Ground and excited electronic state thermodynamics of aqueous carbon monoxide: A theoretical study

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By using the quasi Gaussian entropy theory in combination with molecular dynamics simulations and the perturbed matrix method, we investigate the ground and excited state thermodynamics of aqueous carbon monoxide. Results show that the model used is rather accurate and provides a great detail in the description of the excitation thermodynamics. © 2005 American Institute of Physics. [DOI: 10.1063/1.1870832]

I. INTRODUCTION

In recent papers^{1,2} we showed that it is possible to use the quasi Gaussian entropy (QGE) theory in combination with molecular dynamics (MD) data to obtain a very detailed and accurate description of the partial molar thermodynamics of dilute solutions. In this work we combine such a theoretical approach with a new extension of the perturbed matrix method (PMM), described in the accompanying paper,² which provides a detailed description of the complete vibroelectronic behavior of a quantum center embedded into a complex molecular environment. In this way it becomes possible to rigorously obtain the partial molar thermodynamics of whatever electronic state, without using the approximations of previous papers^{4,5} where vertical electronic excitations were utilized. Application to aqueous carbon monoxide confirms the accuracy of QGE/MD models in reproducing (ground state) thermodynamics and provides a detailed description of the first two electronic excitations which, although degenerate in the isolated carbon monoxide, present a rather different thermodynamics when solute-solvent interactions are considered.

II. THEORY

In this section we summarize the essential derivations of both the QGE theory and the PMM, necessary to obtain partial molecular and electronic properties from MD data. Detailed descriptions can be found in previous papers.^{1–5} Let Q and Q_{ref} be the canonical partition functions for a fluid state system of one solute and n_s solvent molecules, and for a reference system at the same temperature and density but without the potential energy (hence without any inaccessible configuration). We can express the excess (Helmholtz) free energy of such a system, equivalent to the excess (Helmholtz) free energy per solute molecule, as^{2,6–9}

$$A' = A - A_{ref} = -kT \ln(Q/Q_{ref}) = kT \ln\langle e^{\beta \mathcal{U}'} \rangle - kT \ln \epsilon,$$
(1)

$$Q = \frac{8\pi^2 V\Theta}{e^{-1}} \int^* e^{-\beta \mathcal{U}'} \prod_{j=1}^{n_s} (\det \tilde{m}_j)^{1/2} (\det \tilde{M}_{cl})^{1/2} d\mathbf{x}_{in} d\mathbf{x},$$
(2)

$$Q_{ref} = \frac{8\pi^2 V\Theta}{e^{-1}} \int \prod_{j=1}^{n_s} (\det \tilde{m}_j)^{1/2} (\det \tilde{M}_{cl})^{1/2} dx_{in} dx, \quad (3)$$

where \mathcal{U}' is the excess energy (basically the potential energy including the quantum vibrational ground state energy shift from a reference value) of a subsystem made of n_s solvent molecules and a single solute molecule with fixed rototranslational coordinates, \mathbf{x}_{in} are the generalized internal (classical) coordinates of the single solute molecule and \mathbf{x} are the (classical) coordinates of the n_s solvent molecules within the solute molecular volume V (i.e., the integration limits are defined by V). Moreover \tilde{m}_j is the classical coordinate mass tensor block of the *j*th solvent molecule, \tilde{M}_{cl} is the classical coordinate mass tensor block of the solute and Θ is a temperature dependent factor including the quantum corrections¹⁰

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$$\Theta = \frac{(2\pi kT)^{(d+d_s)/2} Q_{ref}^{qm}}{n_s! h^{(d+d_s)} (1+\gamma) (1+\gamma_s)^{n_s}}$$
(4)

with $1 + \gamma$ and $1 + \gamma_s$ the symmetry coefficients for the solute and the solvent, respectively, *d* and *d_s* the number of classical degrees of freedom in the solute and *n_s* solvent molecules, and Q_{ref}^{qm} the quantum vibrational partition function, as defined in previous papers,^{7,10} for the molecules within the solute molecular volume *V*, typically given by the product of the molecular vibrational partition functions. Finally, *h* is the Planck's constant and the star in Eq. (2) denotes an integration only over the accessible configurational space within the solute molecular volume. Note that ϵ , in Eq. (1), is the fraction of available configurational space,⁹

