Ro-vibrational coupling in high temperature thermochemistry of the BBr molecule.

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**Summation of ro-vibrational levels.**

- Future prospects - study of molecular states near dissociation (Perspective: Accurate ro-vibrational calculations on small molecules, J. Tennyson JCP 145, 120901, 2016). 
  "For high temperatures, typically $T \gg 1000K$, experience shows that it is necessary to include, at least approximately, all states in the summation."

- PH$_3$ (phosphine) - 153 million rotation-vibration energy levels; 
  NH$_3$ (ammonia) - 7.3 million rotation-vibration energy levels.
  - reduction of computational cost - not all rotational levels used above certain total angular momentum number; Tennyson et al. 2014.

- CH$_4$ - up to 3000K (+ significant differences between methods; the differences in PESs); Nikitin et al. 2015.
True bound, resonance and scattering states or what is a molecule.

FIG. 4. The calculated bound $\epsilon_{1,100,v} < 0$, and metastable, $\epsilon_{1,100,m} > 0$, states are located in a plot of $v_{1,100}(R)$ for the $l=100$ state of Li$_2$(X $^1\Sigma^+_g$). The vibrational levels $v=0, 10$ define the true bound state portion $q_{1,100}(B)$ of the radial partition function $q_{1,100} = q_{1,100}(B) + q_{1,100}(C)$. The total continuum contribution $q_{1,00}(C) = q_{1,100}(M) + q_{1,00}(F)$ is divided into two components. The finite set of virtual levels $m=1, 7$ predicted to exist behind the rotational barrier $R < R_{Bar}$, and with approximate eigenvalues $0 < \epsilon_{1,100,m} < \epsilon_{Bar}$, define the metastable contribution $q_{1,100}(M)$.
Only true bound states at high T:

- Partition functions and equilibrium constants of 291 diatomic molecules up to 10 000 K; summation of ro-vibrational levels (P.S. Barklem, R. Collet, Astron. Astrophys. 588 (2016) A96)
- Partition functions of 51 molecules up to 6000K (in some cases; not only diatomic) (R.R. Gamache et al. J. Quant. Spectrosc. Radiat. Transfer 203 (2017) 70)
True bound, resonance and scattering states or what is a molecule.

- **Bound and resonance/metastable states:**
  - N$_2^+$, NO, O$_2$, CN, C$_2$, CO, CO$^+$ - summation up to 50000K (Y. Babou et al. Int. J. Thermophys. 30 (2009) 416)
  - $V_J(r) = V(r) + J(J + 1)/(2\mu r^2)$
  - Often idea of excluded volume used: $K = B - b_0$
True bound, resonance and scattering states or what is a molecule.

**FIG. 3.** Calculated equilibrium constant $K_p(T)$ in the range 250–400 K: (—) in the limit $\alpha = 0$, (---) considering the finite value of $\alpha$, (___) from our previous calculation\textsuperscript{30}. Experimental data: (■) results based on the thermal conductivity of steam experiments of Curtiss \textit{et al.},\textsuperscript{13} (♦) Ptashnik \textit{et al.}\textsuperscript{15} high resolution pure water vapor absorption spectra using the Ma and Tipping continuum model; (►) Nicolaisen\textsuperscript{17} IR absorption spectrum of water in CCl\textsubscript{4}. 
True bound, resonance and scattering states or what is a molecule.

**Fig. 2** Percentage difference between present partition functions and results from [9] (left) and from [6] (right)


True bound, resonance and scattering states or what is a molecule.

Water dimer and trimer - bound and metastable states in absorption spectrum. Spectroscopic model - metastable dimer is considered as two monomers almost freely rotating near each other - absorption spectrum modeled as double absorption of the monomer broadened due to a short lifetime of the metastable molecule.

![Absorbance vs Wavenumber graph](image)

*Fig. 4. Decomposition of the experimental absorption spectrum of pure water vapor at 79-atm [16]. Calculated contribution of monomer (M), bound dimer (D), metastable dimer (DM), bound trimer (T) and metastable trimer (TM) are shown.*

True bound, resonance and scattering states or what is a molecule.

- **Bound, resonance, and scattering states:**

  Partition function, $K$, $Na_2$, $Li_2$; ground and 1 excited state.

True bound, resonance and scattering states or what is a molecule.

