Quantum Nature of the Sign Preference in Ion-Induced Nucleation

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(Received 24 July 2005; published 30 March 2006)

Observed first in Wilson's pioneering experiments in the cloud chamber, the sign preference has remained a mystery for more than a century. We investigate the sign preference using a quantum approach and show that this puzzling phenomenon is essentially quantum in nature. It is shown that the effect of the chemical identity of the core ion is controlled by the electronic structure of the core ion through the influence on the intermolecular bonding energies during the initial steps of cluster formation. Our results demonstrate the superiority of the quantum approach and indicate fundamental problems of conventional ion-induced nucleation theories, in which the electronic structure of the core ion is either ignored or not treated rigorously.

DOI: 10.1103/PhysRevLett.96.125701 PACS numbers: 64.60.Qb, 61.46.−w

Nucleation on ions is one of the major nucleation mechanisms in the Earth's atmosphere, and it plays a decisive role in a number of climate-related processes [1–5] and various technologies, including removal of toxic metals from air and fabrication of nanoparticles [6–8]. The presence of ions, which essentially work as a catalyst, helps to overcome the nucleation barrier and leads to significant enhancement in nucleation rates [2,9,10]. Strong interactions between ionic clusters and dipolar atmospheric precursors, common pollutants, and toxic and chemically active substances promote the formation of ultrafine aerosol particles [2,9,11] that are associated directly with adverse public health effects [12–14].

Wilson's 1897 pioneering cloud chamber experiments [15] demonstrated that ions of opposite sign exhibited significantly different nucleation rates. Later nucleation experiments have shown that in a number of systems nucleation rates of positive and negative ions are different [15–21]. This phenomenon is known as the sign preference and has remained a mystery for more than a century [16–28]. Despite impressive progress of experimental methods since Wilson's original work, precise nucleation measurements remain difficult due to uncertainties in their interpretation, and many important experimental results remain controversial [18–21]. A classical example of such a controversy is the sign preference for water. Wilson in his original experiments [15] found that, in the presence of an external electrical field, droplets nucleated more efficiently on negative ions. However, ninety years later, Rabeony and Mirabel [18] reported that the sign preference of water was not detectable if an external electric field was not applied. The uncertainties in the interpretation of the experimental data are largely caused by the lack of a clear and insightful understanding of the molecular nature of the ion-induced nucleation phenomena and the absence of a theory that can properly account for the critically important [17] effect of the chemical identity of the core ion on cluster formation.

Classical bulk liquid theory [28], which has been criticized in a number of studies for the application of bulk surface tension and density to molecular clusters and sensitivity to poorly defined input parameters, is still used almost exclusively in the interpretation of ion-induced nucleation experiments. The theoretical formalism of the classical approach has recently been improved and extended through the incorporation of the effect of the polar host vapor molecule-charged cluster interactions, and some of the serious shortcomings of the original model have been successfully corrected [9,10]. However, a theoretical description of the effect of the chemical identity of the core ion on the gas-to-particle conversion is still lacking.

Continuously growing interest in the ion-induced nucleation during the past decade has resulted in a number of molecular-based theories dedicated to the sign preference. Semiquantitative molecular theory [22,23] explains the sign preference by the ''asymmetric nature of the molecular interactions.'' Recent molecular dynamics work [24] concludes that nucleation of negative ions is stronger because anionic clusters are more compact than cationic. The umbrella-sampling Monte Carlo study [25] suggests that anions are better nucleators because ''the average anion-H distance is considerably shorter than the average cation-O distance.'' Molecular-based theory [26] attributes the sign preference to the asymmetric effect of the electrical field on the surface tension.

Theories [22–26] conclude that the sign preference is governed by the ion sign alone. In contrast, a novel dynamical nucleation theory (DNT) [27] suggests that taking into account the ion sign alone is insufficient and that core ion properties can be adequately described using ion size and ion sign as the key parameters. Despite the difference in the theoretical approaches and explanations given to the sign preference, all the theories [22–27] reach the identical conclusion that ''generally'' water prefers anions.