$$\boldsymbol{\epsilon} = \frac{\int^{*} (\det \tilde{M}_{cl})^{1/2} \prod_{j=1}^{n_s} (\det \tilde{m}_j)^{1/2} d\boldsymbol{x}_{in} d\boldsymbol{x}}{\int (\det \tilde{M}_{cl})^{1/2} \prod_{j=1}^{n_s} (\det \tilde{m}_j)^{1/2} d\boldsymbol{x}_{in} d\boldsymbol{x}}$$
(5)

with the corresponding (temperature independent) entropic term, $k \ln \epsilon$, usually associated to hard-body excluded volume.⁷

The ensemble average in Eq. (1) can also be expressed as

$$\langle e^{\beta \mathcal{U}'} \rangle = \int \rho(\mathcal{U}') e^{\beta \mathcal{U}'} d\mathcal{U}', \qquad (6)$$

where $\rho(\mathcal{U}')$ is the probability distribution function of the excess energy \mathcal{U}' . We showed in previous papers^{1,2,7,9} that one of the simplest distribution, the Gamma distribution, provides a fully physically acceptable theoretical model for solute-solvent systems (Gamma state) giving an excellent description of the fluid state thermodynamics over a wide range of temperature and density. We can rewrite the excess free energy of the considered system as

$$A'(T) = n_s a'_s + a', (7)$$

where a'_s is the partial molecular excess (Helmholtz) free energy of the solvent and a' is the partial molecular excess (Helmholtz) free energy of the solute. It is worth noting that solvent and solute partial molecular excess free energies are obtained at fixed pressure p for the actual fluid and not in general at fixed pressure for the reference state. This is because the reference state is defined with the same volume and molecular number of the actual condition. Hence we obtain^{1,2}

$$a_s' = \mu_s' - p' v_s, \tag{8}$$

$$a' = \mu' - p'v, \tag{9}$$

$$\mu_s' = \mu_s - \mu_{ref,s},\tag{10}$$

$$\mu' = \mu - \mu_{ref},\tag{11}$$

$$p' = p - p_{ref},\tag{12}$$

where v and v_s are the partial molecular volumes of the solute and solvent in the actual fluid (which are in general

different from the ones in the reference state), μ , μ_{ref} , μ_s , $\mu_{ref,s}$ are the chemical potentials in the actual fluid and in the reference condition for the solute and solvent molecules and p_{ref} is the pressure in the reference state.

Assuming that A' can be well modeled by a single Gamma state,⁷ we have

$$U' = U'_0 + (T - T_0) \frac{C'_{V0} T_0}{T(1 - \delta_0) + \delta_0 T_0},$$
(13)

$$A' = U'_0 - T_0 C'_{V0} \Lambda(T) - kT \ln \epsilon, \qquad (14)$$

$$\Lambda(T) = \frac{1}{\delta_0} + \frac{T}{T_0 \delta_0^2} \ln\{1 - \delta(T)\},$$
(15)

$$\delta(T) = \frac{T_0 \delta_0}{T(1 - \delta_0) + T_0 \delta_0},\tag{16}$$

with $U'_0 = U'(T_0)$ and $C'_{V0} = C'_V(T_0)$ the excess internal energy and heat capacity of the system at the reference temperature T_0 , and δ_0 a dimensionless intensive property⁷ independent of the temperature, which in our case (high dilution) is determined by the solvent. Subtracting the solvent partial excess free energy from Eq. (14), we readily obtain

$$a' = A' - n_s a'_s = u'_0 - c'_{V0} T_0 \Lambda(T) - kT \ln \bar{\epsilon},$$
(17)