Resonance and scattering states from semiclassical approximation for the scattering phase shift

<p>| TABLE II. Partition functions for Na₂ (X¹Σ⁺) and Na₂ (a³Σ⁺u). |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|</p>
<table>
<thead>
<tr>
<th>T (K)</th>
<th>Q₁</th>
<th>Q₁(M)</th>
<th>Q₁(B)</th>
<th>Q₁(F)</th>
<th>Q₂</th>
<th>Q₂(M)</th>
<th>Q₂(B)</th>
<th>Q₂(F)</th>
<th>Q₃</th>
<th>Q₃(M)</th>
<th>Q₃(B)</th>
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<td>500</td>
<td>1.074 (11)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>2.615 (4)</td>
<td>0.4697</td>
<td>+0.4720</td>
<td>56.145</td>
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<td>1000</td>
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<td>0.0001</td>
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<td>1500</td>
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<td>2500</td>
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<td>0.1400</td>
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<td>−2.566 (4)</td>
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<td>3500</td>
<td>1.976 (6)</td>
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<td>7000</td>
<td>1.634 (6)</td>
<td>0.2836</td>
<td>0.2096</td>
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<tr>
<td>8000</td>
<td>1.612 (6)</td>
<td>0.3027</td>
<td>0.2438</td>
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<td>1.600 (6)</td>
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<td>0.2776</td>
<td>−1.386 (5)</td>
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<td>1.594 (6)</td>
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True bound, resonance and scattering states or what is a molecule.

![Graph](image)

FIG. 14. Calculated equilibrium constant $K_p^{(3\Sigma_u^+)}$ for the triplet state of Li$_2$. The solid curve is obtained by assuming $Q_{TOT} = Q_3$ and is meant to mimic the qualitative behavior we would expect for a shallow van der Waals type dimer. The bound state contribution $K_p(B)$, shown by the dashed curve, remains positive for all $T$, but the combined quantity $K_p = K_p(B) + K_p(C)$ predicts a negative concentration of dimers for $T > 5500$ K. This effect can be properly described in terms of modified activity for the monomer.

True bound, resonance and scattering states or what is a molecule.

- N\textsubscript{2}, heat capacity, enthalpy up to 25000K, classical approach via virial coefficient (R. Phair, L. Biolsi, P.M. Holland Int. J. Thermophys. 11 (1990) 201)
- O\textsubscript{2}, heat capacity, enthalpy up to 25000K, classical approach via virial coefficient; good comparison with JANAF (up to 6000K) but O\textsubscript{2} is easy - plot form Babou (L. Biolsi, P.M. Holland Int. J. Thermophys. 17 (1996) 191)
- Na\textsubscript{2}, heat capacity, viscosity, thermal conductivity, classical approach via virial coefficient; also repulsive PEC used; at 6000K the heat capacity is twice the NIST result (L. Biolsi, P.M. Holland Int J. Thermophys. 31 (2010) 831)
True bound, resonance and scattering states or what is a molecule.

continued:
For Na$_2$ at 2500K: 31.70J/(molK) (NIST) vs. 31.78J/(molK) (Biolsi,Holland) but without repulsive part 25.43J/(molK)  
Comparison not reliable - NIST values do not take into account unbound states - discrepancy must have different source M.W. Chase J. Phys. Chem. Ref. Data, Monograph 9, 1998

Repulsive part of potential cannot be ignored for the heat capacity of Ag$_2$ (M.L. Biolsi, L. Biolsi, P.M. Holland Paper #368 ACS 228th National Meeting, 2004)
Classical approach to thermochemistry/thermophysics.

The ro-vibrational partition function of diatomic molecule can be calculated classically from Hamiltonian in spherical coordinates following the procedure of Hill with the condition for bound states as

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

\( \sigma \) is given by the \( V(\sigma) = D_e \) condition, \( \gamma \) is the incomplete gamma function, and \( V' = V - \lim_{r \to \infty} V \) with \( \lim_{r \to \infty} V = D_e \) for each PEC considered here.
Classical approach to thermochemistry/thermophysics.

At high temperatures the influence of unbound states is significant, especially heat capacity is a quantity sensitive to unbound states. The inclusion of unbound states is easy in the classical theory because it involves change of \( \exp(-\beta V) \) in

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

for \( \exp(-\beta V) - \exp(-\beta D_e) \)

\[
Q_{rovib} = \frac{1}{2\sqrt{\pi}} \left( \frac{2\mu}{\beta} \right)^{3/2} \int_0^\infty [\exp(-\beta V) - \exp(-\beta D_e)] r^2 dr. \tag{3}
\]
Classical approach to thermochemistry/thermophysics.

Let $H=T+V$ be the Hamiltonian of internal motion of diatomic molecule given as a sum of kinetic energy $T$ and potential energy $V$, by using equality $e^{-\beta V} = (e^{-\beta V} - 1) + 1$ the internal partition function is

$$Q = \frac{1}{(2\pi)^3} \int \int e^{-\beta(T+V)} d\mathbf{p} d\mathbf{r} = \frac{1}{(2\pi)^3} \int e^{-\beta T} \mathbf{p} \int e^{-\beta V} d\mathbf{r}$$

$$= \frac{1}{(2\pi)^3} \int e^{-\beta T} \mathbf{p} \int (e^{-\beta V} - 1) d\mathbf{r} + \frac{1}{(2\pi)^3} \int \int e^{-\beta T} d\mathbf{p} d\mathbf{r},$$

the second term is a partition function of non-interacting atoms (with $V = 0$) which means that the rest contains all interactions (truly bound, metastable, and scattering states).
Classical approach to thermochemistry/thermophysics.

