

## THRESHOLD ION-PAIR PRODUCTION SPECTROSCOPY (TIPPS) of H<sub>2</sub> and D<sub>2</sub>

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Threshold Ion-Pair Production Spectroscopy (TIPPS) can determine field-free energetic thresholds for ion-pair formation<sup>a b</sup> in the same way that pulsed field ionization techniques (ZEKE/MATI) can obtain field-free ionization potentials. H<sub>2</sub> and D<sub>2</sub> were investigated and their ion-pair thresholds were determined to be  $139714.8 \pm 1.0 \text{ cm}^{-1}$  and  $140370 \pm 1.0 \text{ cm}^{-1}$ , respectively. Pulsed field ion-pair formation mostly results from excitation of complex resonances between ion-pairs and electronic Rydberg states of the parent molecule. However, evidence of the direct excitation of ion-pair Rydberg states was also found.

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<sup>a</sup> J. D. D. Martin and J. W. Hepburn, *Phys. Rev. Lett.* **79** (1997).

<sup>b</sup> J. D. D. Martin and J. W. Hepburn, *J. Chem. Phys.* **109** (1998).