Rotational spectrum of *cis–cis* HOONO

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The pure rotational spectrum of *cis–cis* peroxynitrous acid, HOONO, has been observed. Over 220 transitions, sampling states up to $J' = 67$ and $K'_a = 31$, have been fitted with an rms uncertainty of 48.4 kHz. The experimentally determined rotational constants agree well with *ab initio* values for the *cis–cis* conformer, a five-membered ring formed by intramolecular hydrogen bonding. The small, positive inertial defect $\Delta = 0.075667(60)$ amu Å^2 and lack of any observable torsional splittings in the spectrum indicate that *cis–cis* HOONO exists in a well-defined planar structure at room temperature. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1687311]

The radical–radical association reaction

$$OH + NO_2 + M \rightarrow HONO_2 + M$$

terminates several key HO_x and NO_x catalytic free-radical chain reactions in the lower atmosphere and sequesters the reactants into the reservoir species nitric acid, $HONO_2$. The rate of this reaction directly affects ozone concentrations in the stratosphere and photochemical smog production in the troposphere. Thus, detailed knowledge of the $OH + NO_2 + M$ mechanism and rate under all atmospherically relevant conditions is critical for accurate modeling of atmospheric photochemistry. An intensive investigation of discrepancies between low- and high-pressure values of the rate led several groups to propose that a secondary channel

$$OH + NO_2 + M \rightarrow HOONO + M$$
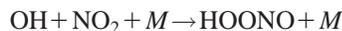
competes with the primary reaction channel at higher total pressures.[1–7] Despite the kinetics evidence, detection of gas-phase HOONO eluded several concentrated detection efforts[2,4,5] and its production as a stable species in the $OH + NO_2 + M$ reaction remained controversial until very recently.

Peroxynitrous acid, HOONO, has long been known as a short-lived intermediate in aqueous solutions, although its spectroscopic characterization in solution has been limited to a broad UV absorption feature.[8–10] In the early 1990s Lee and co-workers identified HOONO infrared spectra after photodissociating $HONO_2$ in cryogenic Ar and N_2 matrices.[11–13] The vibrational frequencies, H/D and $^{14}N/^{15}N$ isotopic shifts, and band intensities recorded in these studies provided the information to distinguish *trans–perp* and *cis–cis* HOONO conformers. The dynamics of $OH + NO_2$ recombination in the matrix sites favored the production of *trans–perp* HOONO; *cis–cis* HOONO was observed only after $HONO_2$ photodissociation at 193 nm.[13]

In 2002 Nizkorodov and Wennberg reported the detection of gas-phase HOONO by recording the vibrational over-tone photodissociation spectrum in the $2\nu_1$ region (6000–7200 cm^{-1}) with ~2 cm^{-1} resolution.[14] They observed a rich vibrational structure with at least seven overlapping HOONO bands. These features were tentatively assigned to both the *cis–cis* and *trans–perp* conformers; however, a reanalysis of this spectral assignment indicates that only *cis–cis* HOONO is present at room temperature, while significant concentrations of *trans–perp* HOONO are observed only below 240 K under moderate flow rates due to rapid isomerization.[15] A number of additional features in this spectrum are assigned to combinations of $2\nu_1$ with the ν_9 torsional mode, indicating a large degree of structural floppiness in HOONO.

This work was followed in rapid succession by detection of the *cis–cis* ν_1 fundamental by Bean *et al.* using cavity ringdown spectroscopy[16] and a high-resolution study of the *trans–perp* $2\nu_1$ band in a supersonically cooled molecular beam by Pollack *et al.*[17] Rotational contour simulations in both studies yielded rotational constants consistent with *ab initio* values. The resolution of individual rotational transitions was not possible due to laser bandwidth limitations in the study of Bean *et al.* and because of dissociative line broadening in the case of the work of Pollack *et al.*

Ab initio calculations have helped guide much of the spectral characterization of HOONO. McGrath *et al.* found stable structures associated with the *cis–cis*, *cis–perp*, and *trans–perp* conformers at the HF/6-31G* and MP2/6-31G* levels of theory.[18] The vibrational frequencies and intensities calculated in this study enabled Lee and co-workers[11,13] to distinguish between the *trans–perp* and *cis–cis* conformers in their matrix IR spectra. McGrath and Rowland subsequently used G2, G2(MP2), QCISD(T)/6-311G(d,p), and MP2 calculations with basis sets up to 6-311+G(3df,2p) to improve characterization of the relative energetics of the three stable conformers.[19] Bean *et al.* found that the *cis–perp* conformer was not a true stationary point at the QCISD(T)/cc-pVTZ or CCSD(T)/cc-pVTZ levels of theory.[16] Bean *et al.* also reported rotational constants and vibrational fre-

