Quantum Microsolvation of Protonated Methane with ⁴He: Large-Amplitude Motion Heavily Influences Bosonic Exchange

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Quantum simulations of small $CH_5^+ \cdot {}^4He_n$ complexes disclose significant and antagonistic impact of small-amplitude local vibrational motion vs large-amplitude global fluxional motion within the CH_5^+ impurity on helium in real and permutation space. While the former significantly enhances bosonic exchange in the surrounding ⁴He microsolvation shell compared to the rigid-body reference, the latter greatly suppresses long permutation cycles, which is traced back to the different nature of these quantum fluctuations. Therefore, it is expected that the resulting impact on local superfluidity is generic for fluctuating impurities in bosonic environments.

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Although superfluidity of bosonic helium clearly is a macroscopic phenomenon, pioneering path integral simulations led to the discovery [1] that finite clusters consisting of only 64 ⁴He atoms already feature manifestations of superfluid behavior below about 2 K that are reminiscent of bulk ⁴He. Indeed, about a decade later, using helium nanodroplet isolation infrared spectroscopy [2,3], superfluidity within ⁴He clusters down to 60 atoms has been revealed [4]. These findings have triggered a plethora of work on impurities *X* interacting with ⁴He, ranging from simple atoms and small molecules to H-bonded clusters [5–9].

When moving from the nanodroplet to the microsolvation limit, it has been found, both experimentally [10–14] and computationally [15–17], that the rotational constant of molecular $X \cdot {}^{4}\text{He}_{n}$ complexes depends strongly and often nonmonotonically on *n*, which has been interpreted in terms of "molecular superfluidity" including even the first solvation shell [18]. Methane $X = \text{CH}_{4}$ certainly belongs to the class of quasirigid molecules subject to only small-amplitude vibrations about a well-defined equilibrium structure much like SF₆, OCS, CO₂, HCN, or H₂O that have been extensively studied as impurities [5–9]. However, adding a proton to CH₄ yields CH₅⁺ and transforms an usual stiff molecule to an utmost floppy species which features dramatically different dynamical properties.

Protonated methane CH_5^+ has been long known to be subject to overriding large-amplitude motion due to an unusually flat potential energy surface (PES) with many degenerate minima separated by tiny energetic barriers as reviewed recently [20]. In a nutshell, this large-amplitude motion vividly changes its molecular structure by inducing intramolecular pseudorotations involving two structural fragments, namely, H₂ and CH₃ yielding an *e*-C_s global minimum (see upper inset of Fig. 1); the details of the mechanism are described in the Supplemental Material [21].



FIG. 1. Distance distribution functions of the helium atoms with respect to the H₂ moiety of CH_5^+ for $CH_5^+ \cdot {}^{4}He_2$ (a) and $CH_5^+ \cdot$ ${}^{4}\text{He}_{4}$ (b); the position of the moiety is defined by its center of mass. The CH_5^+ molecule is either fully frozen in its e- C_s stationary-point structure corresponding to the global minimum (blue), restrained close to its e-Cs structure allowing only for nuclear quantum delocalization due to small-amplitude vibrational motion (green; see text), or fully flexible which additionally allows for largeamplitude fluxional motion and hydrogen scrambling to occur (red). The superimposed open circles denote Maxwell-Boltzmann quantum statistics as obtained by switching off the helium PIMC exchange moves. Only for the purpose of analyzing the restraint and fully flexible path integral trajectories, the molecule has been transformed beadwise to best fit the e-C_s reference structure of the respective frozen simulation by minimizing the site-site rootmean-square deviation (RMSD) of CH₅⁺. The left and right insets in (b) depict the nuclear densities in three-dimensional space at $r = 3.5 \pm 0.01$ Å for $e-C_s$ frozen and at $r = 4.0 \pm 0.01$ Å for fully flexible CH₅⁺, respectively, based on 7500 statistically independent configurations each, where only those helium atoms behind the image plane are shown.

