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## Concluding remarks

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### 1 Overview

The field of cluster dynamics is alive, flourishing and exposing ever new and exciting aspects of the details of molecular motion. The twenty four papers presented here, the stimulating and informative discussions of these papers, and the new posters all demonstrate the extraordinary vitality of cluster dynamics and point the way for future advances. One key theme that appeared regularly throughout our discussions was the beautiful complementarity between theory and experiment, and the mechanisms by which these interactions have enabled us to achieve levels of sophistication in detailed understanding of molecular motion and in complexity of large systems that would not have been possible with either acting more independently. As we extend to larger and larger systems, this paradigm will become the dominant mechanism for advances.

Over the three days of this Faraday Discussion, we explored many aspects of cluster dynamics, with a major focus on the use of clusters to elucidate important intellectual issues in neighboring fields of chemistry, physics and materials sciences. This was a decision arising from the necessity of fitting the Faraday Discussion into three days. Consequently, there was only limited discussion of the importance of specific clusters, reactivity of size-selected small clusters, catalytic properties, *etc.* Such studies will be the focus of other Faraday Discussions in the future, no doubt.

Our meeting began with the Spiers Memorial Lecture given by Prof. Roger Miller.<sup>1</sup> Among many important topics in this lecture, Prof. Miller placed special emphasis upon the unique role of helium clusters as a medium for the assembly of smaller clusters within them. The continuing collisions of the cluster ingredients within the liquid helium drop allows rapid and continual energy removal from the forming cluster and enables Miller to stabilize amazing small clusters in very shallow minima on the cluster potential energy surface. Species that are not seen under any other conditions, for example linear HCN clusters, are readily produced in this fashion.<sup>2</sup> There seems no end to the astonishing array of interesting species that can be produced and studied effectively in this new medium. The subject of liquid helium clusters was further extended through our discussions by presentations by Vilesov<sup>3</sup> and Lehmann.<sup>4</sup> In addition, the array of interesting helium cluster posters attests to the opportunities in this new area of study.

Throughout the course of this Faraday Discussion, a number of themes appeared, and in the remainder of these remarks I will attempt to give a brief perspective on several of these. This is a process I embark upon with some trepidation, for the discussions were much too enjoyable to take the time to write out detailed notes!

### 2 Potential energy surfaces

As Prof. Levy stated in his Concluding remarks at the last Cluster Dynamics Discussion,<sup>5</sup> the accurate characterization of cluster potential energy surfaces is a bread and butter activity of our field. A dominant theme in this aspect of our discussion is the effort from theorists and experimentalists to explore and map out important new regions of the multiple dimensional potential energy

surfaces, especially finding ways to work away from the local minima and to probe those regions important in chemical reactivity. From the high-resolution studies of Saykally<sup>6</sup> to the slightly "lower-resolution" studies of Nesbitt<sup>7</sup> to the IR absorption studies of Zwier<sup>8</sup> and Suhm,<sup>9</sup> we are probing ever more extensive regions of these surfaces. A second theme that emerges from our discussions is the importance of determining the critical degrees of freedom, the process of determining which of these degrees of freedom can be treated classically, which must be treated quantum mechanically,<sup>10</sup> and how accurately each of these degrees of freedom must be treated.<sup>11</sup>

There has been tremendous progress in the accurate characterization of potential energy surfaces for weakly bound systems. It was noted that in the 1988 Faraday Discussion on this subject, Buckingham, Fowler and our organizer Hutson<sup>12</sup> described the Van der Waals minimum as the theoretically intractable intermediate region! We have come a long way, both experimentally and theoretically. As emphasized by Szalewicz,<sup>13</sup> it is essential to extend our view of the intermolecular potential energy surfaces to include those regions that involve monomer distortions. In his words, flexible monomers are **required** in order to have chemistry! We can surely look forward to dramatic increases in computational power and rapid advances in both theory and experiment in addressing these important issues.

### 3 Clusters and the cage effect

While the problem of accurate determination of multidimensional potential energy surfaces for clusters is a daunting one, the problems become compounded when we consider the fact that only rarely does chemistry take place on a single potential energy surface! The cage effect and photodissociation dynamics have traditionally been and to date remain our major testing ground for multisurface, nonadiabatic processes. The active role of the solvent in cage recombination was emphasized by the calculations of Gerber<sup>14</sup> showing solvent insertion into the recombining chromophore and the experimental/theoretical studies of Lineberger<sup>15</sup> and Parson<sup>16</sup> showing solvent-driven curve crossings and emphasizing the importance of the solvent field on the recombining chromophore. In addition, the femtosecond photoelectron spectroscopy experiments of Neumark<sup>17</sup> show clearly the different timescales involved in recombination, vibrational relaxation and energy transfer to the solvent. The interplay between theory, experiment and simulation is nowhere more productive than in these complex, multisurface complexes.

### 4 Reactive complexes and transition state spectroscopy

One of our very important tools in the quest for details of extended regions of potential energy surfaces has been the use of clusters to probe normally unreachable sections of surfaces. Neumark<sup>17–20</sup> and Lineberger<sup>21,22</sup> utilize negative ion photodetachment of ionic clusters to probe transition state regions, while Polanyi<sup>23</sup> photoexcites neutral complexes at geometries near transition states to obtain spectroscopic information on this part of the surface. Lester<sup>24–26</sup> has demonstrated a remarkable ability to stabilize very weakly bound reactive complexes in the entrance channels, and has demonstrated that many of them (OHCO) play a key role in important reactions and are the cause of unusual temperature dependences. Using helium droplets to remove rapidly the association reaction exothermicity, Miller<sup>1</sup> expects to stabilize even more reactive species as, for example, (OH)<sub>n</sub>. In all of these systems, it appears likely that we will be able to add solvent molecules and carefully study the effect of stepwise solvation on reaction dynamics. Indeed, Neumark<sup>17</sup> has already demonstrated the effect of Ar solvation on IHI transition state. This is truly an exciting and rapidly developing area.

### 5 Conclusions

In the seven years since the last Cluster Dynamics meeting, we have seen dramatic increases in our theoretical comprehension, in the ability to simulate large systems and in the experimental tools and complexity of systems that can be addressed. The field is truly exciting and growing rapidly in breadth and in depth. It seems assured that there will be a Durham 2006 Faraday Discussion on Cluster Dynamics. The interesting speculation concerns what we will have seen by then, and what

will be the thrust of this next meeting. Using a murky crystal ball, I predict to see the following areas of emphasis:

- (i) Focus on multisurface processes and nonadiabatic transitions.
- (ii) Ultrafast dynamics probe of new regions of reactive surfaces.
- (iii) Spectacularly accurate surfaces for small systems, such as the water dimer and small cluster ions.
- (iv) Spectacular state/size/temperature selectivity.
- (v) Characterization of solvation and solvent role through the first solvent shell.
- (vi) Time dependence of “real” chemical reactions in size selected clusters.
- (vii) Helium clusters with biomolecules.
- (viii) And the most exciting developments will undoubtedly not be included above!

A more complex question concerns what will we do with these multidimensional surfaces. Will we have the tools to visualize them and gain intuition from motion in so many dimensions? This is unclear to me. What is clear is that all of these advances will result primarily from the vitality of the scientists and from the very close coupling between theory, experiment and simulation. We close with our great thanks to Jeremy Hutson for organizing this meeting, and look forward to our next gathering.

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