Critical test of quantum cluster equilibrium theory: Formic acid at B3LYP/6-31+G* hybrid density functional level

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Critical test of quantum cluster equilibrium theory: Formic acid at B3LYP/6-31+G* hybrid density functional level

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The recently developed quantum cluster equilibrium (QCE) theory is used at the B3LYP/6-31+G* level of hybrid density functional theory to calculate the equilibrium cluster populations for formic acid vapor, whose quantitative cluster composition was determined by Coolidge and others through precise spectroscopic and vapor-density measurements over a wide range of temperature and pressure. Unlike previous experimental tests of QCE theory in which T,P-dependent cluster polpulations enter only indirectly (e.g., through convolutions with calculated cluster spectroscopic properties, yielding comparison with inhomogeneously braodened ''average'' spectral features), the present comparison is able to *directly* test the QCE population distributions. Nearly exact agreement between theory and experiment is found over the entire span of measurements, confirming that QCE theory satisfactorily predicts the T,P-dependent concentrations of individual cluster species, as well as the cruder population-weighted averages that enter less-sensitive comparisons with experiment. © *1998 American Institute of Physics.* [S0021-9606(98)30438-9]

Quantum cluster equilibrium (QCE) theory, recently developed and applied by our group,[1–5] has provided a new and remarkably detailed picture of the equilibrium cluster structures and thermodynamic properties of hydrogen-bonded fluids. QCE theory is based on full quantum-mechanical treatment of structures, binding energies and vibrational frequencies of H-bonded clusters, which are considered to constitute the basic microscopic units of both gaseous and liquid phases (connected by the fundamental continuity of the gas/liquid critical point). The *ab initio* cluster partition functions, corrected for residual cluster–cluster interactions and volume effects,[6] are employed within the rigorous framework of quantum statistical thermodynamics to solve for the QCE cluster population distributions that dictate thermodynamic behavior. In effect, QCE theory assumes that a ''snapshot'' of the system would reveal a specific distribution of clusters, each exhibiting large-amplitude, nonequilibrium displacements characteristic of thermally excited soft vibrational modes (somewhat related to Stillinger and Weber's picture[7] or the liquid structures proposed by Benson[8]).

While the lifetimes of individual clusters are expected to be much shorter than those of molecular isomeric species, the QCE methodology should correctly model the long-time thermodynamic and spectroscopic responses, as long as cluster binding energies appreciably exceed kT (a condition readily achieved for H-bonded liquids). Note that the QCE-predicted cluster structures depend sensitively on enthalpic (binding energy) and entropic (vibrational) factors of quantal character,[1] and thus differ significantly from those inferred from conventional molecular dynamics simulations employing empirical potentials of electrostatic/polarization form.

Previous tests of QCE theory involved liquids such as water,[2] formamide,[2] and ammonia[9] for which suitable T,P-dependent spectroscopic comparisons were available. However, such liquid-phase comparisons are generally limited by the characteristic experimental difficulties (such as spectral broadening of IR lines) as well as by the required theoretical convolutions (involving averaging over both cluster components and overall cluster populations) to relate theory to experiment. Gas-phase measurements, although inherently of higher accuracy, commonly provide fewer checks on the accuracy of QCE theory since the vapor-phase cluster distribution is typically dominated by monomers and exhibits no significant T,P-dependent detail. See Refs. 4 and 5 for a more detailed account of QCE theory.

Formic acid represents a well-known exceptional case. Notorious difficulties (including decomposition to H_2O and $CO^{10,11}$) render many liquid HCOOH measurements problematic. Furthermore, the unusual degree of HCOOH clustering in the vapor phase[10] complicates routine determination of gas/liquid thermodynamic properties. For example, the critical point of HCOOH has not been satisfactorily measured,[12] and the standard enthalpy of vaporization (ΔH_{vap}) cannot be reliably determined from vapor pressure measurements, due to complete breakdown of the Clausius–Clapeyron approximation. Furthermore, ΔH_{vap} for HCOOH is known to exhibit a highly anomalous *increase* with temperature over the liquid range, contrary to the ''expected'' decrease that is observed in most liquids. Thus, formic acid presents a unique challenge to conventional pictures of the liquid phase.