As a result of such large-amplitude motion, all five protons in CH₅⁺ can be exchanged upon successively combining the two aforementioned transformation pathways, which leads to what is called "hydrogen scrambling" as confirmed using partial deuteration experiments [46]. Importantly, this scrambling motion cannot be frozen by lowering the temperature: CH_5^+ is quantum fluxional [47]. Even attaching a few He atoms has been shown more recently [48] to not affect hydrogen scrambling within CH_5^+ . In stark contrast to He atoms, however, attaching additional H₂ molecules is a severe perturbation and affects both low-temperature scrambling dynamics and vibrational spectroscopy [49–51] of CH_5^+ . All this is the reason why this conceivably simple but exceptionally fluxional molecule CH_5^+ has been dubbed recently "the enfant terrible of chemical structures," given that even "the very concept of molecular structure becomes problematic" [52]. More generally speaking, CH₅⁺ has long been considered to serve as the archetype of the vast class of fluxional (aka floppy or superflexible) molecules that challenges both theory and spectroscopy for decades up to the present day [52–58]. Having fundamentally understood the most difficult representative is expected to pave the way to quickly elucidate other fluxional molecules. In addition, soft van der Waals and H-bonded clusters being characterized by many low-barrier intramolecular vibrational-rotational degrees of freedom that get easily excited already at ultracold conditions are other vast classes of fluxional species, e.g., water clusters which are well known to be subject to pronounced large-amplitude vibration-rotation tunneling dynamics.

Here, we pose the question: Might there be an impact of large-amplitude motion and fluxionality on the microsolvation shell that emerges upon attaching a few ⁴He atoms to CH_5^+ ? Moreover, using bosonic helium offers the opportunity to probe possible perturbations of the quantumstatistical exchange properties of indistinguishable particles obeying Bose-Einstein statistics in the presence of strongly quantum-fluctuating local impurities, where CH₅⁺ serves again as the generic representative. Beyond the specific case, it is expected that the fundamental understanding of differences of quantum solvation of fluxional vs quasirigid molecules will have direct ramifications on (i) relating (measured) effective rotational constants of polyatomic impurities X to the (computed) molecular superfluidity of bosonic solvents (such as ⁴He atoms and para-H₂) molecules [9-17,59,60]) in case of intramolecular largeamplitude motion within the impurity X and on (ii) treating pseudorotations of nonrigid quantum impurities X which interact with bosonic environments [61].

Methods.—Addressing these questions requires an efficient finite-temperature bosonic path integral simulation approach that considers the full molecular flexibility of X within $X \cdot {}^{4}\text{He}_{n}$ complexes at 1.25 K, thus, transcending

rigid-body approaches to investigate the (micro-) solvation of (quasi-) rigid molecules (such as SF₆, OCS, ...) by superfluid helium. To this end, we employ our hybrid PIMD/ PIMC approach [62] where PIMD and PIMC denote path integral molecular dynamics and Monte Carlo simulations, respectively. Therein, helium is sampled using bosonic exchange path integral Monte Carlo simulations [63] to establish Bose-Einstein statistics, whereas the molecule is propagated using Maxwell-Boltzmann path integral molecular dynamics; see the Supplemental Material [21] for details and a validation of neglecting the protonic Fermi-Dirac statistics when sampling the quantum-average structure of CH_5^+ at ultralow temperatures (based on analyzing the lowest-energy Pauli-allowed vs Pauli-forbidden wave functions [56]).

Results and discussion.--A first impression of the microsolvation shell of $CH_5^+ \cdot {}^4He_n$ can be gleaned from the distance distribution function of the helium atoms around the H_2 moiety shown as the red lines in Fig. 1. The corresponding distance distribution function is found to be bimodal where the peak around 2.5 Å corresponds to those helium atoms that are close to the H₂ moiety in accord with the optimized e-C_s structure (see upper inset of Fig. 1). But what is the origin of the second peak at about 4.0 Å? Visual inspection reveals that this is not due to the formation of a second helium solvation shell of the H₂ moiety. Rather, this maximum stems from the first solvation shell around the CH₃ tripod where helium atoms populate the spatial region that is diametrically opposite the H_2 moiety; see right inset in Fig. 1(B). Given that helium interactions with the H₂ moiety are energetically favorable for all *n* (see Fig. 1 in the Supplemental Material [21]), this phenomenon must be exclusively induced by nuclear quantum-fluctuation effects at such ultralow temperatures.

