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Quantum-mechanical solution to fundamental problems of classical theory of water vapor nucleation

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The inconsistent temperature dependence of nucleation rates, disagreement of theoretical critical or onset supersaturations with experimental data, and insufficiently accurate predictions of nucleation rates are fundamental problems of the classical nucleation theory (CNT) of water vapors, which is a foundation of various multicomponent nucleation models widely used in the aerosol microphysics, physical chemistry, and chemical technology. In the present study, a correction to the CNT obtained from "first principles" has been derived and significant progress has been made in solving the fundamental problem of predicting nucleation rates of water vapors. The modified model with the quantum-mechanical correction incorporated is in very good agreement with experiments over the full range of temperatures ($T=210-290$ K), saturation ratios ($S=2-100$), and nucleation rates ($J=\sim 10^{1}-10^{17}$ cm^{-3}).

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INTRODUCTION

The formation of the new disperse phase via homogeneous nucleation is important wherever the first-order phase transitions occur. New particle formation is an important source of atmospheric aerosols, which are largely responsible for the uncertainties in global climate change predictions, and plays a critical role in a number of technologies related to synthesis of nanomaterials, air quality, and chemical industry [1–4]. The classical theory of homogeneous nucleation of water vapor is a foundation of multicomponent water-trace gases and water-organics nucleation models used to predict the atmospheric aerosol formation and simulate technological processes [5–11]. The classical nucleation theory (CNT) was originally derived by Volmer and Weber [12] and Becker and Doring [13]. The commonly used Becker and Doring [13] version of the CNT (BD) [see Fig. 1(a)] provides a qualitative agreement with experiments; however, temperature and, at a lesser degree, saturation dependencies of predicted nucleation rates are inconsistent with experimental data.

In addition to the above-mentioned predictivity issues, there exist serious problems with the theoretical foundation of the BD model, which include the violation of the mass action law and mismatch for i-mers at $i=1$ in the cluster distribution caused by a mistaken assignment of nonzero Gibbs free energy to the $0\rightarrow 1$ transition. These fundamental shortcomings have been corrected [19–22]; however, the more robust model [19], best known as the self-consistency corrected classical theory [SCC CNT, Fig. 1(b)], grossly overpredicts nucleation rates [noting that lines in Fig. 1(b) are scaled by a factor of 0.001]. A number of attempts to correct the theory of homogeneous nucleation in water vapors have been made in the past by using empirical scaling factors to the CNT [23–25] and molecular models based on empirical interaction potentials [26–30]. The empirical scaling allows achieving agreement between theory and experiments; however, it is unable to provide any new information about the molecular nature of nucleation phenomena. More advanced molecular-based methods have also been used to study the water vapor nucleation; however, the molecular-based predictions of nucleation rates are available at few temperatures only. Merikanto with co-workers [29,30] have carried out Monte Carlo TIP4P simulations of nucleation rates at $T=240$ K; however, a scaling factor of $10^{2}-10^{3}$ is needed in order to achieve the agreement between their model and experiments. The predictions by dynamical nucleation theory (DNT) [28] at 244 K are in agreement with the experimental data at 240 K. The observed agreement is not a sign of perfection because a factor of $\sim 10^{2}$ should be applied to the computed nucleation rates in order to account for the temperature difference.

It is clear that the accurate theoretical description of nucleation phenomena in water vapors is critically important, and that the further progress in the development of muticomponent nucleation theories may be achieved with the reduction of uncertainties in the CNT, on which most of the existing multicomponent nucleation theories are based. In order to reduce these uncertainties, the fundamental problems of the CNT must be resolved.

In the present paper, we attack the fundamental problems of the CNT by applying the quantum-mechanical correction to the CNT thermochemistry. The thermodynamical properties of i-mers obtained from the "first principles" have been incorporated in the framework of the self-consistency corrected CNT, and a modified model of the homogeneous nucleation in water vapor has been derived.