where u'_0 and c'_{V0} correspond to the solute partial molecular excess internal energy and heat capacity, evaluated at the reference temperature T_0 , and $-kT \ln \bar{\epsilon}$ is the corresponding partial molecular excess free energy due to the confinement ($\bar{\epsilon}$ is the confinement term of the solute). Using general thermodynamic relations, we can obtain the Gamma state expressions for any thermodynamic property at high dilution, e.g., the solute partial molecular internal energy u' and heat capacity c'_V ,^{1,2}

$$u' = \left(\frac{\partial U'}{\partial n}\right)_{p,n_s,T} = u'_0 + (T - T_0) \frac{c'_{V0}T_0}{T(1 - \delta_0) + \delta_0 T_0},$$
$$c'_V = \left(\frac{\partial C'_V}{\partial n}\right)_{p,n_s,T} = c'_{V0} \left[\frac{T_0}{T(1 - \delta_0) + \delta_0 T_0}\right]^2.$$

Using the expression of Eq. (13) to fit the average potential energy of the whole system, as provided by MD simulations at various temperatures, we can obtain the excess chemical potential via^{1,2}

$$\mu' = \mu^* - kT \left(\frac{\partial \ln \varepsilon}{\partial n}\right)_{V,n_s},\tag{18}$$

$$\mu^* = \Delta A^* = u_0' - c_{V0}' T_0 \Lambda(T) + p^* v, \qquad (19)$$

$$A^* = A' + kT \ln \varepsilon, \qquad (20)$$

where ΔA^* and p^* are respectively the change of the excess free energy between the solute-solvent and the pure solvent systems and the excess pressure, disregarding the corresponding confinement terms, and $(\partial \ln \epsilon / \partial n)_{V,n_s} = (\mu^* - \mu')/(kT)$ can be obtained simply performing at one

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temperature a thermodynamic integration (TI) calculation to evaluate the excess chemical potential.²

The general previous derivations, although typically refer to the excess thermodynamics for the electronic ground state of the system (i.e., all the molecules are in their electronic ground states), can be utilized, as well, for a given solute electronic excited state. Hence, similarly to our previous studies on formaldehyde in water⁴ and water in water,¹¹ we can evaluate the solute electronic excitation thermodynamics, combining the QGE theory with the PMM.^{3,12,13} PMM has been recently developed and successfully applied to a large variety of quantum centers (QC) embedded into a complex molecular environment,^{3,5,14–16} proving to be a very powerful tool in the theoretical study of electronic properties.

Defining with r_n the nuclear coordinates of the QC and x the coordinates of the solvent providing the (classical) perturbing field we can write, within certain approximations,^{4,13} the perturbed electronic Hamiltonian matrix of the QC (in our case a carbon monoxide) as

$$\widetilde{H}(\boldsymbol{r}_{n},\boldsymbol{x}) \cong \widetilde{H}^{0}(\boldsymbol{r}_{n}) + q_{T} \mathcal{V}(\boldsymbol{r}_{0},\boldsymbol{x}) \widetilde{I} + \widetilde{Z}_{1}(\boldsymbol{E}(\boldsymbol{r}_{0},\boldsymbol{x}),\boldsymbol{r}_{n}) + \Delta V(\boldsymbol{r}_{n},\boldsymbol{x}) \widetilde{I}, \qquad (21)$$