In view of this finding, we ask how the optimized global minimum structure of CH_5^+ gets solvated when adding *n* quantum ⁴He atoms. The dark blue lines in Fig. 1 are obtained by clamping all six nuclei of CH₅⁺ in threedimensional space according to its e-Cs stationary-point configuration (see upper inset of Fig. 1) while simultaneously sampling rigorously the ⁴He quantum distribution. This so-called "e-C_s frozen" treatment represents the space-fixed "rigid-body approximation of protonated methane" and excludes the impact of both small- and largeamplitude motion of CH_5^+ on the surrounding ⁴He atoms. For n = 2 [see Fig. 1(A)], the distance distribution with its well-localized symmetric maximum around 2.5 Å implies that both atoms are exclusively solvating the H_2 moiety, thus populating only the energy minimum of the PES (see upper inset of Fig. 1) subject to trivial quantum smearing. This is in stark contrast to the flexible case which implies that this rigid-body approximation artificially overlocalizes helium around CH_5^+ .

After having added four ⁴He atoms to CH_5^+ (see Fig. 1(B)], the distribution remains sharply peaked at

2.5 Å, but there now is a pronounced wing that extends up to ≈ 4 Å away from the H₂ moiety. A more refined analysis presented in the left inset of Fig. 1(B) makes clear that this tail is not due to helium atoms that microsolvate the CH₃ tripod (as seen in the right inset for the fully fluxional case) but only delocalize into the equatorial plane between the moiety and tripod. We conclude that neglecting all intramolecular quantum fluctuations does not provide a physically meaningful description of ⁴He-tagged CH₅⁺ complexes.

These dramatic differences between the fully flexible and fully frozen scenario provoke the question if they are due to (quasiharmonic) vibrational motion around some reference structure, such as e-C_s, or if they are induced by the fluxional dynamics of CH_5^+ . We thus set out to disentangle nuclear quantum (delocalization) effects stemming exclusively from small-amplitude quantum fluctuations (as also present in quasirigid molecules) from those effects that get solely imprinted by large-amplitude scrambling by performing simulations where the CH_5^+ core in $CH_5^+ \cdot {}^{4}He_n$ has been restrained as described in the Supplemental Material [21]. The resulting " $e-C_s$ restraint" treatment provides a "quasi-rigid-body approximation of protonated methane" that allows for small-amplitude vibrations, while the influence of large-amplitude motion (i.e., pseudorotations and hydrogen scrambling) of CH_5^+ on the ⁴He environment is fully suppressed.

It can be seen with the naked eye that according to this quasirigid approximation of protonated methane (see green lines in Fig. 1), the distribution functions are unimodally peaked around 2.5 Å with a smoothly decaying broad wing extending toward 4.5 Å. Moreover, the behavior of CH_5^+ · ${}^{4}\text{He}_{2}$ and $\text{CH}_{5}^{+} \cdot {}^{4}\text{He}_{4}$ becomes virtually identical if CH_{5}^{+} is allowed to perform small-amplitude vibrations with respect to its e-C_s structure, at variance with the rigid-body scenario discussed. The long-ranged tail in the two quasirigid n = 2, 4 cases is very similar to what happens in the frozen scenario for n = 4, the only difference being a somewhat enhanced probability in the former case. Therefore, it is exclusively large-amplitude fluxionality and thus hydrogen scrambling within the $X = CH_5^+$ core in these $X \cdot {}^{4}\text{He}_{n}$ complexes (and not simply the smallamplitude vibrational nuclear quantum delocalization of individual nuclei within X) that is responsible for the distinctly different microsolvation patterns depending on the level of approximation. In other words: In view of the low-lying rovibrational excitations [54-58] of bare CH⁺₅ and the weak He \cdots CH⁺₅ interactions [64], it is mandatory to account for pseudorotational and scrambling motion within the CH_5^+ impurity in order to provide the correct picture of these $CH_5^+ \cdot {}^4He_n$ complexes.

