0}{r} \exp(-\beta_1 r) + \sum_{i=1}^9 a_i [r \exp(-\beta_2 r)]^i, \quad (5)$$

and the parameters in this expression are given in Table 1. The results were calculated with the explicit $1^3\Sigma_u^+$ (statistical weight 3), $^3\Pi_u$ (statistical weight 6), and $^1\Sigma_u^+$ (statistical weight 1) states. The $^3\Sigma_g^+$, $^1\Pi_u$, $^1\Sigma_g^+$ states were approximated with $^3\Sigma_g^+$ (with statistical weight 6), and the $^1\Pi_g$, $^3\Pi_g$, $2^3\Sigma_u^+$ states were approximated with the $^1\Pi_g$ state (with statistical weight 11).

The energy shift between the states dissociating to the 3s+3s and 3s+3p limits is $\Delta E = 0.07255E_h$ [14]. Finally, the expression for the internal partition function of the Na₂ molecule is

$$Q_{int} = Q_{int}(X^1\Sigma_g^+) + 3Q_{int}(1^3\Sigma_u^+) + e^{-\beta\Delta E} [6Q_{int}(^3\Pi_u) + Q_{int}(^1\Sigma_u^+) + 6Q_{int}(^3\Sigma_g^+) + 11Q_{int}(^1\Pi_g)]. \quad (6)$$

The above expression in its full form or with the chosen electronic states is used to obtain the results in the following section.

3 Results

Heat capacity—ground and the first excited state Comparing different approaches one can see that for the ground state at high temperatures inclusion of the unbound states plays a very significant role (Table 2, the upper entries—the results are based on the CBS PES, for the lower entries—the results are based on the IRM PES). At 2500 K, the

Table 1 Parameters of the fits to Konowalow data with Eq. 5

	$1^3\Sigma_u^+$	$3\Pi_u$	$1^1\Sigma_u^+$	$3^3\Sigma_g^+$	$1^1\Pi_g$
a_0	1360.491 653	3.747 024 542	1.144 429 410	1.730 230 037	4.593426118r
a_1	-0.0069 549 798 197	0.0	0.0	0.0	0.0
a_2	-0.04091 745 793	-0.08 899 981 630	-0.03 926 042 290	-0.01 069 642 562	0.0
a_3	0.5 715 556 185	0.0	0.0	0.0	0.0
a_4	-2.549 438 894	0.04048 723 955	0.000 568 355	-0.002 487 249 959	0.0
a_5	9.238 779 840	0.0	0.0	0.0	0.0
a_6	-20.79 211 128	0.0	0.0	0.0	0.0
a_7	29.03 994 607	0.0	0.0	0.0	0.0
a_8	-22.58 787 238	0.0	0.0	0.0	0.0
a_9	7.539 412 612	0.0	0.0	0.0	0.0
β_1	3.018 139 348	0.7 650 584 306	0.2 120 271 489	0.3 555 527 001	1.076476 159
β_2	0.4 307 030 965	0.3 129 811 451	0.2 310 664 856	0.2 140 515 091	0.0

Table 2 The ground state heat capacity based on the bound states (C_p^B), exclusion of negative contribution (C_p^{NE}), and unbound states (C_p^U); the upper entries—the results based on the CBS PES, the lower entries—the results based on the IRM PES compared to the Song [4] results

T (K)	C_p^B	C_p^{NE}	C_p^U	Song
2000	30.58	35.68	35.33	~ 39
	31.19	36.82	36.49	
2500	27.41	32.67	32.22	~ 37
	27.73	33.29	32.89	
3000	25.42	30.55	30.03	~ 35
	25.59	30.86	30.40	

difference between the bound and unbound heat capacities is $4.81 \text{ J} \cdot (\text{molK})^{-1}$; Biolsi [9] also reports a significant discrepancy but in this case the method of comparison is not specified. The results in Table 2 were restricted to 3000 K to minimize the influence of the excited states.