We applied QCE theory to formic acid, based on nine basic cluster species (one monomer, three dimers, three trimers, two tetramers) calculated at the B3LYP/6-31+G* level of hybrid density functional theory, as implemented in GAUSSIAN 94.[13] Of these nine clusters, only four were found

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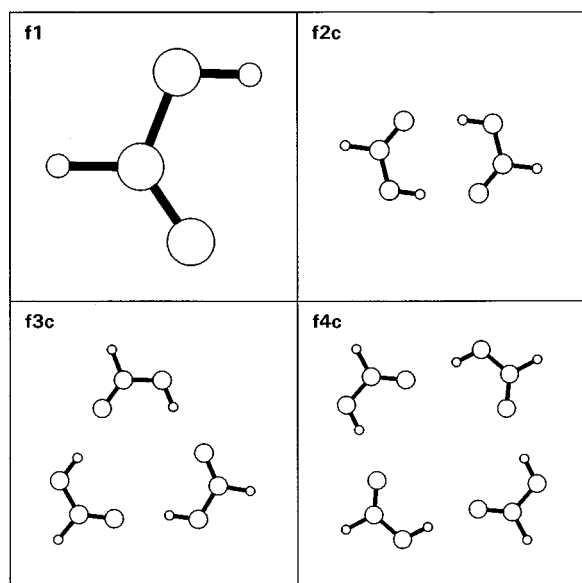
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FIG. 1. Optimized B3LYP/6-31+G* structures for leading formic acid clusters of the QCE liquid/vapor distributions.
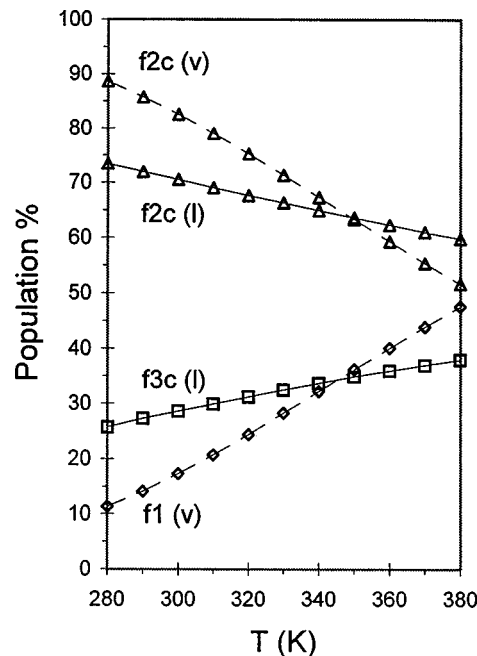

FIG. 2. T-dependence of QCE predicted populations for coexisting liquid and vapor phases of HCOOH in the range 280–380 K. Note that the plotted populations give the percent of clusters (not molecules) present; at 280 K, for example, 26% of the clusters are $f3c$, corresponding to 34% by weight in this cluster.

to have significant populations and are shown in Fig. 1. Figure 2 exhibits the calculated QCE population distributions of coexisting liquid and gaseous phases of HCOOH over the approximate liquid range 280–380 K. As shown in this figure, the QCE liquid phase consists primarily of cyclic dimer ($f2c$) and trimer ($f3c$), with trace ($\sim1\%$) contributions from cyclic tetramer and higher clusters. The absence of monomer in the liquid over this temperature range is consistent with IR and Raman spectra taken over the range 283–353 K.[14] Surprisingly, the proportion of larger $f3c$ clusters is

found to *increase* with temperature in this range, contrary to the pattern commonly seen in other liquids. The calculated QCE ΔH_{vap} is 14.9 kJ/mol at standard-state conditions and increases with T to 21.3 kJ/mol at the normal boiling point, qualitatively consistent with the experimental values of 20.1 and 22.3 kJ/mol.[10] Enthalpic and entropic origins of the ''in-
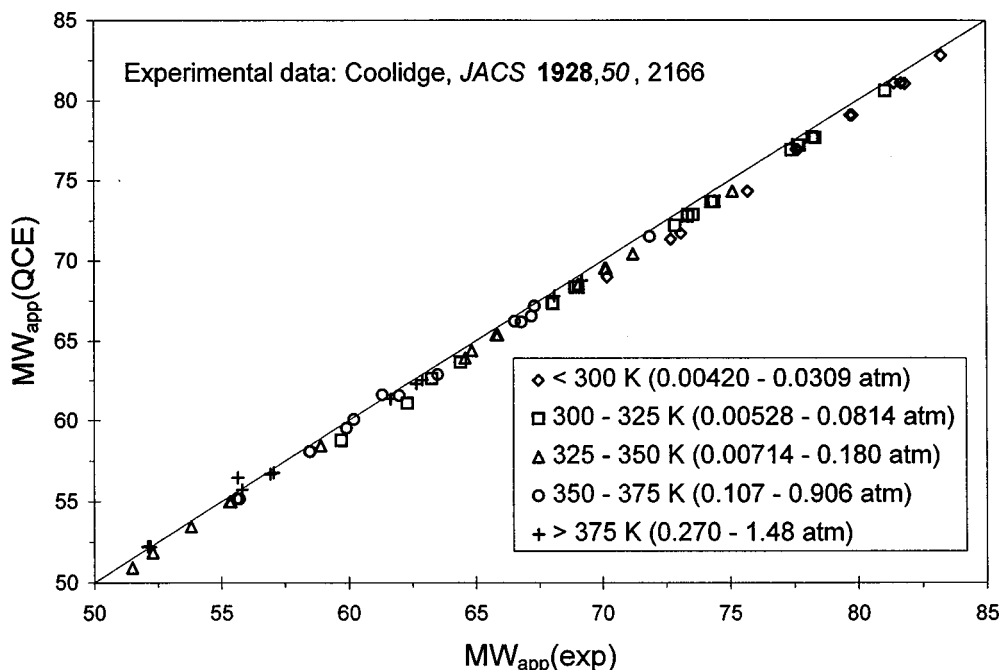

