

Microwave spectroscopy at the dissociation limit

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We have developed an ion beam technique in which a mass selected ion beam passes through a microwave absorption cell, followed by an electric field lens. Weakly bound energy levels lying close to the lowest dissociation asymptote fragment in the lens, and the resulting fragment ions are energy analysed with a electrostatic sector and detected. Spectroscopic transitions induced in the microwave cell produce population changes which result in changes in fragment ion intensity. The technique has extremely high sensitivity and in some cases we detect transitions involving levels with populations as low as 100 ions per second.

Although microwave spectroscopy is conventionally associated with rotational transitions, the nature of the closely spaced levels lying near the dissociation limit means that, in different cases, we observe electronic and vibrational as well as rotational transitions. Spectroscopic analysis and assignment is often extremely difficult, but once accomplished we obtain a detailed and accurate description of the long-range interaction potential. The work will be illustrated with reference to recent investigations of the Ne_2^+ and HeH_2^+ species.

**TRANSIENT FREQUENCY MODULATION SPECTROSCOPY OF
MOLECULAR FREE RADICALS**

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Phase modulation of narrow line light at radio frequencies coupled with detection at the modulation frequency allows one to approach shot-noise-limited absorption sensitivity. Such frequency modulation methods were developed 20 years ago and applied to the spectroscopy of static samples of chemically unreactive molecules. We have adapted the method to record spectra of chemically reactive species and this talk describes some of our recent work on carbenes. New spectra of the simplest (methylene, CH_2) have been obtained using a new spectrometer based on a simple and inexpensive tunable diode laser system in the near-infrared. A considerable number of new vibronic states have been identified. Chloro- and bromo-methylene have also been studied. These species possess a singlet electronic ground state, in contrast to CH_2 where the ground state is triplet, and the singlet-singlet rovibronic spectra recorded for the halomethylenes are considerably simpler to interpret than those observed for the parent radical.

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