In order to solve the fundamental problem of the sign preference, one has to address the following questions:

(a) What are the mechanisms responsible for and what are the key parameters controlling the sign preference? (b) Which stage/stages of the cluster growth play a decisive role in the formation of the sign preference?

In this Letter, we attack the fundamental problem of the sign preference by employing a higher level theory such as quantum mechanics. It has long been known that the chemical identity of an atom, molecule, or molecular ion relates directly to its electronic structure or, in other words, the space distribution of the electronic density, which is described by a wave function [29]. In order to study the structure and thermodynamic properties of clusters formed over the core ions of different sign and chemical composition, the quantum density functional theory at the PW91PW91/6-311 + $+G(3df, 3pd)$ level has been applied. The choice of the PW91PW91 method [30] is based on comprehensive study [31] and our own tests [32]. The 6-311 + $+G(3df, 3pd)$ basis set [33] has been selected based on its size, a moderate basis set superposition error, and the ability to reproduce with sufficient accuracy (within less than 1% in the dipole moment) the distribution of the electronic density on the water molecule. Core ions (Li^+, Na^+, OH^-, H_3O^+, and Cl^-) have been selected in such a way so as to represent species of different chemical nature (alkali metals, hydrogen bonded complexes, and halogen) and sign. Optimized cluster geometries reported in Refs. [34–39] were used as initial geometries for $Li^+(H_2O)_n$ and $Na^+(H_2O)_n$, $OH^-(H_2O)_n$, $Cl^-(H_2O)_n$, and H_3O^+ $[(H_2O)_n]$, respectively. Figure 1 presents examples of the optimized structures of the most stable water clusters formed over different core ions and electrostatic potential (ESP) for monohydrates formed over a water cation and anion.

Although the theoretical formalism of the classical [9,28] and molecular-based approaches [22–27] is generally different, they have a lot in common. Most of the ion-induced nucleation theories treat the cluster thermodynamics using one or more bulk liquid properties (density, surface tension, vapor pressure) and assume that a spherical liquidlike cluster or droplet with a spherically symmetric electrostatic potential is formed over the spherical core containing a point charge at its center. Figure 1 shows that clusters formed over different core ions have a variety of shapes and they do not look like uniform compact spheres. It is important to note that these molecular clusters are too small to bring the surface forces [26] into play. As seen from Figs. 1(f) and 1(g), the ESP for both $OH^-(H_2O)$ and $H_3O^+(H_2O)$ formed over a water anion and a cation, respectively, has a complex nonspherical shape. Another important detail is that the O-O distances for water molecules bonded directly to each other in clusters formed over different core ions are in the range of ~2.8–2.9 Å that is typical for ice rather than for bulk liquid water. Conclusions about the structure of anionic and cationic clusters containing an equal number of water molecules made in recent molecular-based theories [24,25] were not confirmed in the present study. We found that in a number of cases the average anion-H distance can be longer than the average cation-O distance and that a maximum interatomic distance in a cationic cluster can be shorter than that in an anionic cluster.