where $\tilde{H}^0(\mathbf{r}_n)$ is the unperturbed Hamiltonian matrix which can be built by standard electronic structure calculations in vacuo, $\mathcal{V}(\mathbf{r}_0, \mathbf{x})$ and $\mathbf{E}(\mathbf{r}_0, \mathbf{x})$ are the (perturbing) electric potential and electric field at r_0 , typically the QC geometrical center, $\tilde{Z}_1(\boldsymbol{E}, \boldsymbol{r}_n)$ is the perturbation energy matrix explicitly given by $[\tilde{Z}_1]_{l,l'} = -\boldsymbol{E} \cdot \langle \Phi_l^0 | \hat{\boldsymbol{\mu}} | \Phi_{l'}^0 \rangle$ and $\Delta V(\boldsymbol{r}_n, \boldsymbol{x})$ approximates the perturbation due to all the higher-order terms as a simple short range potential. Moreover, Φ_l^0 are the unperturbed Hamiltonian (electronic) eigenfunctions and all the matrices used are expressed in this unperturbed basis set. From the MD trajectory of the whole system, we obtain the electric potential and electric field acting onto the QC and, hence, the perturbed Hamiltonian matrix at each MD frame. The diagonalization of such a matrix provides a trajectory of the perturbed eigenvalues and eigenvectors and therefore of whatever perturbed electronic property. In the accompanying paper,³ where we further extend PMM in order to treat explicitly quantum nuclear vibrations coupled to electronic states, we obtained the complete vibroelectronic behavior, including all the energetical and geometrical details associated to quantum vibrational states. Following the theory described in that paper we may calculate all the terms necessary to express the excitation free energy, without using the approximations utilized in previous papers.^{4,5} Hence, from the previous QGE equations and using the fact that for a given electronic state the QC mass tensor is virtually fixed, as indeed explicitly obtained for carbon monoxide,³ we may define the Helmholtz free energy associated to a given electronic transition of the solute, as^{2-4}

$$\Delta A_{ex} = -kT \ln \frac{\Theta_l \int e^{-\beta \mathcal{U}_l'} (\det \tilde{M}_{cl,l})^{1/2} d\mathbf{x}}{\Theta_0 \int e^{-\beta \mathcal{U}_0'} (\det \tilde{M}_{cl,0})^{1/2} d\mathbf{x}}$$

$$= -kT \ln \langle e^{-\beta (\mathcal{U}_l' - \mathcal{U}_0')} \rangle_0 - kT \ln \frac{Q_{v,l}}{Q_{v,0}}$$

$$- 2kT \ln \frac{|\langle \beta_{0,l} \rangle_l|}{|\langle \beta_{0,0} \rangle_0|}$$

$$\cong -kT \ln \langle e^{-\beta (\mathcal{U}_l' - \mathcal{U}_0')} \rangle_0 - kT \ln \frac{Q_{v,l}}{Q_{v,0}}$$

$$- 2kT \ln \frac{|\langle \beta_{0,l} \rangle_0|}{|\langle \beta_{0,0} \rangle_0|}, \qquad (22)$$

$$\mathcal{U}_{l}' = \varepsilon_{l} + \Delta \mathcal{U}_{v,l,0} + \mathcal{U}_{env,l}',$$

where $\langle \rangle_l$ indicates the ensemble average in the *l*th electronic state condition (l=0 clearly indicates the ground state), ε_l is the perturbed eigenvalue of H, obtained at the QC minimum energy internal configuration of the corresponding electronic state, $\mathcal{U}'_{env,l}$ is the (excess) internal energy of the solvent, excluding the interaction with the QC and obtained when the QC is in the *l*th electronic state and all the water molecules are in their electronic ground states. $Q_{v,l}$ is the molecular quantum vibrational partition function for the *l*th electronic state of carbon monoxide obtained by the corresponding vibrational frequency of the isolated carbon monoxide (reference frequency) and $\Delta U_{v,l,0}$ is the QC ground state vibrational energy shift (from the reference ground state vibrational energy) of the *l*th electronic state, as obtained by the perturbed quantum vibrational energies' (we assume that solvent quantum vibrational energies are independent of the QC electronic state). Moreover, the *l* subscript of Θ and \tilde{M}_{cl} means that these properties refer to the *l*th electronic state and we removed from the integral dx_{in} as no classical internal coordinates are present in carbon monoxide. Finally, $\beta_{0,l}$, the QC intramolecular coordinate equilibrium position (minimum energy configuration) for the electronic *l*th state that, as shown in the accompanying paper,³ is virtually fixed at its average value is due to the mass tensor determinant,³ which is also virtually independent of the solute-solvent configuration, and in Eq. (22) we used $\langle \beta_{0,l} \rangle_l \cong \langle \beta_{0,l} \rangle_0$. Hence, considering the confinement term as independent of the electronic excitation, we have

$$\Delta A'_{ex} = -kT \ln \langle e^{-\beta(\mathcal{U}'_l - \mathcal{U}'_0)} \rangle_0, \qquad (23)$$