Having discovered exceptionally pronounced largeamplitude effects on the solvation pattern of $CH_5^+ \cdot {}^4He_n$ complexes, the next—possibly provocative—question suggests itself: Is there any impact of the fluxional nature of this impurity $X = CH_5^+$ on Bose-Einstein quantum statistics of the solvating ⁴He atoms? The obvious approach would be to compute the superfluid fraction f_s within CH_5^+ . ⁴He_n in the presence of either a frozen, restrained, or fully flexible CH_5^+ core. The superfluid fraction can be related to the effective quantum moment of inertia of the entire complex that, in turn, can be converted into an effective rotational constant, which is an observable and thus an experimental probe of molecular superfluidity [9]. Unfortunately, as is well known, the existing estimator for f_s (that has been devised originally to quantify superfluidity in nanodroplet-sized $n \gg 1$ bosonic clusters [1]) provides a non-negligible superfluid fraction even in the limit of a single ⁴He atom in the system. On the other hand, it has been demonstrated repeatedly that the probability of "sufficiently long" permutation cycles can serve as a useful proxy to quantify superfluidity in finite boson systems [65,66]. Therefore, and in view of the small number of bosons $n \leq 4$, we analyze in the following the probability that all n ⁴He atoms are involved in a single permutation cycle within $CH_5^+ \cdot {}^{4}He_n$, dubbed "full exchange." Evidently, having no practical formalism to compute f_s rigorously for small nimplies that it is impossible to meaningfully compute effective rotational constants in the present case. Nevertheless, measuring the effective rotational constants of chemically similar fluxional vs quasirigid systems, such as CH_5^+ vs CH_4 , seems highly promising if carried out from very small to large *n*.

Using the pragmatic proxy approach [65,66], the flexible simulation of $CH_5^+ \cdot {}^4He_2$ provides fully exchanging configurations with a probability of 4.8%, whereas that number drops to only 1.0% if CH_5^+ is frozen. There are two plausible origins of this surprising decrease in bosonic exchange upon clamping the impurity X. Either the effect is due to the usual quantum delocalization of the nuclei, or it is caused, again, by large-amplitude scrambling motion in the $X = CH_5^+$ core. The restrained simulation, surprisingly, provides much enhanced bosonic permutations leading to a full exchange probability of 12.5%. This is completely different from all that we have found so far: Largeamplitude motion of X actually counteracts bosonic exchange. In other words, exciting only small-amplitude (vibrational) fluctuations enhances bosonic exchange compared to the zero-amplitude (frozen) fluctuation limit, whereas liberating the large-amplitude (scrambling) fluctuations greatly reduces exchange. We note in passing that despite this deep impact of fluxionality on the permutation space, the feedback of bosonic exchange on the microsolvation pattern in real space is very small (compare Maxwell-Boltzmann to Bose-Einstein statistics in Fig. 1).

Is this puzzling finding valid beyond the simplest possible case involving just two ⁴He atoms? The answer clearly is "yes": The probability of full exchange cycles in

frozen, restraint, and flexible simulations amounts to 0.2, 14.3, and 4.1% for n = 3 and to 4.7, 9.2, and 2.1% for n = 4, respectively. We must conclude that large-amplitude scrambling motion of $X = CH_5^+$ counteracts these manifestations of superfluid behavior, whereas the rigid-body approximation of the molecular impurity *X* severely and artificially suppresses exchange of bosonic helium in $CH_5^+ \cdot {}^4He_n$. Perhaps the most intriguing species is n=4: Fully flexible $X = CH_5^+$ suppresses full exchange even below that of fully clamped *X*.

How can these intricate observations be understood at the molecular level by tracing back qualitative differences in permutation space to fluctuations of $CH_5^+ \cdot {}^4He_n$ in real space? For n = 2 [see Fig. 2(A)], the frozen CH₅⁺ core strongly localizes the ⁴He atoms close to their minima on the very anisotropic PES (recall Fig. 1) where they are kept rather far apart around the H₂ moiety. As is well known, the efficiency of bosonic exchange depends exponentially on interparticle distance [63]. Thus, the rigid-body approach to X prevents vivid exchange by localizing the 4 He atoms sufficiently far from each other due to anisotropic $X \cdots$ He interactions. This changes drastically when allowing for vibrations of the impurity X, thus, exciting small-amplitude quantum fluctuations, in the restraint scenario in Fig. 2(D). Because of this local quantum broadening of X, the two ${}^{4}\text{He}$ atoms can delocalize much more themselves while they are still kept in sufficient proximity to each other in the hemisphere around the H₂ moiety. The resulting overlap along the Trotter axis (i.e., in imaginary time) greatly enhances the efficiency of exchange permutations [63]. However, upon exciting large-amplitude motion on top, CH₅⁺ undergoes full hydrogen scrambling which implies that the H₂ moiety is vividly pseudorotating and eventually covers the full sphere as seen in Fig. 2(G); note that this purely intramolecular motion is unrelated to overall rotations of X which are allowed in the fully flexible and restrained simulations. This utmost delocalization, in turn, pulls all helium atoms apart from each other on that sphere since the energetically attractive energy minima close to the H_2 moiety (see upper inset of Fig. 1) are now fully isotropically delocalized as well, thus suppressing close ${}^{4}\text{He}\cdots{}^{4}\text{He}$ contacts in imaginary time (whereas the realspace population by ⁴He atoms is very similar in the full and no exchange cases; compare Fig. 2(E) to Fig. 2(D) and Fig. 2(H) to Fig. 2(G). This explains why the probability to involve all ⁴He atoms in a single permutation cycle decreases systematically, and therefore, also full exchange and manifestations of superfluid behavior.