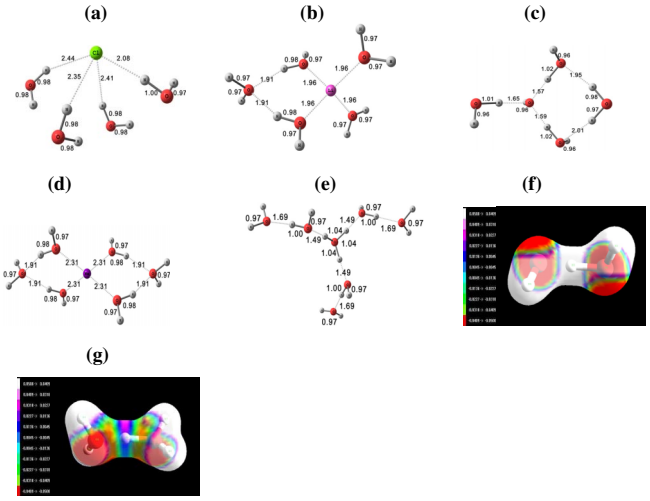

FIG. 1 (color online). Optimized structures and bond lengths (Å) of most stable isomers of (a) $Cl^-(H_2O)_4$, (b) $Li^-(H_2O)_5$, (c) $OH^-(H_2O)_4$, (d) $Na^+(H_2O)_5$, and (e) $H_3O^+(H_2O)_6$ and ESP for (f) $OH^-(H_2O)$ and (g) $H_3O^+(H_2O)$. ESP of $OH^-(H_2O)$ and $H_3O^+(H_2O)$ ground states is mapped onto the electron density surface for the ground state. The color map shows the electrostatic potential energy (in hartrees) for the various colors. The red end of the spectrum shows the regions of highest stability for a positive test charge, while magenta/blue shows the regions of least stability for a positive test charge.

These findings lead us to conclude that the simplistic representation of a cluster formed over a core ion as a uniform liquidlike sphere carrying a centered point charge, an approximation commonly used within the nucleation field, is unlikely realistic.

Figure 2 compares the Gibbs free energies $\Delta G_{n,n-1}$ obtained in the present study with experimental data [40–44] and predictions of recent molecular-based theories [25,27]. $\Delta G_{n,n-1}$, which controls the cluster stability, is expressed as

$$\Delta G_{n,n-1} = \Delta H_{n,n-1} - T\Delta S_{n,n-1}, \quad (1)$$

where $\Delta H_{n,n-1}$ is the enthalpy change, $\Delta S_{n,n-1}$ is the entropy change, subscript $n, n-1$ refers to the $X^{\pm}(H_2O)_{n-1} + H_2O = X^{\pm}(H_2O)_n$ process, $X^{\pm}$ refers to the core ion, and T is the ambient temperature.

As seen from Fig. 2(a), quantum theory predicts, in good agreement with the experimental data, a very strong influence of the chemical nature of the core ion on the thermodynamics of the first several steps of the cluster growth. Moreover, there is a clearly visible difference in the thermodynamics of ions of like sign but different chemical nature. The difference in thermodynamic stability between dimers formed from different solvated monomers exceeds ~15 kcal mol^{-1}; however, it decreases quickly as the clus-

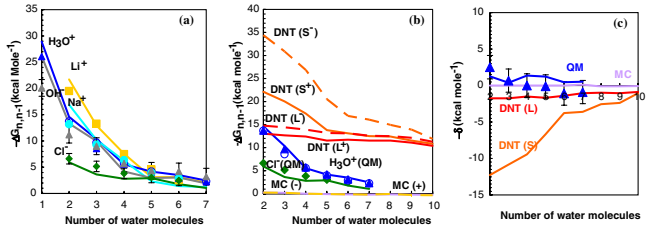

FIG. 2 (color online). Comparison of experimental and theoretical values of the Gibbs free energy $\Delta G_{n,n-1}$ for $X^{\pm}(H_2O)_{n-1} + H_2O = X^{\pm}(H_2O)_n$ reactions [(a),(b)] and the difference in the Gibbs free energy $\delta(j)$ between j-mers formed over core ions of opposite sign (water cation and water anion) (c). Curves and symbols of the same color refer to theoretical results and experimental data, respectively. Abbreviations DNT, MC, and QM refer to the dynamic nucleation theory [27], the Monte Carlo study [25] (four-point transferable intermolecular potential water), and the present study, respectively. Symbols L and S refer to core ions of indeterminate composition of 0.1 and 1 nm radius, respectively [27]. Subscripts "+" and "−" refer to the charge polarities. Experimental data for $Li^-(H_2O)_n$ [42], $Na^+(H_2O)_n$ [42], $OH^-(H_2O)_n$ [44], $H_3O^+(H_2O)_n$ [40,41], and $Cl^-(H_2O)_n$ [43] were used. Experimental values of $\delta(j)$ [blue triangles in Fig. 2(c)] were calculated from the experimental data for $H_3O^+(H_2O)_n$ [41] and $OH^-(H_2O)_n$ [44]. The calculations were performed at the ambient temperature of 298.15 K and ambient pressure of 101.3 KPa.