METHODS

The homogenous nucleation in water vapors is described schematically by the $(H_2O)_{i-1}+H_2O\rightarrow(H_2O)_i$ reaction underlying the i-mer formation by addition of monomer. The nucleation rate [31] is expressed as

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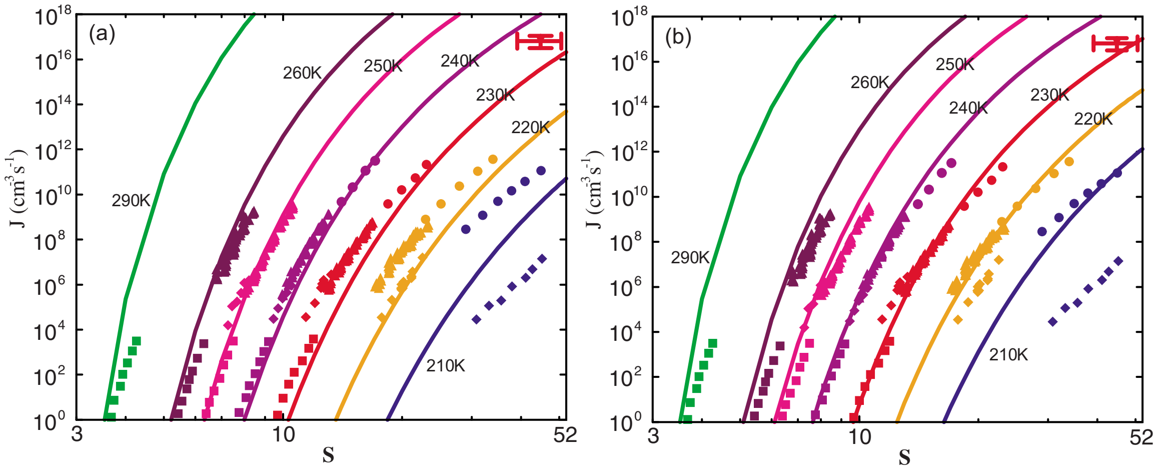

FIG. 1. (Color online) The comparison of theoretical predictions of nucleation rates J ($\mathrm{cm}^3\ \mathrm{s}^{-1}$) given by the (a) original Becker-Doring theory and (b) self-consistency corrected classical theory (scaled by a factor of 0.001) with the experimental data [14–18]. Lines (theoretical predictions) and symbols (experimental data) of the same color are for the same temperature.

$$J = N_1\left(\sum_{i=1}^{\infty}\frac{1}{\beta_i f_i}\right)^{-1}, \tag{1}$$

where β_i is the cluster forward rate, N_1 is the monomer concentration, and f_i,

$$f_i = \exp\left(-\frac{\Delta G_i(N_1,T)}{kT}\right), \tag{2}$$

is controlled by the Gibbs free energy change ΔG_i. The total Gibbs free energy change associated with the i-mer formation is expressed in the SCC CNT by the following equation:

$$\Delta G_i^{SCC} = -(i-1)kT\ln S + 4\pi(r_i^2 - r_1^2)\sigma, \tag{3}$$

where S and $\sigma=\sigma(T)$ are the saturation ratio of nucleating species defined as the ratio between the pressure of nucleating vapor and saturated vapor pressure, and specific surface free energy, respectively.