Other approaches - use second virial coefficient:
\[ B(T) \sim \int (e^{-\beta V} - 1)dr \]

- \[ K = -B_b - B_m \]

- \[ Q = -Q_{tr}B, \quad K = K(B) + K(M) + K(C) \] (repulsive part of PEC - negative effect)

- \[ K = -B \]

- idea of excluded volume: \[ K = -(B - b_0)/RT \]
The potential energy curve (PEC) for the ground electronic state \( ^1\Sigma \) was modeled with the improved Manning-Rosen oscillator

\[
V_g(r) = D_e \left( 1 - \frac{e^{\alpha r_e} - 1}{e^{\alpha r} - 1} \right)^2, \tag{5}
\]

where \( D_e = 0.14904 \text{a.u.} \), \( r_e = 3.5659 \text{a.u.} \), and \( \alpha = 0.699176 \text{a.u.} \). The low lying excited states are described with the Morse PECs, the \(^3\Pi\) state with

\[
V_{e1}(r) = 0.081216 \left( 1 - e^{-1.1477(r-3.517)} \right)^2 + 0.067824, \]

and the \(^1\Pi\) state with

\[
V_{e2}(r) = 0.016537 \left( 1 - e^{-2.1270(r-3.545)} \right)^2 + 0.132503.
\]

The other thermochemical quantities that is internal thermal energy $E_{int}$, internal heat capacity $C_{p, int}$, and internal entropy $S_{int}$ are calculated as

$$E_{int} = - \frac{d \ln Q}{d \beta},$$  \hspace{1cm} (6)

$$C_{p, int} = \beta^2 \frac{d^2 \ln Q}{d \beta^2},$$  \hspace{1cm} (7)

$$S_{int} = \ln Q + \beta E_{int},$$  \hspace{1cm} (8)

$$C_p = C_{p, int} + (5/2)R,$$  \hspace{1cm} (9)

$$S = S_{int} + (5/2)R + \ln \left[ \left( \frac{m}{2\pi\beta} \right)^{3/2} \frac{1}{\beta P} \right] R,$$  \hspace{1cm} (10)

with $P = 1\text{ atm}$.
**BBr high temperature thermochemistry.**

Table: The heat capacities of the BBr molecule

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$C_{p,int}^B (g)$</th>
<th>$C_{p,int}^B (g^{2e})$</th>
<th>$C_{p,int} (g^{2e})$</th>
<th>$C_p (g^{2e})$</th>
<th>$C_{p,NIST}$</th>
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<tbody>
<tr>
<td>300K</td>
<td>2.016</td>
<td>2.016</td>
<td>2.016</td>
<td>37.59</td>
<td>32.68</td>
</tr>
<tr>
<td>500K</td>
<td>2.027</td>
<td>2.027</td>
<td>2.027</td>
<td>37.68</td>
<td>35.50</td>
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<tr>
<td>1000K</td>
<td>2.057</td>
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<td>2.057</td>
<td>37.93</td>
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<td>2.128</td>
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<td>0.3029</td>
<td>0.5044</td>
<td>24.99</td>
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</table>

BBr high temperature thermochemistry.

**Figure:** The ground state potential energy curve and the related thermal energies (dots) related to energy at inflection point (dashed line).

**Figure:** Influence of ro-vibrational coupling on the partition function $Q_{\text{int}}^B(g)$, the thermal energy $E_{\text{int}}^B(g)$, the heat capacity at constant pressure $C_{p,\text{int}}^B(g)$, and the entropy $S_{\text{int}}^B(g)$ given as the percent difference between the exact value with respect to separated rotations value.
Figure: The partition function of the bound molecule on the ground electronic state $Q^B_{int}(g)$ compared with the partition function based on the ground and excited electronic states $Q^B_{int}(g+2e)$, and with the partition function based on both all electronic states and unbound states $Q_{int}(g+2e)$.
Figure: The energy of the bound molecule on the ground electronic state $E_{int}^B(g)$ compared with the energy based on the ground and excited electronic states $E_{int}^B(g + 2e)$, and with the energy based on both all electronic states and unbound states $E_{int}(g + 2e)$. 

Figure: The heat capacity of the bound molecule on the ground electronic state $C_{p,\text{int}}^B(g)$ compared with the heat capacity based on the ground and excited electronic states $C_{p,\text{int}}^B(g+2e)$, and with the heat capacity based on both all electronic states and unbound states $C_{p,\text{int}}(g+2e)$.
Figure: The entropy of the bound molecule on the ground electronic state $S_{int}^B(g)$ compared with the entropy based on the ground and excited electronic states $S_{int}^B(g + 2e)$, and with the entropy based on both all electronic states and unbound states $S_{int}(g + 2e)$.