ter grows, approaching ~ 2 kcal mol^{-1} at $n = 5$. Since the typical experimental uncertainty is on the order of several kcal mol^{-1} [45], the difference in $\Delta G_{n,n-1}$ at $n \geq 5$ between clusters formed over ions of different chemical nature cannot be distinguished statistically anymore. This finding is supported by the analysis of the large NIST database [45] on water clustering, which shows [46] that experimental $\Delta G_{5,4}$ and $\Delta G_{6,5}$ for clusters formed over core ions of different chemical nature and sign ($C_6H_{15}O^+$, O_2^-, OH^-, H_3O^+, Br^-, NH_4^+, K^+, Li^+, Na^+, Pb^+, Rb^+, Cl^-, Bi^+, Ag^+, CH_3O^+, CH_4NO^+, CH_5O^+, $C_2H_4N^+$, $C_2H_5O^+$, $C_2H_7O^+$, $C_2H_8N^+$, $C_3H_7O^+$, $C_3H_9O^+$, $C_4H_{11}O_2^+$, Cu^+, F^-) and (OH^-, H_3O^+, Br^-, NH_4^+, K^+, Li^+, Na^+, Pb^+, Bi^+, Ag^+, CH_3O^+, CH_5O^+, $C_2H_4N^+$, $C_2H_5O^+$, $C_2H_7O^+$, $C_3H_9O^+$, $C_4H_{11}O_2^+$, F^-) are in the range of $\sim 3.6 \pm 1.6$ kcal mol^{-1} and $\sim 2.8 \pm 0.8$ kcal mol^{-1}, respectively. This means that the difference in the formation free energy $\Delta G_j^{A^\pm} - \Delta G_j^{B^\pm} = \sum_2^j (\Delta G_{n,n-1}^{A^\pm} - \Delta G_{n,n-1}^{B^\pm})$ between j-mers formed over core ions $A^\pm$ and $B^\pm$ is controlled by the initial growth stages. Another important detail is that, at $n = 7$, $\Delta G_{n,n-1}$ for clusters formed over different core ions is close to the bulk value for water that likely indicates quite rapid transition of molecular clusters to the state of bulk liquid.

These findings are consistent with the short-ranged nature of charge-related interactions that leads to the quick decrease of the influence of the electronic structure of the screened core ion with the number of molecules in the screening cluster. Our results and analysis of the experimental data [45] rule out a generally negative sign preference for water, because in a number of cases the hydration free energy $\Delta G_{n,n-1}$ for a cation is more negative than that for an anion. It is important to note that the sign preference depends on the chemical nature of cations and anions in general, and, thus, the sign preference for ions (A^+, B^-) and (C^+, D^-) nucleating in the same host vapor may be different.

We would like to emphasize that the quantum approach, in addition to good overall agreement with experimental data, can accurately account for the effect of the internal structure on the cluster thermodynamics. Quantum theory predicts a change in the slope of the $\Delta G_{n,n-1}$ curve for $H_3O^+(H_2O)_n$ at $n = 4$, which is associated with the formation of the second solvation shell. This prediction is in very good agreement with recent measurements [41].

Comparison of curves in Fig. 2(b) shows that molecular theories have failed in predicting both the formation free energy and its size dependency, including the asymptotical behavior of $\Delta G_{n,n-1}$ at large j. DNT [27] overestimates the reaction free energy associated with the formation of hexamer from the solvated dimer $H_3O^+(H_2O_2)_2$ by ~ 40 kcal mol^{-1}, while the corresponding free energy predicted by the Monte Carlo model [25] is ~ 35 kcal mol^{-1} lower than the experimental value. These deviations cause excessively large uncertainties of 29 and 25 orders of magnitude, respectively, in the $H_3O^+(H_2O)_2 + 3H_2O \rightarrow H_3O^+(H_2O)_5$ reaction rate. Another important detail is that $\Delta G_{n,n-1}$ for n-mers formed over Li^+ of atomic radius $r_{Li}^a = 0.145$ nm, Na^+ ($r_{Na}^a = 0.178$ nm), and both the water cation H_3O^+ and anion OH^- of ~ 0.2 nm in size is more negative than that of Cl^- of atomic radius $r_{Cl}^a \approx 0.1$ nm. This means that the core ion effect cannot be adequately described using the ion sign, either alone or in a combination with the mean atomic size, as the key parameter.