It is long known that the application of the bulk liquid-capillarity approximation to treat the thermodynamic properties of molecular clusters in the CNT can be an important source of uncertainties in nucleation rates. Recent theoretical [30,32] and experimental studies [33] suggest that the failure of the capillarity approximation is associated with initial ($i < \sim 10$) growth steps. In the present study, the SCC CNT has been corrected using enthalpies, entropies, and Gibbs free energies for small clusters $(H_2O)_i$ ($i=1-10$) calculated using highly accurate *ab initio* based model chemistries. The thermochemical properties of the small clusters are calculated assuming well-defined geometries. The thermochemical data for larger clusters $(H_2O)_i$ ($i>10$) were derived using the standard capillarity approximation. The key difference between the classical theory and the modified nucleation model is that the first formation steps, to which the capillarity approximation is not applicable, are treated using more rigorous quantum methods. Computational quantum methods G3 and G3MP2 used in the present study were developed to predict highly accurate energies and they are often used as the reference methods in energy calculations due to the high reliability. These theories have been tested on hundreds of species [34,35] and have been proven to be highly accurate in predicting the cluster energies. Both G3 and G3MP2 are compound *ab initio* based methods involving a number of basis sets and advanced theoretical corrections to provide good energy calculations. The G3 and G3MP2 methods are effectively at the QCISD(T) level (quadratic configuration interaction with single and double excitations and triple excitations added perturbatively) with prescribed large basis sets and provide accurate energies of the formation well within the uncertainties in the experimental data for a large set of test molecules and complexes. The vibrational frequencies in both methods are scaled in order to achieve a good agreement between the theory and experiments and to account for the vibrational anharmonicity. Both G3 and G3MP2 agree with experimental water dimerization free energy at 298 K well within the experimental uncertainty [36]. The test results show that G3 and G3MP2 predictions for $i=2-6$ agree within ~ 0.3 kcal mole^{-1}. Although large number of quantum-chemical studies of water clusters has been published in the past, the information on thermodynamics of $(H_2O)_i$ clusters became available only recently. Dunn *et al.* [36] have performed a comprehensive study of thermochemical properties of $(H_2O)_i$ ($i=2-6$) using several model chemistries. They concluded that *ab initio* based model chemistries CBS-APNO, Gaussian-2 (G2), and Gaussian-3 (G3), which were developed to provide accurate energies and are often used as the reference methods in energy computations, give very close results. Due to the prohibitively high computational costs, no thermochemical data for larger clusters are available at the present time. In the present study, recently published G3 data [36] were used for $(H_2O)_i$ ($i=1-6$). A more affordable, yet accurate, G3MP2 method [37] was employed to study $(H_2O)_i$ ($i=6-10$) in the present work. The computations have been carried out using the GAUSSIAN 03 suite of programs [38]. The thermochemical properties of individual conformers have been calculated using equilibrium (optimized) geometries and calculated vibrational frequencies. The vibrational anharmonicity in both G3 and G3MP2 methods is accounted for by using the scaling fac-

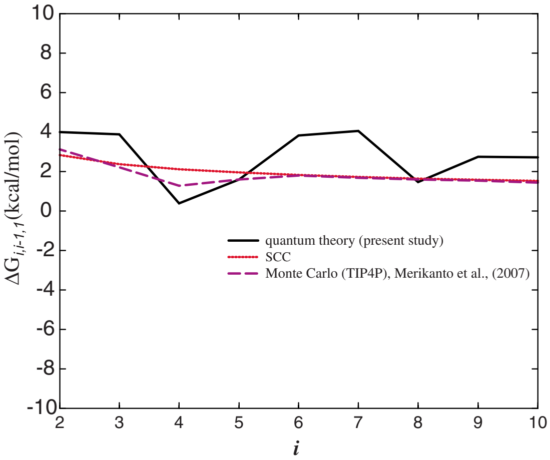

FIG. 2. (Color online) Comparison of stepwise Gibbs free energy changes $\Delta G_{i,i-1,1}$ associated with formation of neutral clusters via $(H_2O)_{i-1}+H_2O \rightarrow (H_2O)_i$ reaction at $T=298$ K and $S=1$.

TABLE I. Calculated stepwise $\Delta H^0_{i,i-1,1}$ and $\Delta G^0_{i,i-1,1}$ of the reaction: $H_2O_{n-1}+H_2O=H_2O_n$ by G3, G3MP2, classical nucleation theory, and experimental studies.

	$\Delta H^0_{i,i-1,1}$ (kcal/mol)		$\Delta G^0_{i,i-1,1}$ (kcal/mol)		
n	G3,[a] G3MP2[c]	Expt.[b]	G3,[a] G3MP2[c]	Expt.[b]	CNT
1					2.77
2	−3.51[a]	−3.59 ± 0.5	1.94[a]	1.95 ± 0.9	0.78
3	−8.52[a]		1.83[a]		0.32
4	−10.46[a]		−1.66[a]		0.07
5	−7.43[a]		−0.46[a]		−0.1
6	−6.96[a]		1.77[a]		−0.23
7	−6.89[c]		2.00[c]		−0.33
8	−1.50[c]		−0.60[c]		−0.41
9	−6.57[c]		0.69[c]		−0.48
10	−8.67[c]		0.66[c]		−0.53

[a] Reference [36].
[b] Reference [47].
[c] G3MP2 data (this study).

tors providing a good agreement between the theory and experiments.

