Addressing Discrepancies in the NF_3 Photoelectron Spectrum

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Due to a large change in geometry upon ionization of NF_3, the photoelectron spectrum of NF_3 observed by Berkowitz and Greene [1] exhibits a vibrational progression that spans roughly 1.5 eV. The width of this progression is enough to surmount the barrier to planarity in NF_3^+, the value of which is assigned based on arguments pertaining to so-called 'quantum monodromy' [2] and accounts for the observed change in vibrational spacing on either side of the peak maximum at 13.75 eV. The experimental ionization onset is quoted to be 13.0 eV, a value that is consistent with previous experimental work but is, however, at (eV) considerable odds with mid-level calculations, which report a value almost 0.4 eV lower in energy. To address this inconsistency, we perform high-accuracy HEAT-345(Q) [3] calculations to determine the adiabatic origin of the spectrum to within 0.01 eV. Moreover, we determine the cation inversion barrier height to be 0.24 eV lower than the value predicted by Berkowitz, throwing into question the origin of the change in vibrational spacing in the experimental spectrum. We present Franck-Condon simulations (accounting for anharmonicity) that attempt to alleviate discrepancies between calculated and experimental assignments of the NF_3 photoelectron spectrum.

References

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