

Nadykto *et al.* Reply: In our Letter [1], we have applied a quantum approach for studying the sign preference and performed a first systematic quantum study of this puzzling phenomenon. Quantum methods have been progressing continuously since Schrödinger's original work [2], and their development has reached the stage when "chemical properties can often be calculated with wave function-based methods as well or better than they can be measured" [3].

Based on the additional information provided by Kathmann, Schenter, and Garrett [4], we can conclude that their curves [5] for positive and negative ions given in Fig. 2(b) should be simultaneously scaled by 8.63 kcal mole⁻¹. Scaled curves for X^+ (SM) and X^- (LG) are quite close to both our results and experimental data for $\text{Na}^+(\text{H}_2\text{O})_n$ and $\text{Cl}^-(\text{H}_2\text{O})_n$, respectively. However, the simultaneous scaling of curves [5] for positive and negative ions does not affect $\Delta G_{i,i-1}^{A\pm} - \Delta G_{i,i-1}^{B\pm}$ controlling the sign preference [Fig. 2(c) in Ref. [1]]. The temperature difference is not an issue either. Accounting for the difference in the temperature leads to a simultaneous scaling of both our results and experimental data, and, thus, the pattern of $\Delta G_{i,i-1}^{A\pm} - \Delta G_{i,i-1}^{B\pm}$ remains virtually unchanged. This means that the predictions given in Ref. [5] deviate from both experiments and our results [1] regardless of the scaling. These considerations lead us to the original conclusion [1] that molecular-based nucleation models using semi-empirical potentials were unable to predict the sign preference in agreement with experiments and quantum theory.

Since the ionic systems studied in Ref. [5] are essentially model ones with undetermined chemical identities, this deviation itself is not a sign of trouble. However, it shows clearly that an explicit identification of the chemical identity of the core ion controlled by the wave function [2] is absolutely necessary when a sign preference of a substance is studied. It is also important to note that the above-mentioned conclusions do not imply that molecular-based methods using empirical potentials are generally invalid or defective. However, they indicate (i) that empirical potentials must provide an adequate description of the thermochemistry of initial cluster growth steps and (ii) that care should be taken when using such potentials in the nucleation studies.

Another important detail is that the statement concerning the thermodynamic instability of the prenucleation clusters made in the Comment is inaccurate. It is well known that ion-induced nucleation is barrier-free in the case when none of the routes of the Kelvin-Thomson equation is real.

Kathmann, Schenter, and Garrett [4] suggest that rigid-rotor harmonic oscillator approximation (RRHOA) free energies obtained in Ref. [1] "are inadequate to conclude that the sign preference is essentially quantum in nature." We disagree. The accuracy of the commonly used RRHOA

or, in plain words, harmonic approximation (HA) has been studied in detail in the past. The difference between theoretical harmonic frequencies and experimental data is expressed via the scaling factor [6]. The scaling factor for the PW91 method used in [1] is close to unity (see, e.g., [7]). These considerations undermine Kathmann, Schenter, and Garrett's conclusion about HA Gibbs free energies [1]. Rigorous theoretical treatment of anharmonic effects is important indeed. Unfortunately, uncertainties in the theoretical anharmonic predictions of low-lying frequencies responsible for the vibrational contribution to the cluster Gibbs free energy are excessively large. For example, they exceed 400 cm⁻¹ or 500% (see, e.g., [8]) in the case of the water dimer.

We agree that issues related to sampling of configurations may be important in the case when the cluster is large. However, ionic clusters studied in Ref. [1] are small, and, thus, "global anharmonicity" is not relevant to our study. Another important detail is that the stepwise Gibbs free energy tends to approach a bulk value quickly [1]. This means that, in order to derive a rigorous "first principles" thermochemical model, one probably will not need to compute the structure and properties of numerous configurations of large clusters composed of an astronomic number of molecules. The derived model can be used for explicit kinetic simulations of the cluster formation. This approach does not involve any sampling of configurations.

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