These effects are particularly severe for n = 4. Here, the two additional helium atoms compared to n = 2 are forced to populate side minima [compare Figs. 1(C), 1(F), and 1(I) to Figs. 1(A), 1(C), and 1(G) in the Supplemental Material [21]], which leads to particularly favorable spatial overlap in imaginary time, thus enhancing exchange in the frozen



FIG. 2. Visualization of the helium atom densities of $\text{CH}_5^+ \cdot {}^4\text{He}_n$ for n = 2 and 4 around CH_5^+ frozen in its $e\text{-C}_s$ stationarypoint structure (top row), restrained close to this $e\text{-C}_s$ structure (center row), and fully flexible CH_5^+ (bottom row) based on 300 statistically independent configuration snapshots each (where only helium atoms behind the image plane are shown). Left column panels correspond to $\text{CH}_5^+ \cdot {}^4\text{He}_2$ configurations where the two ${}^4\text{He}$ atoms do not exchange, while all other panels correspond to full exchange (see text) for n = 2 (center column) and n = 4 (right column). Note that $\text{CH}_5^+ \cdot {}^4\text{He}_n$ has been transformed beadwise to best fit the optimized $e\text{-C}_s$ structure to allow for visualization. The helium atoms involved in full exchange cycles are shown in green, whereas in the left column, blue and red highlight the two distinct helium atoms that are located left and right in (a) and (d) and upper and lower in (g).

limit [compare Fig. 2(C) to Fig. 2(B)]. The fully flexible case, in contrast, is unusually unfavorable for $CH_5^+ \cdot {}^4He_4$ since now all four ⁴He atoms must fuse into full exchange cycles that are forced to cover isotropically the entire surface of the sphere for the same reason as explained for n = 2.

Conclusions and outlook.—Our simulations of CH_5^+ · ⁴He_n complexes up to n = 4 disclosed a hitherto unknown but striking impact of both small-amplitude and large-amplitude quantum fluctuations within a molecular impurity $X = CH_5^+$ not only on its microsolvation structure in real space but also on the Bose-Einstein exchange statistics of ⁴He in permutation space. While the former fluctuations

being local vibrations with respect to a quasirigid molecular structure significantly increase long permutation cycles and thus enhance manifestations of superfluid behavior, the global fluxionality of X was found to dramatically suppress exchange. Beyond the specific example, this implies that the computed superfluid response of quasirigid polyatomic molecules X interacting with a few bosonic species, be it ⁴He or para-H₂, gets systematically underestimated when neglecting small-amplitude vibrational motion. This effect will impact the interpretation of experimental effective rotational constants in the sense of the evolution of molecular superfluidity from small n toward the nanodroplet limit. Applying such a rigid-body treatment to fluxional molecules will even introduce qualitative artifacts without considering explicitly the discovered impact of large-amplitude motion on bosonic exchange. Moreover, the resulting intricate coupling will add complexity to the intriguing five-dimensional super-rotor description of extremely flexible molecules in terms of a second-order SO(5) Casimir Hamiltonian [57] introduced for bare CH_5^+ when they interact with bosonic species. Since CH_5^+ is the archetype of such superflexible molecules, our insights are expected to be fundamental to understanding fluxional impurities interacting with bosonic solvents way beyond this specific case. Last but not least, even the low-frequency degrees of freedom of soft van der Waals and H-bonded clusters, such as water clusters subject to large-amplitude vibration-rotation tunneling, might leave similar footprints in the superfluid properties of bosonic environments.