For each class of *i*-mers a number of isomers were sampled and the obtained optimized equilibrium structures of global and local minima have been used to compute the standard partition functions and the Boltzmann-Gibbs average energy for each *i*. The conformational search for $(H_2O)_n$ ($n=6-10$) have been performed in the present study using optimized structures obtained in the most complete up-to-date studies of water clusters [36,39–41] as some of the guess geometries. The corresponding partition functions have been computed and the contribution of local minima to the total Gibbs free energy of *i*-mers has been calculated. The calculations show that the contribution of local minima to the total Gibbs free energy of *i*-mers formation is mild (<0.23 kcal mole^{-1} for the total Gibbs free energy changes associated with the 10-mer formation). The information on the optimized structures and energies of 6, 7, 8, 9, and 10-mers obtained in the present study (over 30 equilibrium conformers in total) can be found in the supplementary information [42]. The Gibbs free energies computed by quantum-chemical methods have been used for the calculations of stepwise changes in the Gibbs free energy associated with $(H_2O)_{i-1}+H_2O \rightarrow (H_2O)_i$ reaction. The obtained stepwise changes in the Gibbs free energy have been used for kinetic calculations of cluster distributions and nucleation rates using Eqs. (1) and (2).

RESULTS

Figure 2 shows the stepwise Gibbs free energy changes ($\Delta G_{i,i-1,1}$) associated with formation of $(H_2O)_i$ ($i=2-10$) via $(H_2O)_{i-1}+H_2O \rightarrow (H_2O)_i$ reaction at $T=298$ K and $S=1$. The derivation of $\Delta G_{i,i-1,1}$ in Fig. 2 is based on the stepwise Gibbs free energy changes ($\Delta G^0_{i,i-1,1}$) at standard state ($T=298$ K and $P=1$ atm) which is given in Table I. The details on the $\Delta G_{i,i-1,1}$ derivation were given in supplementary information [42]. The comparison of curves in Fig. 2 presenting calculations of stepwise Gibbs free energy changes shows that the difference between the classical theory, molecular-based Monte Carlo TIP4P study [30], and quantum methods in the region of small *i* is considerable. Another interesting observation is that $\Delta G^0_{i,i-1,1}$ for neutral $(H_2O)_i$ clusters converges to the bulk value a bit slower than that for ions [32] and at $i=10$ $\Delta G^0_{i,i-1,1}$ was not yet fully converged into the bulk value. At the present time, no data needed for a thorough assessment of this phenomenon are available and thus further experimental work is needed in order to assess this issue. The comparison of the modified model predictions with the experimental data [14–18] and most accurate empirical scaling nucleation models [23–25] in terms of nucleation rate and onset saturation ratio are presented in Figs. 3 and 4, respectively.

As seen from the comparison of curves for nucleation rates in Figs. 1 and 3, the modified nucleation model using thermodynamics obtained from "first principles" agrees well with experimental data over the full range of experimental conditions and outperforms both SCC CNT and BD theories. A comparison of curves in Figs. 3 and 4 also shows that the temperature and saturation dependencies of theoretical nucleation rates and onset saturations given by the modified model are in agreement with experiments. This is a clear indication that a significant progress has been made in solving the fundamental problem of predicting nucleation rates of water vapors. The modified model agrees well with experiments [43] [see Fig. 4(a)], in which the number of molecules in the critical cluster is ~10–20 (based on the classical theory). However, the nucleation rates obtained in [44] at similar conditions are ~3–4 orders of magnitude higher. Further experimental work is needed to identify the source of the experimental uncertainties.

The comparisons of nucleation rate and onset saturation given in Figs. 3 and 4 show that the modified model with the quantum-mechanical correction incorporated agree well with experiments in nearly all the cases studied here. The modified model outperforms both BD theory, SCC CNT, and