The difference between the IRM [4] and CBS PECs is also notable (the lower and upper entries): for the bound version of the heat capacity it is $0.61 \text{ J} \cdot (\text{molK})^{-1}$ at 2000 K and for the unbound the corresponding discrepancy is $1.16 \text{ J} \cdot (\text{molK})^{-1}$. It means that the whole range is important for the results, and this fact is a guideline for PEC construction—it is important to provide accurate results not only in the vicinity of the minimum but also at the high and low inter-atomic distances. Note that Musiał et al. [12] and Zhang et al. [13] calculate the energies for inter-atomic distances only down to around $2a_0$ but for Konowalow's results the lowest distance is $3.8a_0$ (and highest distance is $15a_0$ while the integration had to be done to $20a_0$ or more for fully converged results). This problem is also important for shallow excited states. The low lying $1^3\Sigma_u^+$ state of Na_2 will, especially, be affected: the correct partition function for this state is negative at higher temperatures so that, in case of inaccuracies, even a wrong sign of contribution is possible. This can cause a serious problem for heat capacity which is a very sensitive quantity for all kind of effects [2,8,15].

For comparison, Table 2 shows the results of Song et al. [4] (approximate values read out from the plot) based on the IRM ground state PEC which differs because of two reasons—neglecting the unbound contribution and the separation of rotations and vibrations.

Finally, note that heat capacity is a sum of the internal and translational contributions so that all inaccuracies in a total value are relatively more pronounced in the internal contribution. The internal part of the heat capacity is more important than the translational contribution at lower temperatures, whereas at higher temperatures the translational part dominates (Fig. 1).

To investigate the accuracy of the lowest excited state ($1^3\Sigma_u^+$) PEC, the respective partition functions were calculated at 2000 K and 6000 K for both PECs. First, the analytical PEC was obtained by the fit to Konowalow data. Second, the CBS PEC of Zhang et al. [13], because of the incorrect behavior at small inter-molecular distances, was approximated by the infinite wall at distances smaller than $2.5a_0$. The results are presented in Table 3. The results were compared with those of Mies and Julienne [7] for the partition functions for this electronic state. The infinite wall (hard spheres) approximation fails for this shallow potential at both temper-

Fig. 1 Ratio of the internal to translational contributions to heat capacity $C_{p,int}/C_{p,trans}$ —dependence on temperature

Table 3 Partition functions of $1^3\Sigma_u^+$ based on the PECs of Konowalow and Zhang—infinite wall approximated. The results of Mies and Julienne are also given

T (K)	Konowalow fit	Zhang—infinite wall	Mies Julienne
2000	$-5.612 \cdot 10^3$	$6.911 \cdot 10^3$	$1.316 \cdot 10^3$
6000	$-1.297 \cdot 10^5$	$-3.216 \cdot 10^5$	$-1.216 \cdot 10^5$

atures and it cannot be used, unlike for the deeper ground state [11]. The other results are similar only at 6000 K, showing the importance of the shallow electronic states and that there is not necessarily a bigger discrepancy at higher temperatures.

The heat capacities for the ground and the first excited state were calculated and the results are compared with the use of Konowalow fit to study the sensitivity of the heat capacity to the differences in the lowest excited state. The bound (excluding the negative contribution) and unbound versions of heat capacity are compared in Table 4. The NIST [1] data and Biolsi's results for the ground and first excited state are also displayed [9]. Inclusion of the first excited state changes all the results especially those with all unbound states (C_p^U) even at the lowest temperature of 2000 K which is actually not surprising because it is a low excited state dissociating to the same limit as the ground state. The results in the present study are significantly below Biolsi's results, whereas the NIST data are mostly much higher than all the others. It should be noted that the NIST data also contain some of the higher electronic states.

Heat capacity—ground and all excited states The results obtained with all excited states are summarized in Table 5. The values here are generally closer to the NIST ones, whereas Biolsi's results are much lower at most temperatures.