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- P. Sindzingre, M. L. Klein, and D. M. Ceperley, Phys. Rev. Lett. 63, 1601 (1989).
- [2] S. Goyal, D. L. Schutt, and G. Scoles, Phys. Rev. Lett. 69, 933 (1992).
- [3] G. Scoles and K. K. Lehmann, Science 287, 2429 (2000).
- [4] S. Grebenev, J. P. Toennies, and A. F. Vilesov, Science 279, 2083 (1998).
- [5] K. B. Whaley, Int. Rev. Phys. Chem. 13, 41 (1994).
- [6] C. Callegari, K. K. Lehmann, R. Schmied, and G. Scoles, J. Chem. Phys. 115, 10090 (2001).
- [7] J. P. Toennies and A. F. Vilesov, Angew. Chem., Int. Ed. 43, 2622 (2004).

- [8] M. Y. Choi, G. E. Douberly, T. M. Falconer, W. K. Lewis, C. M. Lindsay, J. M. Merritt, P. L. Stiles, and R. E. Miller, Int. Rev. Phys. Chem. 25, 15 (2006).
- [9] T. Zeng and P.-N. Roy, Rep. Prog. Phys. **77**, 046601 (2014).
- [10] J. Tang, Y. Xu, A. R. W. McKellar, and W. Jäger, Science 297, 2030 (2002).
- [11] Y. Xu, W. Jäger, J. Tang, and A. R. W. McKellar, Phys. Rev. Lett. 91, 163401 (2003).
- [12] J. Tang, A. R. W. McKellar, F. Mezzacapo, and S. Moroni, Phys. Rev. Lett. **92**, 145503 (2004).
- [13] A. R. W. McKellar, Y. Xu, and W. Jäger, Phys. Rev. Lett. 97, 183401 (2006).
- [14] L. A. Surin, A. V. Potapov, B. S. Dumesh, S. Schlemmer, Y. Xu, P. L. Raston, and W. Jäger, Phys. Rev. Lett. 101, 233401 (2008).
- [15] F. Paesani, A. Viel, F.A. Gianturco, and K.B. Whaley, Phys. Rev. Lett. **90**, 073401 (2003).
- [16] S. Moroni, A. Sarsa, S. Fantoni, K. E. Schmidt, and S. Baroni, Phys. Rev. Lett. 90, 143401 (2003).
- [17] F. Paesani, Y. Kwon, and K. B. Whaley, Phys. Rev. Lett. 94, 153401 (2005).
- [18] This class of experiments, where exploring the quantum nature of the solvent ⁴He is the focus of interest and investigated by using molecular impurities X as probe species, is truly complementary to He-tagging action spectroscopy [19]. In that case, very few ⁴He atoms attached to X are used as gentle probe species to record the (action) IR spectrum of that molecule by detaching the weakly bound ⁴He messengers using IR radiation [19].
- [19] J. Roithova, A. Gray, E. Andris, J. Jasik, and D. Gerlich, Acc. Chem. Res. 49, 223 (2016).
- [20] S. D. Ivanov, A. Witt, and D. Marx, Phys. Chem. Chem. Phys. 15, 10270 (2013).
- [21] See Supplemental Material at http://link.aps.org/ supplemental/10.1103/PhysRevLett.123.123002 for additional information and computational details, which includes Refs. [22–45].
- [22] D. Marx and A. Savin, Angew. Chem., Int. Ed. 36, 2077 (1997).
- [23] M. E. Tuckerman, Statistical Mechanics and Molecular Simulations (Oxford University Press, Oxford, 2008).
- [24] D. Marx and J. Hutter, Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods (Cambridge University Press, Cambridge, England, 2009).
- [25] F. Uhl, D. Marx, and M. Ceriotti, J. Chem. Phys. 145, 054101 (2016).
- [26] R. A. Aziz, V. P. S. Nain, J. S. Carley, W. L. Taylor, and G. T. McConville, J. Chem. Phys. **70**, 4330 (1979).
- [27] F. Uhl, Ł. Walewski, H. Forbert, and D. Marx, J. Chem. Phys. 141, 104110 (2014).
- [28] R. P. Feynman, *Statistical Mechanics* (Addison-Wesley, Redwood City, 1988).
- [29] X.-G. Wang and T. Carrington, Jr., J. Chem. Phys. 129, 234102 (2008).
- [30] M. Kolbuszewski and P. R. Bunker, J. Chem. Phys. 105, 3649 (1996).
- [31] Ł. Walewski, H. Forbert, and D. Marx, J. Chem. Phys. 140, 144305 (2014).
- [32] CP2k Developers Group, www.cp2k.org.