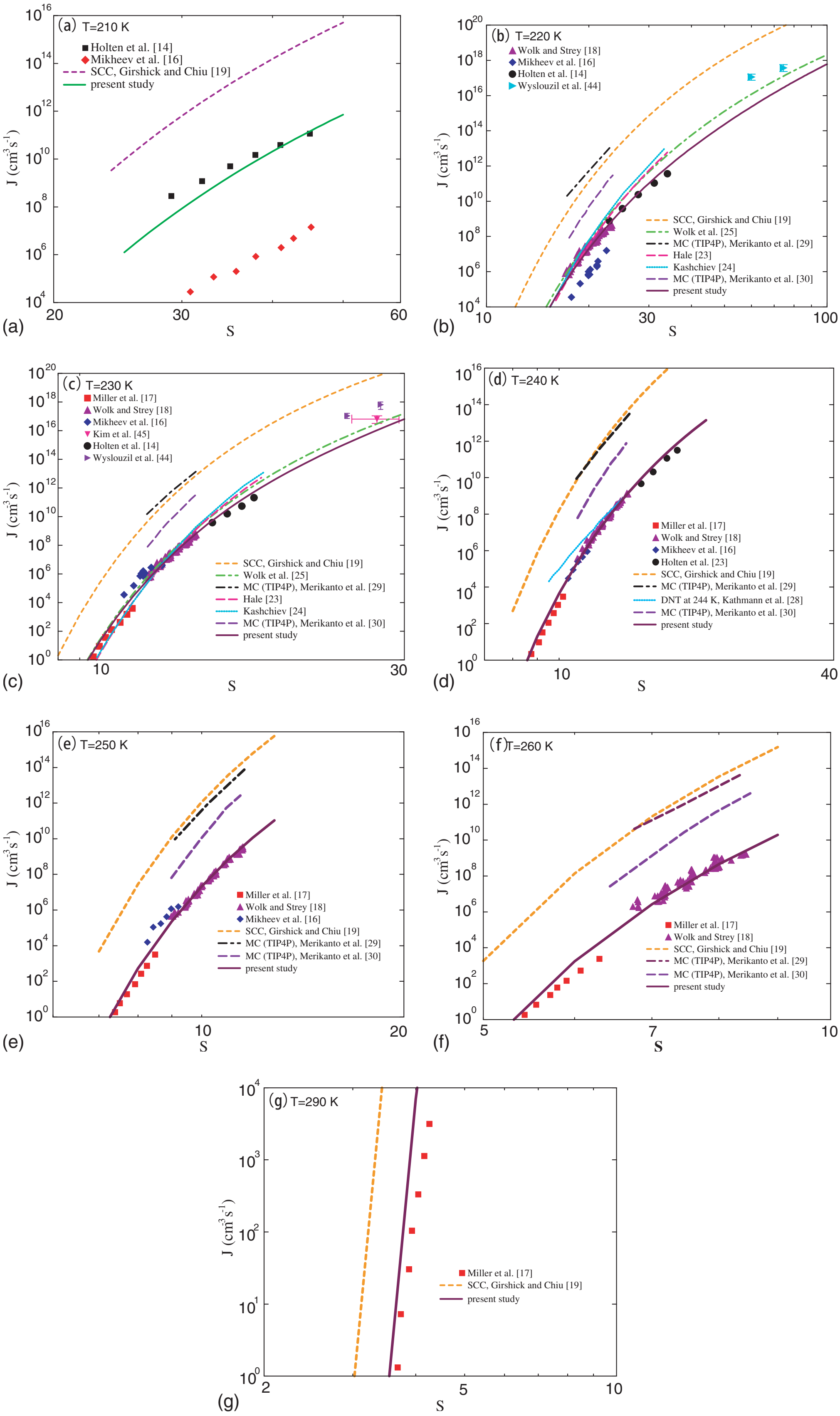

FIG. 3. (Color online) A comparison of nucleation rates J (cm^3 s^{-1}) obtained using the modified model derived in the present study with the experimental data [14–18,43,44].