In order to look for a possible source of the discrepancy, the results of this study were recalculated removing some of the electronic states. This test was done at a temperature of 6000 K. The results for the ground and the first excited state followed the

Table 4 The heat capacities based on the ground and the first excited state ($1^3\Sigma_u^+$); bound states versions (C_p^B) based on Konowalow (K) excited state PEC; negative contribution excluded versions (C_p^{NE}), and unbound C_p^U versions. The NIST and Biolsi's results are also given

T (K)	C_p^B K	C_p^{NE} K	C_p^U K	NIST	Biolsi
2000	30.87	37.46	33.06	32.78	35.13
2500	27.62	33.93	28.64	31.70	31.64
3000	25.57	31.37	25.38	34.42	29.17
3500	24.27	29.65	22.94	40.75	27.46
4000	23.41	28.49	20.99	47.51	26.26
4500	22.82	27.69	19.33	52.18	25.36
5000	22.41	27.12	17.81	54.01	24.67
5500	22.11	26.71	16.35	53.09	–
6000	21.88	26.40	14.90	49.94	23.65

Table 5 The heat capacities with all electronic states and all unbound contributions based on Konowalow (K) first excited state PECs

T (K)	C_p^U K	NIST	Biolsi
2000	33.63	32.78	35.16
2500	31.60	31.70	31.78
3000	34.13	34.42	29.52
3500	40.94	40.75	28.09
4000	49.61	47.51	27.19
4500	56.83	52.18	26.57
5000	60.39	54.01	26.14
5500	60.12	53.09	–
6000	57.19	49.94	25.54

Biolsi pattern, so the $^3\Pi_g$ state that is missing in Biolsi's calculations was suspected. Removal of the $^3\Pi_g$ state gives a value of 58.04, removing all states which were approximated (i.e., leaving three excited states) yields 52.80. Removing the two lowest states dissociating to the $3s+3p$ limit ($^3\Pi_u$, $^1\Sigma_u^+$) from the calculation yields 46.63.

Another way to analyze the influence of the excited states is the convergence diagram. Figure 2 shows the influence of consecutive terms describing the excited states partition functions in Eq. 6 for the unbound version of the heat capacity. As is already known, the inclusion of the first excited state lowers the heat capacity and adding more and more states increases and keeps the heat capacity at higher levels again. It is tempting to attribute that increase in value to the second excited state ($^3\Pi_u$) but excluding only this state from the full calculation also gives a similar value ($51.38\text{ J} \cdot (\text{molK})^{-1}$).

The final conclusion about this behavior is that, in general, the higher excited states (dissociating to the $3s+3p$ limit) increase the heat capacity again. Note that it is not possible to attribute this to any given electronic states because heat capacity is not additive with respect to the partition functions of the electronic states (the reason for that is the logarithm in Eq. 1), meaning it is not possible to split the total heat capacity between the heat capacities of the electronic states. Because of the second derivative in the definition of heat capacity, it can also be concluded that all higher excited states have similar second derivatives.

Fig. 2 The influence of consecutive terms (n) describing the excited states partition functions in Eq. 6 for heat capacity. Unbound version of heat capacity is presented. The $C_p(0)$ is heat capacity based on ground state only

The specific source of the discrepancy for the low values at high temperatures in Biolsi's results must then be attributed generally to the differences in the higher electronic states. The difference in the partition functions of electronic states, which can seem unimportant, can lead to a big difference in the second derivative.

The present results of heat capacity with all the excited electronic states were fitted to the function similar to the Shomate equation, as in the NIST database, with the result $C_p = 751.766 - 0.589972T + 0.000187928T^2 - 2.58304 \cdot 10^{-8}T^3 + 1.28916 \cdot 10^{-12}T^4 - 4.15595 \cdot 10^8/T^2$, where T is the temperature in Kelvin. The difference between the calculated points and the values of this equation is in the range of 0.01 % to 0.3 %.

4 Conclusions

Heat capacity at high temperatures is a thermophysical quantity which is very sensitive to the accuracy of the partition function of all the electronic states. The exact calculations require knowledge of the exact PECs of many electronic states, as in case of weakly bounded molecules as the Na_2 molecule. In light of the present results, it is crucial to have more exact results than the old Konowalow data and to use analytical representations which are more sophisticated than the Hulburt–Hirschfelder potential used by Biolsi which is known to be unsatisfactory at low inter-atomic distances [16]. Both the present results and those of Biolsi certainly suffer from inaccuracies at the low inter-atomic part of PECs so that it is important that the PECs are calculated at very small inter-atomic distances. If the results at even higher temperatures are to be calculated reliably, the electronic states dissociating to the $3s+4s$ limit will also have to be taken into account, but unfortunately analytical PECs are not available for these.

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