- [33] J. Hutter, M. Iannuzzi, F. Schiffmann, and J. VandeVondele, WIREs Comput. Mol. Sci. 4, 15 (2014).
- [34] M. E. Tuckerman, in *Quantum Simulations of Complex Many-Body Systems: From Theory to Algorithms*, edited by J. Grotendorst, D. Marx, and A. Muramatsu (John von Neumann Institute for Computing, Jülich, 2002), p. 269.
- [35] L. J. LaBerge and J. C. Tully, Chem. Phys. 260, 183 (2000).
- [36] M. Ceriotti, G. Bussi, and M. Parrinello, J. Chem. Theory Comput. 6, 1170 (2010).
- [37] M. Ceriotti, M. Parrinello, and D. E. Manolopoulos, J. Chem. Phys. **133**, 124104 (2010).
- [38] M. Ceriotti and D. E. Manolopoulos, Phys. Rev. Lett. 109, 100604 (2012).
- [39] D. M. Ceperley and E. L. Pollock, Phys. Rev. Lett. 56, 351 (1986).
- [40] M. P. Deskevich and D. J. Nesbitt, J. Chem. Phys. 123, 084304 (2005).
- [41] M. P. Deskevich, A. B. McCoy, J. M. Hutson, and D. J. Nesbitt, J. Chem. Phys. **128**, 094306 (2008).
- [42] D. Marx and M. Parrinello, Nature (London) 375, 216 (1995).
- [43] D. Marx and M. Parrinello, Z. Phys. D 41, 253 (1997).
- [44] S. J. A. van Gisbergen, F. Kootstra, P. R. T. Schipper, O. V. Gritsenko, J. G. Snijders, and E. J. Baerends, Phys. Rev. B 57, 2556 (1998).
- [45] D. M. Bishop and B. Lam, J. Chem. Phys. 88, 3398 (1988).
- [46] S. D. Ivanov, O. Asvany, A. Witt, E. Hugo, G. Mathias, B. Redlich, D. Marx, and S. Schlemmer, Nat. Chem. 2, 298 (2010).
- [47] D. Marx and M. Parrinello, Nature (London) 375, 216 (1995).
- [48] F. Uhl and D. Marx, Angew. Chem., Int. Ed. Engl. 57, 14792 (2018).

- [49] D. W. Boo, Z. F. Liu, A. G. Suits, J. S. Tse, and Y. T. Lee, Science 269, 57 (1995).
- [50] A. Witt, S. D. Ivanov, and D. Marx, Phys. Rev. Lett. 110, 083003 (2013).
- [51] A. Esser, H. Forbert, and D. Marx, Chem. Sci. 9, 1560 (2018).
- [52] T. Oka, Science 347, 1313 (2015).
- [53] G.E. Scuseria, Nature (London) 366, 512 (1993).
- [54] A. L. L. East, M. Kolbuszewski, and P. R. Bunker, J. Phys. Chem. A 101, 6746 (1997).
- [55] O. Asvany, K. M. T. Yamada, S. Brünken, A. Potapov, and S. Schlemmer, Science 347, 1346 (2015).
- [56] R. Wodraszka and U. Manthe, J. Phys. Chem. Lett. 6, 4229 (2015).
- [57] H. Schmiedt, P. Jensen, and S. Schlemmer, Phys. Rev. Lett. 117, 223002 (2016).
- [58] X.-G. Wang and T. Carrington, Jr., J. Chem. Phys. 144, 204304 (2016).
- [59] H. Li, R. J. Le Roy, P.-N. Roy, and A. R. W. McKellar, Phys. Rev. Lett. **105**, 133401 (2010).
- [60] P. L. Raston, W. Jäger, H. Li, R. J. Le Roy, and P.-N. Roy, Phys. Rev. Lett. 108, 253402 (2012).
- [61] M. Lemeshko, Phys. Rev. Lett. 118, 095301 (2017).
- [62] Ł. Walewski, H. Forbert, and D. Marx, Comput. Phys. Commun. 185, 884 (2014).
- [63] D. M. Ceperley, Rev. Mod. Phys. 67, 279 (1995).
- [64] D. Kuchenbecker, F. Uhl, H. Forbert, G. Jansen, and D. Marx, Phys. Chem. Chem. Phys. 19, 8307 (2017).
- [65] W. Krauth, Phys. Rev. Lett. 77, 3695 (1996).
- [66] F. Mezzacapo and M. Boninsegni, Phys. Rev. Lett. 100, 145301 (2008).