The approach also introduces an adiabaticity parameter that gives insight into the competing effects between quantum mechanical overlap and vibrational reorganization, allowing a rough estimation of when vibronic corrections will be needed. An increase in the rate of energy transfer of up to $3.5\times$ is predicted in relation to Förster theory. At ambient temperatures and once disorder is taken into account, the improvement is estimated to be around 10%. This prediction is in line with theoretical work indicating that quantum electronic-vibrational interactions can enhance a figure of merit in the scenario of a quantum heat engine with parameters of PC645.9

The theoretical analysis by Dean et al. considers only the effect of a single vibrational frequency while ignoring all other environmental effects. Incorporating a wider range of quantized vibrations could make the predicted enhancements more robust to disorder. The insights presented also rely largely on the quasi-local character of the intermolecular vibronic states. This therefore encourages a careful investigation of the overall advantages of vibronic coupling when exciton states with large delocalizations are also involved and the quasi-local picture breaks down. Indeed, a systematic investigation is needed before these findings can be generalized to all light-harvesting antennae or reactions centers, where coherence beating has also been observed. Although 2D optical spectroscopy has shown to be a powerful technique for unveiling details of ultrafast excited-state dynamics, the congested nature of these spectra hinders unambiguous signatures of excited-state coherences. Furthermore, the ensemble nature of the measurement also means that a certain amount of information is washed out. Complementary experimental efforts to probe coherence—whether at the ensemble or the single-molecule level—are therefore much needed.

ACKNOWLEDGMENTS
Financial support from the Engineering and Physical Sciences Research Council (EPSRC UK) and the EU FP7 Project PAPETS (GA 323901) is gratefully acknowledged.


In Situ Detection of Organics in the Comet 67P/Churyumov-Gerasimenko
Alexandre Bergantini1,2 and Ralf I. Kaiser1,2,*

Comets are fascinating objects transporting complex organic molecules from the outer to the inner solar system. A paper published in Nature by Fray and co-workers presents key results of the Rosetta mission by collecting in situ data of refractory grains from comet 67P/Churyumov-Gerasimenko in 2014.

The underlying physicochemical processes leading to the formation of complex organic molecules (COMs) in distinct interstellar (cold molecular clouds, young stellar objects, and protostellar envelopes) and solar system environments (planets, moons, asteroids, and comets) has fascinated chemists and astronomers since the discovery of the very first diatomic molecule methylidyne (hydridocarbon, CH) in the interstellar medium in the plane of the Milky Way almost 80 years ago.1 The detection of nearly 200 molecules in interstellar and circumstellar environments—more than one-third of which, including vital precursors to molecular

1. W.M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA
2. Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA
*Correspondence: ralfk@hawaii.edu
http://dx.doi.org/10.1016/j.chempr.2016.11.001
building blocks of life, such as glycolaldehyde (2-hydroxyacetaldehyde, HCO-CH$_2$OH), can be classified as complex organics—and the elucidation of potential formation routes in the gas and condensed phase (ices) eventually led to the rise of a new interdisciplinary research field: astrochemistry.

Among these almost 200 molecules detected in outer space, the identifications range from simple species, such as molecular hydrogen (H$_2$), to large COMs containing as many as 13 atoms, such as methyl acetate (CH$_3$OC(O)CH$_3$), propylcyanide (butanenitrile, C$_3$H$_7$CN), and even carbon-only molecules, such as C$_{60}$ and C$_{70}$ fullerenes. The ultimate goal of astrochemistry is to exploit astronomical observations, missions, theory, models, and laboratory experiments on the chemical interactions among gas, ice, dust, and ionizing radiation in astrophysical environments to elucidate the inherent formation of new molecules in astrophysical and solar system environments. This also helps us understand how the chemical building blocks of all known forms of life on Earth—sugars, lipids, and amino acids—are formed in distinct astrophysical environments and which processes limit their chemical complexity.