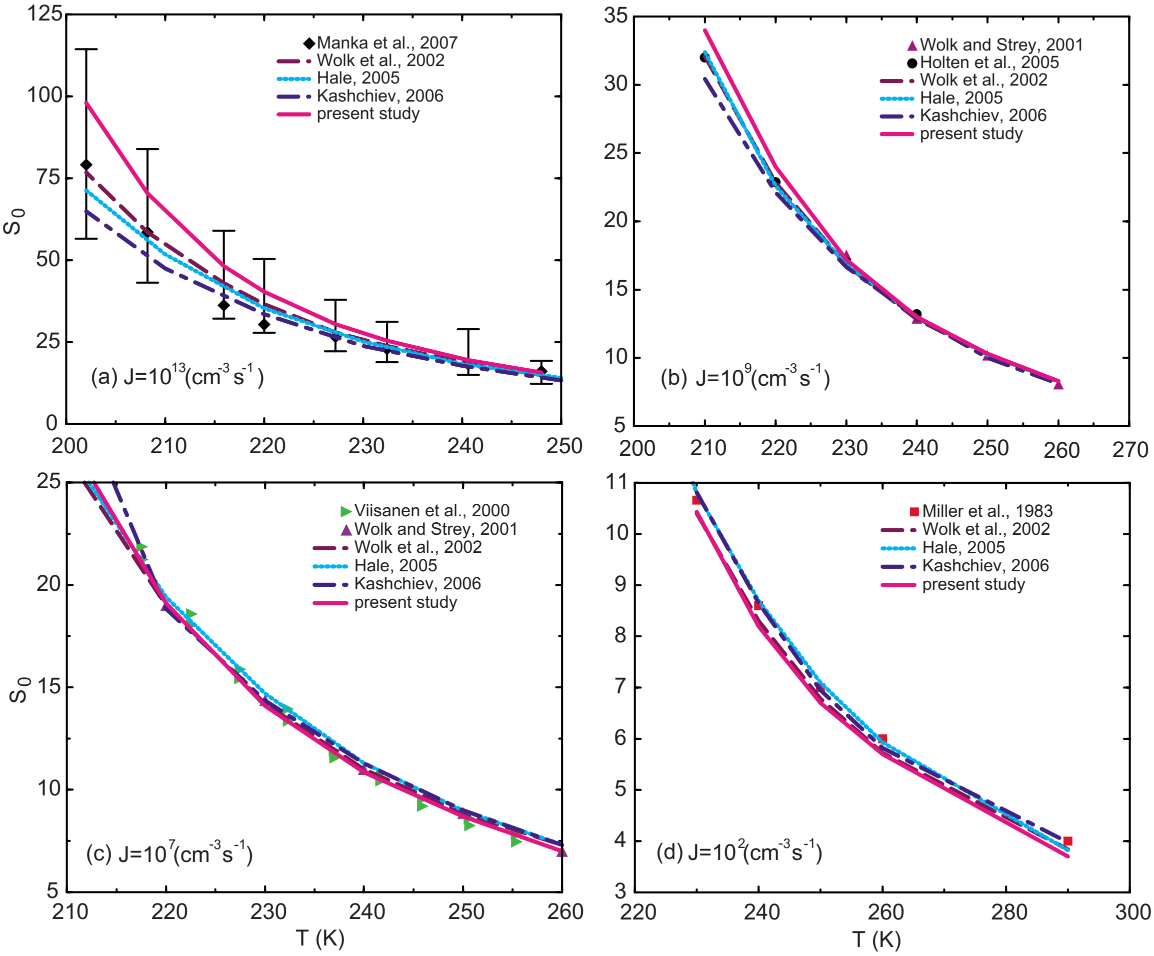

FIG. 4. (Color online) Comparison of predicted onset saturation ratios with experiments [14–18,43,45–47] and empirical scaling models [23–25] for (a) $J = 10^{13}$ cm^{-3} s^{-1} (b) $J = 10^{9}$ cm^{-3} s^{-1}; (c) $J = 10^{7}$ cm^{-3} s^{-1}; (d) $J = 10^{2}$ cm^{-3} s^{-1}. The error bars for Fig. 4(a) were estimated from the experimental uncertainties in the nucleation rates using [25].

molecular-based nucleation models [28–30] and stays in line with the most accurate empirical scaling models [23–25].

SUMMARY

In this paper, a modified model of nucleation in water vapor has been derived and fundamental problems of temperature and saturation dependencies of nucleation rates in the CNT have been largely solved. The modified model is an extension of the classical nucleation theory, and can explain the disagreement between theory and experiments. The disagreement that is caused by the inappropriate treatment of the thermodynamic properties of small water clusters in classical nucleation theory has been resolved in the present study. It has been pointed out that the application of the quantum-chemical methods systematically improves the CNT predictivity, substantially reduces uncertainties in nucleation rates, and allows achieving good quantitative agreement between the theory and experiments. The modified model with the quantum correction incorporated is in very good agreement with experiments over the full range of temperatures ($T = 210-290$ K), saturation ratios ($S = 2-100$), and nucleation rates ($J = \sim 10^{1}-10^{17}$ cm^{-3}). The present work highlights the critical importance of the rigorous (presumably quantum) treatment of pre-nucleation clusters, and its results are encouraging for the further applications of the quantum-chemical approach to multicomponent nucleation models widely used in the atmospheric research, physical chemistry, and chemical technology.

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