As seen from Fig. 2(c), our results, which are in agreement with the experimental data on ion clustering [41,44] within the uncertainty range and a nucleation study [18], show a weak (slightly positive) sign preference for water, while DNT [27], in contrast, gives a much stronger negative sign preference. DNT predicts that an addition of 40 water molecules to a 1 nm core ion, which is more than 5 times larger than a water molecule, is still not enough to reach the limit where the effects of electrical fields of positively and negatively charged core ions become undistinguishable. This prediction contradicts both our results and experiments [41,44]. The negligible sign preference given by the Monte Carlo model [25] arises from inaccurately calculated formation free energies, which are close to zero within the whole range of cluster sizes, and the agreement with the experiment [18] is coincidental. The present work leads us to conclude that:

(a) The influence of the core ion on the n-mer formation free energy is associated mainly with the first several growth steps, where the effect of the core ion properties on the cluster thermodynamics is very large. This means that an answer to a practical question "Which ion is a

better nucleator?'' can be obtained by carrying out a relatively simple quantum mechanics study or by looking at the data on the thermochemistry of cluster ions available for a number of substances [45].

(b) The strong effect of the chemical nature of the core ion on the conversion of vapor molecules to clusters is essentially quantum in nature, and, thus, systematic accounting for the actual core species is impossible without taking into account the actual electronic structures of the core ions. Ignorance or approximation of the actual electronic structure, which is the key parameter controlling the sign preference, by oversimplified electrostatic models leads to the failure of existing nucleation theories [9,22,27,28].

In this Letter, the nature of and the key parameters controlling the sign preference have been identified, and a fundamental problem of the effect of the chemical identity of the core ion on the formation of ionic clusters has been largely solved. It has been demonstrated that a quantum theory that treats the cluster microphysics rigorously provides a solid foundation for the development of a new first-principles ion-induced nucleation theory. We also suggest that further experiments on clustering of various ions with large j would be very helpful for the understanding of the molecular nature of ion-induced nucleation and ionic molecular cluster-bulk liquid transitions.

Unlike the existing nucleation models [9,22–28], which are sensitive to poorly defined input parameters, the quantum theory can treat a system of an arbitrary chemical composition and be applied to a large number of problems related to the physics and chemistry of atmospheric aerosols, cloud microphysics, technologies of the nanoparticle fabrication and removal of toxic metals, environmental safety, and air quality research.

Support of this work by the U.S. National Science Foundation and useful discussions with Professor C. Walcek and Mr. A. Tsoyref are gratefully acknowledged. We thank the CSC-Center for Scientific Computing (Espoo, Finland). K. V. M. thanks the Danish Natural Science Research Council, DCSC, the Danish Technical Research Council, and the EU network NANOQUANT for support.

