

directly ionized, and every possible vibrational state of HCl^+ can be photodissociated. The main channels seen in the velocity map images shown in Fig. 2 are from photoionization of $\text{H}^*(n = 2)$ in the H^+ image; photoelectrons from the photoionization of $\text{H}^*(n = 2)$ and $\text{Cl}^*(4p(2D))$ in the electron image; and from the photoionization of $\text{Cl}^*(4p(2D))$ atoms in the Cl^+ image. The minor channels seen in all three images correspond to the production and subsequent photodissociation of HCl^+ to form $\text{H} + \text{Cl}^+$, or $\text{H}^+ + \text{Cl}$. Very similar results have been found for REMPI of molecular oxygen.³⁸ An added dimension of the velocity mapping is that the angular distributions are determined for all of the channels mentioned above, and that photodissociation proclivities for each vibrational level of HCl^+ are determined. Interpretation of the angular distributions is straightforward for HCl^+ photodissociation, but for the photoelectron angular distributions, many interesting and complex processes such as interference from shape resonances add extra dimensions and complications to the analysis.

4. Conclusion

A few of the most active applications of velocity mapping in studies of the photodissociation and photoionization of small molecules have been surveyed in this chapter. There are, of course, many other areas in these research fields that can profit from the relatively high angle velocity resolution of the mapping process. A recent example is the observation of dissociative ionization processes such as $\text{H}_2^* \rightarrow \text{H} + \text{H}^+ + e^-$, which is a three-body dissociation process. In this case, continuous energy distributions are observed for the photoelectrons and H^+ ions instead of the sharp rings of the Newton spheres. It should also be noted that the same technique can also be applied to other nascent molecules such as those formed, for example, in crossed-beam scattering, where again, the Newton spheres for the processes are directly observed. Velocity mapping, which has now opened the full potential of ion imaging to the study of molecular dynamics processes, is without doubt only a forerunner of increasingly more powerful techniques we can expect in the future.

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