quencies for cis–cis and trans–perp HOONO for QCISD and CCSD(T) calculations. At the CCSD(T)/cc-pVTZ level of theory, the cis–cis conformer was found to be 3.4 kcal/mol more stable than the trans–perp conformer (including zero-point correction) (Ref. 16) with a best estimate of $D_{0}(\text{HO–ONO})_{\text{cis–cis}} = 18.3$ kcal/mol at the CCSD(T)/CBS level of theory.\(^{20}\)

There now exists an abundance of convincing spectroscopic evidence supporting a significant HOONO channel in the gas-phase reaction of OH + NO\(_2\).\(^{14–17}\) However, the lack of rotationally resolved spectra in any of these studies has hampered efforts to provide an unambiguous assignment of the observed spectral features or to quantify the relative yields of cis–cis and trans–perp HOONO produced under different experimental conditions. Our past success in producing, detecting, and analyzing the pure rotational spectra of free radicals and reactive intermediates with the JPL submillimeter spectrometer\(^{21–25}\) prompted us to initiate a search for HOONO. Submillimeter spectroscopy provides several advantages over the techniques that have previously been used to characterize HOONO: excellent detection sensitivity, superb spectral resolution, and unequivocal molecular specificity for assigned transitions. Additionally, molecular concentrations can be accurately measured from the intensities of pure rotational transitions once the molecular dipole moment is known. Here we report an analysis of the cis–cis HOONO submillimeter spectrum.

The JPL submillimeter spectrometer has been described in detail previously.\(^{26}\) Spectra were recorded by flowing the vapors from a 70% hydrogen peroxide solution (FMC Corporation) over a sample of solid NOBF\(_4\) (Aldrich) placed in a shallow Pyrex boat in the bottom of the absorption cell. The hydrogen peroxide flow rate was adjusted to maximize the cis–cis HOONO signal. Typical cell pressures were 15–20 mtorr. Small amounts of nitric acid (HONO\(_2\)) (Ref. 27), peroxyxynitric acid (HOONO\(_2\)) (Ref. 27), and hydroxyfluoroborane (BF\(_2\)OH) (Ref. 28) were observed as side products. The chemistry used in this study has the advantage of selectively generating cis–cis HOONO without large interferences from HONO\(_2\).

All spectral fitting and simulations were performed using Pickett’s SFIT program suite.\(^{29}\) An illustration of the cis–cis HOONO molecular structure in its principal axis system is given in Fig. 1. Simulations of the cis–cis HOONO rotational spectrum, based on ab initio rotational constants and dipole moments,\(^{16}\) predicted the presence of characteristic asymmetry doublets of both a- and b-type transitions (i.e., quartets) for low-$K_a$ R-type transitions near 400 GHz. Survey scans in the 399–454 GHz region revealed quartet patterns consistent with the cis–cis HOONO simulations. The compact origins of several patterns are shown in Fig. 2. Termed “R bunches,” these patterns occur for oblate limit transitions at intervals of $2\Sigma$ ($\sim$11.5 GHz) with $J + K_a =$ const. The initial assignments for R bunches with $K_a < 5$ were used to refine the spectroscopic parameters and generate new predictions. New transitions were assigned and the fitting process iteratively repeated. Additional spectra were recorded in the 179–183, 269–284, and 627–640 GHz regions to extend the $J$ and $K_a$ range of transitions in the data.