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 $D_0(\text{HO–ONO})_{cis–cis} = 18.3$ 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 $\text{OH} + \text{NO}_2$.[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), peroxynitric acid (HOONO_2) (Ref. 27), and hydroxy-fluoroborane (BF_2OH) (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 SPFIT 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 $2C$ ($\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
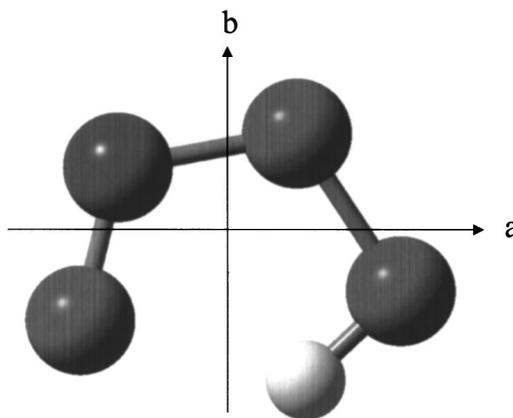

FIG. 1. *cis–cis* HOONO depicted in its principal axis system. The *c* axis is perpendicular to the molecular plane. The structure is taken from the CCSD(T)/cc-pVTZ calculations of Bean *et al.* (Ref. 16).
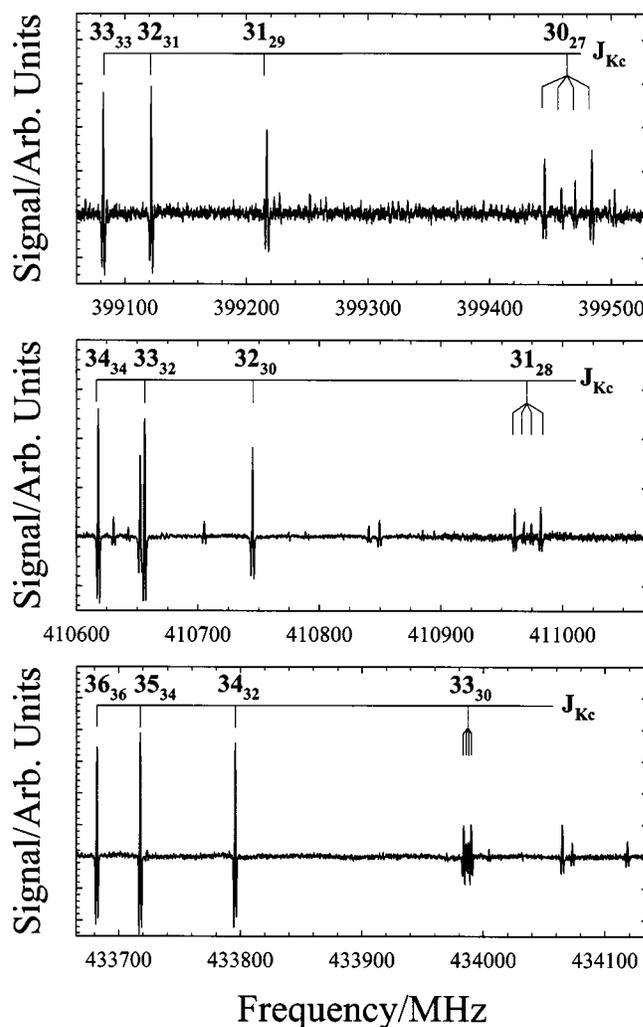

FIG. 2. Submillimeter spectra of *cis–cis* HOONO *R*-bunch origins in the 400 GHz region displaying the characteristic pattern used to make the initial identification. The separation of the first resolved quartet from the first transition of each sequence and the splitting within the quartet both decrease with increasing frequency. The approximate intensity ratio within each quartet reflects the relative magnitudes of $\mu_b^2 : \mu_a^2 : \mu_a^2 : \mu_b^2$. The unmarked features in these spectra are due to HONO_2, HOONO_2, or other *cis–cis* HOONO transitions.