with $\Delta A'_{ex}$ the excitation excess free energy. In the case where the environment energy is basically independent of the electronic state of the QC, as we assume neglecting atomic polarization, then $\mathcal{U}'_l - \mathcal{U}'_0 = \varepsilon_l - \varepsilon_0 + \Delta \mathcal{E}_{v,l} - \Delta \mathcal{E}_{v,0}$ (this last equation has been used for the calculation of the excitation free energy). Assuming that both the ground and excited states can be well described by the Gamma state model and have virtually identical partial molecular volumes, we obtain

$$\Delta A'_{ex} = \Delta U'_0 - T_0 \Delta C'_{V0} \Lambda(T), \qquad (24)$$

which can then be used to obtain a theoretical model by fitting the crude excitation excess free energies, given by

TABLE I. Parameters of the QGE (ground state) theoretical models for pure water [SPC (Ref. 20) at 55.32 mol/1, Ref. 1 and 2] and aqueous carbon monoxide. Reference temperature, T=300 K.

	u'_0 (kJ/mol)	$c'_{V0} \ ({ m kJ}\ { m mol}^{-1}\ { m K}^{-1})$	δ_0
SPC	-41.4	0.046	0.6565
CO	-4.4	0.044	0.6565

PMM (Ref. 3) and Eq. (23), as a function of the temperature. Finally, the theoretical model for the complete excitation free energy

$$\Delta A_{ex} \cong \Delta A'_{ex} - kT \ln \frac{Q_{v,l}}{Q_{v,0}} - 2kT \ln \frac{|\langle \beta_{0,l} \rangle_0|}{|\langle \beta_{0,0} \rangle_0|}$$
(25)

in combination with $\Delta A_{ex} = \Delta \mu_{ex}$ and the related expressions,³ provides the complete thermodynamic behavior for any electronic excitation.

III. SIMULATION METHODS

The MD simulations and quantum chemical calculations used in this paper are described in detail in the accompanying paper.³ Here we only need to describe the computational method used to obtain the confinement term via thermodynamic integration (TI) (see theory section). We performed TI calculations at 300 and 800 K, to evaluate the corresponding excess chemical potentials. This was done using the GROMACS^{17–19} routine for TI (soft core potential with α =1.51, σ =0.3 nm) to perform 21 perturbation simulations at each temperature: time length=250 ps, time step=2 fs at 300 K and time length=125 ps, time step=1 fs at 800 K, with a 0.9 nm cutoff radius for treating molecular interactions. TI free energy error was estimated by propagating the noise of the free energy gradients in the integration. The noise of each free energy gradient was obtained by the standard deviation of the perturbation energy derivative divided by the square root of the number of statistically independent evaluations (obtained using the autocorrelation function).



FIG. 1. The isochoric excess internal energy change due to (ground state) aqueous carbon monoxide, as obtained by MD data (circles) and QGE model (solid line). The error bars are given by a standard deviation.



FIG. 2. The excess chemical potential (solid line) and excess partial molar internal energy (dotted line) of (ground state) aqueous carbon monoxide, as obtained by the QGE model.

Note that TI excess chemical potential at 800 K was used to obtain the QGE model confinement term while the TI value at 300 K was utilized for comparing with QGE data.

IV. RESULTS

We parameterized our model for the ground state of carbon monoxide, as described in the theory section, by means of the average potential energy (excess internal energy) and the pure solvent pressure in the whole temperature range, i.e., by fitting these values with the corresponding theoretical models. The partial molecular properties of the solute are obtained, according to the theory section, via $\mu^* = \Delta A^*$. Note that, when calculating μ^* , it is very important to use exactly the same temperatures for the evaluation of the overall excess free energies of the solute-solvent and pure solvent systems. This is because even a slight systematic error in these two excess free energies would result in an inaccurate μ^* .



FIG. 3. The excess partial molar entropy (dotted line) and excess (isochoric) heat capacity (solid line) of (ground state) aqueous carbon monoxide, as obtained by the QGE model.

