

Vibrational Spectroscopy and Ab-Initio Computational Investigations into the Structure, Symmetry, and Dynamics of Molecules and Ions of Atmospheric Relevance

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The spectroscopic characteristics of atmospheric molecules play an essential role in determining their reactivity on the macroscopic as well as atomic scale. Due to the complex balance of the non-equilibrium atmospheric system, overall global effects are not directly proportional to molecular concentration, and thus it is essential to develop detailed models for a large variety of atmospheric molecules. Gas-phase vibrational spectroscopy allows for an investigation into intramolecular dynamics which can then be incorporated into a model of overall reactivity. In addition to this practical motivation, there is ample opportunity in the interplay of modern spectroscopic and computing capability to investigate problems of purely physical interest. The development and implementation of novel methods of vibrational spectroscopy for laboratory and atmospheric analysis is explored. These efforts are complemented by molecular orbital calculations useful for guiding spectral interpretation and developing models of bonding and reactivity. Examples include interpretation of solar and open-path atmospheric FT-IR absorption spectra, plasma absorption and pyrolysis emission spectra, and spectroscopic characterization of many interesting large molecules such as the highly symmetric $C_{60}Br_{24}$. Ab-initio investigations particularly facilitate analysis of reactive species such as molecular anions, providing a means for interpretation of recent photoelectron and IR-MPD spectra of SF_6^- . The importance of molecular symmetry in electron transfer processes is explored as the experimental results of SF_6^- IR-MPD spectroscopy are incorporated within a theoretical framework for the auto-ionization lifetimes of polyatomic anions. Based upon agreement with recent experiments, an explanation for a long-standing discrepancy in reported experimental values for the autodetachment lifetime of this interesting anion is proposed.