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TABLE I. Fitted *cis–cis*-HOONO Hamiltonian parameters.[a]

Parameter	Units	Value
$(B+C)/2$	MHz	6869.52786(32)
$A-(B+C)/2$	MHz	14536.8651(10)
$(B-C)/4$	MHz	539.26307(12)
$-\Delta_J$	kHz	−8.05340(26)
$-\Delta_{JK}$	kHz	16.0335(11)
$-\Delta_K$	kHz	−59.9854(46)
δ_J	kHz	−2.47179(11)
δ_K	kHz	−13.7320(20)
Φ_J	mHz	−15.005(68)
Φ_{JJK}	mHz	184.55(53)
Φ_{JKK}	mHz	−883.1(21)
Φ_K	Hz	1.0996(56)
ϕ_J	mHz	−5.385(29)
ϕ_{JK}	mHz	−55.11(76)
ϕ_K	mHz	388.7(46)
σ_{fit}/No. lines	kHz	48.4/225

[a]Values in parentheses represent 1σ uncertainties in units of the least significant figure.

set. The final data set included 225 transitions sampling states with J up to 67 and K_a up to 31. The least-squares fit yielded an rms uncertainty of 48.4 kHz and accurately predicted all ground-state *cis–cis* HOONO features with sufficient intensity to be identifiable in the spectra recorded.

Measured and calculated frequencies and quantum number assignments can be found in the JPL millimeter and submillimeter spectral line catalog online at http://spec.jpl.nasa.gov/catalog. Rotational constants and distortion constants up to sixth order were determined using the Watson A reduction. The parameters determined in the least-squares fit are given in Table I.

The A, B, and C rotational constants were determined from the fitted Hamiltonian parameters. These values are given in Table II along with the rotational constants determined from the optimized CCSD(T)/cc-pVTZ structure reported by Bean *et al.*[16] The inertial defect $\Delta = I_{cc} - I_{aa} - I_{bb}$ is 0.076 amu Å[2], consistent with the small, positive inertial defects that have been observed for planar ring molecules such as furan and pyrrole.[30] This evidence indicates that *cis–cis* HOONO is a planar molecule with small out-of-plane deformations caused by zero-point vibrational motion. The lack of any observed torsional splittings in the submillimeter

TABLE II. *cis–cis* HOONO rotational constants, moments of inertia, and inertial defect.[a]

Parameter	Experiment	CCSD(T)/cc-pVTZ Ref. 16
A (MHz)	21406.3930(10)	21310
B (MHz)	7948.05399(43)	8081
C (MHz)	5791.00173(35)	5859
I_{aa} (amu Å[2])	23.6087915(11)	23.715
I_{bb} (amu Å[2])	63.5852588(34)	62.54
I_{cc} (amu Å[2])	87.2697149(53)	86.26
Δ (amu Å[2])	0.0756646(64)	0.00

[a]Values in parentheses represent 1σ uncertainties in units of the least significant figure.

spectrum of the vibrational ground state further suggests that intramolecular hydrogen bonding prevents any significant large-amplitude motion.

Our findings of well-defined planarity in *cis–cis* HOONO contrast with the significant levels of torsional excitation that Nizkorodov and Wennberg observed in the $2\nu_1$ region and their conclusion that HOONO exhibits a large degree of structural floppiness.[14] The most likely reasons for this discrepancy lie in the experimental measurements: the submillimeter spectrum detects molecules near the minimum of the potential energy surface while the Nizkorodov–Wennberg experiment detects exclusively molecules that have undergone vibrational photodissociation. HOONO molecules with internal energies above the HO–ONO dissociation threshold might be expected to display significant torsional excitation as they dissociate. Torsional excitation may even enhance the dissociation rate near D_0(HO–ONO) and thermal excitation of torsional vibrations can promote dissociation for molecules nominally excited below D_0(HO–ONO). The variation of the rigidity of the planar structure as a function of vibrational-mode excitation and total internal energy as well as how the deviation from planarity affects the near-threshold dissociation dynamics are clearly areas for further investigation.

The intensities of the various observed rotational transitions can be used to estimate the relative values of the μ_a and μ_b dipole moment components. The $J_{Kc} = 30_{27}$, 31_{28}, and 33_{30} quartets shown in Fig. 2 are especially useful for this since the two central components in each quartet are a-type transitions while the highest- and lowest-frequency transitions in each quartet are b-type transitions. After removal of the J- and K-dependent matrix elements, the relative intensities of the quartets suggest that $\mu_b^2/\mu_a^2 \sim 3$. Simulations using $\mu_a = 0.66$ D and $\mu_b = 1.14$ D produced good agreement with comparable *cis–cis* HOONO transition intensities.

Experiments to measure selected lower-J transitions at millimeter wavelengths to determine μ_a, μ_b, and μ_{tot} are under way. Once experimental values for μ_a, μ_b, and μ_{tot} have been determined, millimeter and submillimeter spectroscopy will provide an excellent method for accurately quantifying *cis–cis* HOONO number densities. This will enable us to quantify the OH + NO$_2 \rightarrow cis-cis$ HOONO yields under atmospherically relevant conditions. A combined submillimeter and infrared experiment could also be used to quantify the band strengths of the infrared transitions.[14,16,17]

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