FIG. 3. Global comparison of theoretical (QCE, this paper) vs experimental (Coolidge, Ref. 10) vapor-density for HCOOH, expressed in terms of apparent molecular weight (MW_{app}). The inset identifies temperature and pressure ranges for each set of data points, spanning all measurements of Ref. 10. The solid line represents a theoretically ''perfect'' fit with zero intercept and unit slope.

verted'' T-dependent clustering patterns, as well as more detailed comparisons with liquid-phase experimental properties, will be discussed elsewhere.

However, the vapor phase provides a much cleaner and more stringent test of QCE predictions, based on previous experimental studies of its cluster composition. Coolidge's vapor-density measurements[10,11] (supplemented and confirmed by Stout[15]), coupled with Millikan and Pitzer's conclusive IR identification[16] as well as Bertie and Michaelian's Raman identification[17] of gaseous $f1$, $f2c$ species, provide a definitive experimental measure of the $f1/f2c$ population ratio over a remarkably broad range of T, P conditions. As shown in Fig. 2, QCE correctly predicts that the HCOOH vapor phase consists primarily of $f1$ and $f2c$ clusters (with $\sim 1\%$ of $f3c$), consistent with spectroscopic evidence. Coolidge[10] expressed his measurements in terms of the ''apparent'' molecular weight (MW_{app}) at each $T, P,$ obtaining values that varied widely (50–85 amu) with respect to the true molecular weight of 46 amu.

We carried out a direct comparison of MW_{app}(QCE) vs MW_{app}(exp) for all of Coolidge's measurements by simply computing the corresponding QCE-weighted MW_{app}(QCE) from QCE vapor populations at each T, P, as summarized in Fig. 3. Clearly, the QCE results are in excellent agreement with experiment, with the best regression fit (slope=1.018, intercept=-0.676, R^2=0.999) differing only insignificantly from the theoretically ''perfect'' fit with zero intercept and unit slope (shown in the figure). As shown in the figure inset, the measured points of Fig. 3 span a wider range of T, P than in Fig. 2, including values far from the standard-state conditions where the two QCE ''empirical parameters''[6] were determined. It is therefore gratifying that the accuracy of the QCE results appears rather uniformly high over this range. Compared to experiment, the QCE results suggest very slightly higher average monomer concentration, with a standard deviation of only 0.7% for *all* temperatures and pressures measured, well within the expected experimental and theoretical uncertainties.[18]

The present work provides the first direct and detailed test of QCE-predicted cluster populations for a vapor-phase system in equilibrium with a dense fluid in which hydrogen-bond clustering can be clearly quantified. The high accuracy of the QCE predictions for formic acid vapor offers considerable support for the general usefulness of B3LYP/6-31+G* binding energies and vibrational frequencies, as well as the reasonableness of QCE model assumptions. A more comprehensive discussion of QCE liquid and vapor cluster compositions of formic acid, individual cluster species, and comparisons with experiment will be presented in a full paper.

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[6] Neglected cluster–cluster interactions are approximated by a simple mean-field corrections factor (a_{mf}), proportional to system density. Estimated molecular volumes (based on empirical van der Waals radii) are corrected by an overall scaling factor (b_{vol}) to fix system density at a single point. In the present case, the two QCE correction factors were taken as $a_{mf}=0.165(\times 10^{-6})$, $b_{vol}=1.613$ to fix the boiling point (373.65 K) and molar density (37.7 mL/mol) of HCOOH at standard-state conditions; see Ref. 1.

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[18] For example, the average 1.1% difference in monomer population could arise from only a 0.2 kJ/mol error in dimer binding energy.