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[1] F. Arnold, Nature (London) **284**, 610 (1980).
[2] F. Yu and R. P. Turco, Geophys. Res. Lett. **27**, 883 (2000).
[3] S.-H. Lee *et al.*, Science **301**, 1886 (2003).
[4] M. Kulmala, Science **302**, 1000 (2003).
[5] L. Laakso *et al.*, Atmos. Chem. Phys. **4**, 2353 (2004).
[6] M. Adachi *et al.*, Appl. Phys. Lett. **75**, 1973 (1999).
[7] J. L. Katz, U.S. Patent No. 6 663 690 (2003).
[8] M. Adachi *et al.*, Adv. Powder Technol. **16**, 549 (2005).
[9] A. B. Nadykto and F. Yu, Phys. Rev. Lett. **93**, 016101 (2004).
[10] F. Yu, J. Chem. Phys. **122**, 084503 (2005).
[11] F. Yu, J. Geophys. Res. **107**, 1118 (2002).
[12] P. Penttinen *et al.*, Eur. Respir. J. **17**, 428 (2001).
[13] M. Knaapen *et al.*, Int. J. Cancer **109**, 799 (2004).
[14] D. Saxon and D. Diaz-Sanchez, Nature Immunol. **6**, 223 (2005).
[15] C. T. R. Wilson, Phil. Trans. R. Soc. A **189**, 265 (1897).
[16] L. B. Loeb, A. F. Kip, and A. W. Einarsson, J. Chem. Phys. **6**, 264 (1938).
[17] A. W. Castleman and I. N. Tang, J. Chem. Phys. **57**, 3629 (1972).
[18] H. Rabeony and P. Mirabel, J. Phys. Chem. **91**, 1815 (1987).
[19] M. Adachi, K. Okuyama, and J. H. Seinfeld, J. Aerosol Sci. **23**, 327 (1992).
[20] T. Seto *et al.*, J. Chem. Phys. **107**, 1576 (1997).
[21] K. Nagato *et al.*, J. Aerosol Sci. **36**, 1036 (2005).
[22] I. Kusaka, Z. Wang, and J. H. Seinfeld, J. Chem. Phys. **102**, 913 (1995).
[23] I. Kusaka, Z. Wang, and J. H. Seinfeld, J. Chem. Phys. **103**, 8993 (1995).
[24] E. P. Brodskaya, A. P. Lyubartsev, and A. Laaksonen, J. Phys. Chem. B **106**, 6479 (2002).
[25] K. J. Oh, G. T. Gao, and X. C. Zeng, Phys. Rev. Lett. **86**, 5080 (2001).
[26] V. B. Warshavsky and X. C. Zeng, Phys. Rev. Lett. **89**, 246104 (2002).
[27] S. M. Kathmann, G. K. Schenter, and B. C. Garrett, Phys. Rev. Lett. **94**, 116104 (2005).
[28] M. Volmer, *Kinetik der Phaseenbinding* (Steinkopff, Dresden, 1939).
[29] E. Schrodinger, Ann. Phys. (Berlin) **79**, 361 (1926).
[30] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[31] S. Tsuzuki and H. P. Lüthi, J. Chem. Phys. **114**, 3949 (2001).
[32] A. Al Natsheh *et al.*, J. Phys. Chem. A **108**, 8914 (2004).
[33] M. P. McGrath and L. Radom, J. Chem. Phys. **94**, 511 (1991).
[34] D. Feller *et al.*, J. Chem. Phys. **103**, 3526 (1995).
[35] T. Tsurusawa and S. Iwata, J. Phys. Chem. A **103**, 6134 (1999).
[36] J. J. Novoa *et al.*, J. Phys. Chem. A **101**, 7842 (1997).
[37] M. Masamura, J. Mol. Struct., Theochem **498**, 87 (2000).
[38] R. W. Gora, S. Roszak, and J. Leszczynski, Chem. Phys. Lett. **325**, 7 (2000).
[39] Ya. Kim and Yo. Kim, Chem. Phys. Lett. **362**, 419 (2002).
[40] P. Kebarle *et al.*, J. Am. Chem. Soc. **89**, 6393 (1967).
[41] K. D. Froyd and E. R. Lovejoy, J. Phys. Chem. A **107**, 9800 (2003).
[42] I. Dzidic and P. Kebarle, J. Phys. Chem. **74**, 1466 (1970).
[43] K. Hiraoka and S. Mizuse, Chem. Phys. **118**, 457 (1987).
[44] M. Meot-Ner (Mautner) and C. V. Speller, J. Phys. Chem. **90**, 6616 (1986).
[45] NIST Standard Reference Database No. 69, edited by P. J. Linstrom and W. G. Mallard (National Institute of Standards and Technology, Gaithersburg, MD, 2005), http://webbook.nist.gov.
[46] See EPAPS Document No. E-PRLTAO-96-067613 for the thermochemical analysis, structural data, and a detailed description of methods used in this study. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.