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TABLE II. Comparison of the excess chemical potentials at 300 K and $\Delta(\beta\mu') = \Delta(\beta\mu^*)$ for the 300–800 K temperature change of (ground state) aqueous carbon monoxide, as obtained by QGE and TI calculations. The errors are given by a standard deviation.

	μ' (kJ/mol)	$\Delta(eta\mu')$
QGE	12.9 ± 0.6	3.1 ± 0.46
TI	14.4 ± 0.5	2.5 ± 0.42

(ground state) QGE models are given in Table I. In Fig. 1 we compare the isochoric energy change $(\partial U' / \partial n)_{n_{\star},T,V}$ as obtained by MD simulation data, with the curve provided by the theoretical (ground state) QGE model. From this figure it is evident the high accuracy, within the noise, of the QGE model, confirming previous results.^{1,2} In Figs. 2 and 3 we show the carbon monoxide excess chemical potential and partial molar internal energy (Fig. 2), as well as the excess partial molar entropy and (isochoric) heat capacity (Fig. 3), as obtained by the (ground state) QGE model. Interestingly, from Fig. 2 the expected instability of aqueous carbon monoxide is evident. Note that the excess chemical potentials as obtained by the QGE model and TI calculations at 300 K are, within the noise, virtually identical further indicating the model accuracy, see Table II. In Table III we compare some experimental solute excess thermodynamic properties, with the corresponding values provided by our model. From this table it is clear that the force field used in the simulations is reasonably correct as the QGE model reproduces rather well the experimental data.

Finally, in Figs. 4 and 5 we illustrate the thermodynamic effect of the remarkable result obtained by using PMM: the breaking of the degeneration of the first two electronic excited states in aqueous carbon monoxide.³ In Fig. 4 we show the excitation free energy for the first two electronic transitions, as given by our model and including all the terms of Eq. (25), and in Fig. 5 we report the corresponding excitation excess free energy ($\Delta A'$), subtracted of the unperturbed minimum energy shift from the ground state minimum, as obtained by PMM and Eq. (23) as well as by the fitted QGE model [Eq. (24)]. These figures show a very clear difference in the excitation thermodynamics for the two electronic transitions, confirming our results on vibroelectronic behavior,³ and hence pointing out the relevant effect of the solvent in destroying the unperturbed degeneracy. Moreover, from Fig.

TABLE III. Comparison of aqueous carbon monoxide thermodynamic properties at 298 K as obtained by the (ground state) QGE model, with the corresponding experimental data: partial molar volume v, excess chemical potential μ' , excess partial molar enthalpy h', and excess partial molar entropy s'.

QGE	Expt.
0.024	0.037
12.7	9.3
-6.3	-8.8
-64.0	-60.0
	QGE 0.024 12.7 -6.3 -64.0



FIG. 4. The excitation free energy for the first two electronic transitions, as obtained by PMM and QGE theory. In this figure we include all the terms of Eq. (25).

5 it is also evident the accuracy, within the noise, of the QGE Gamma state model to describe the excitation excess thermodynamics.

V. CONCLUSION

By combining QGE theory, PMM, and MD simulations we were able to describe the complete partial molar thermodynamics of aqueous carbon monoxide, including its excitation thermodynamic properties as obtained, with great detail, via the PMM extension described in the accompanying paper.³ The results confirm the accuracy of the QGE model in reproducing the simulation thermodynamics and the comparison with the experimental data show that the computational model used is also rather accurate. Finally, the PMM-QGE model for the excitation thermodynamics, now including all the possible terms and without using the approximations utilized in previous papers, opens the way to a



FIG. 5. The excitation excess free energy (subtracted of the unperturbed minimum energy shift from the ground state, T_e) for the first two electronic transitions, as obtained by PMM and QGE theory. The circles correspond to the crude PMM free energies as obtained by Eq. (23), subtracting the unperturbed T_e , and the error bars are given by a standard deviation.

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deep understanding of those chemical-physical events involving electronic excited states in local thermodynamic equilibrium, e.g., chemical reactions, photochemical processes, etc.

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