The recent Rosetta mission by the European Space Agency to explore comet 67P/Churyumov-Gerasimenko (2014) represents an exceptional success in terms of both scientific findings and engineering achievements. 67P, a short-period comet, was discovered by K. Churyumov and S. Gerasimenko on photographs taken of 32P/Comas Sola in September 1969 at Alma Ata. From a chemical point of view, comets are among the most primitive objects in the solar system. With the exception of main-belt comets, they originate either from the Oort Cloud (long-period comets) or from the Kuiper Belt (short-period comets) beyond the orbit of Neptune. These objects have preserved material from the interstellar medium and also from the early stages of the formation of our solar system. Given that the Kuiper Belt and Oort Cloud reside at distances of about 30 AU and up to 100,000 AU, respectively, away from the Sun, the surface temperature of the comets is extremely low, just a few tens of degrees above absolute zero; this implies that objects originating from the Kuiper Belt carry frozen volatiles. Considering the evolution of planetary systems, it is believed that the chemical composition of such objects is very similar to the chemical composition of the molecular cloud that collapsed to form the solar system. Therefore, comets are considered to be “natural time capsules” offering a unique opportunity for us to look back in time directly into the dawn of our solar system.

In the October 6, 2016, edition of Nature, Fray et al. report fascinating discoveries made by Rosetta, which was launched in 2004 to rendezvous with the 67P/Churyumov-Gerasimenko comet in 2014. The raw data presented by Fray et al. were collected by the Cometary Secondary Ion Mass Analyzer (COSIMA), which is collecting solid material from the comet to be analyzed by time-of-flight secondary ion mass spectrometry (TOF-SIMS). One of the most interesting characteristics of the mission is that the particles were collected at low speeds (a few meters per second), unlike in previous “cometary hunt” missions, such as Stardust (6 km/s) and Giotto (68 km/s). The fact that the particles were collected at low speeds ensures their molecular integrity. More than 27,000 particles were detected, and close to 200 were analyzed. From these, the authors present the analysis of two representative particles named Kenneth and Juliette.

The main results from the COSIMA instrument are the detection of organic matter in the particles collected from the comet 67P/Churyumov-Gerasimenko. The TOF-SIMS spectra show signatures of carbon compounds, such as the positive ions C$_+$, CH$_+$, CH$_2+$, CH$_3+$, and C$_2$H$_3+$, with m/z ratios of 12.00, 13.01, 14.02, 15.02, and 27.02, respectively, as well as the negative ions C$_-$ and CH$_-$, plus a weak contribution signal from CH$_2$. The authors point out that the carbon-bearing species in the particles collected from the 67P comet present similarities with the spectrum of insoluble organic matter extracted from carbonaceous chondrite meteorites used for comparison, which is indicative of the presence of high-molecular-weight organic matter in the particles of 67P. Organic molecules such as carboxylic acids, polycyclic aromatic hydrocarbons, and amino acids have not been detected by the COSIMA instrument yet, although another instrument, named the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSIMA), detected volatile organics such as methyl formate (HCOOC$_2$H$_3$) and formamide (NH$_2$CHO) in the gas phase of the comet.

It is important to note that the dust particles were analyzed a few weeks after they were collected and that these particles were kept on the substrates at temperatures of about 280 K; therefore, any possible volatiles, especially any “ices,” even water, would have been lost by the time of the analyses. This represents one of the weakest aspects of the research presented by Fray et al., given that a crucial set of information not only about the comet itself but also about the formation stages of the solar system could have been obtained from the in situ analysis of the comet’s volatiles.

Fray et al. also mention that volatile organic molecules were detected on particles ejected by the lander Philae and that those detections are consistent with ices processed by photolysis or radiolysis. But the statement that this sample was processed before the
formation of the comet is not supported by measurements made by the Rosetta mission. Additionally, Fray et al. could not find a chemical connection between the species detected in the solid phase by the COSIMA instrument and the molecules probed in the gas phase by, e.g., ROSINA. Their conclusion is that the volatile and solid materials in the comet 67P have distinct origins. A much simpler explanation could be the fact that the samples were collected in very distinct temperatures—probably a couple hundred Kelvin of difference—so any low-volatile molecules possibly left on the surface of the comet by Philae and the carbonaceous material collected in the coma by COSIMA were simply lost because of sublimation.

Finally, Fray et al. conclude that their detection of high-molecular-weight organic matter both in the particles from the comet and in meteorite samples such as ultracarbonaceous Antarctic micrometeorites suggests that comets and asteroids share common characteristics, at least in a phase where the volatiles are gone. This is not necessarily a new idea (see, e.g., Chyba et al.10).

In conclusion, the fact that 67P is naturally poor in volatiles—as speculated from the analysis of the fragments by the COSIMA instrument—regardless of the original sample’s characteristics, most likely represents an artifact of the enhanced storage temperature of the grains, suggesting that we may have missed the possibility of detecting CHON-bearing species, which are the epicenter of the attention of the astrochemistry community.10