

Cis-cis and trans-perp HOONO: Action spectroscopy and isomerization kinetics

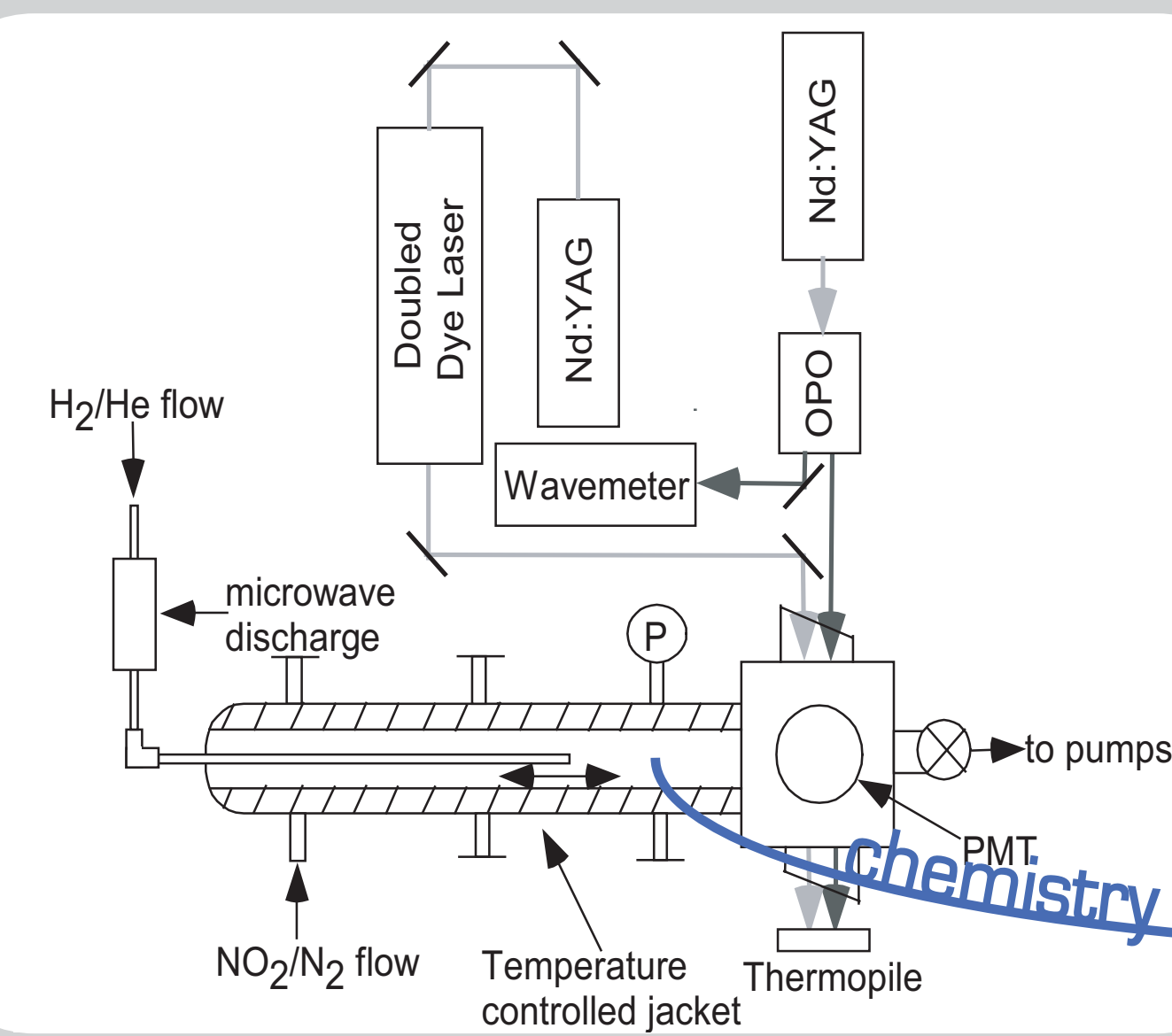
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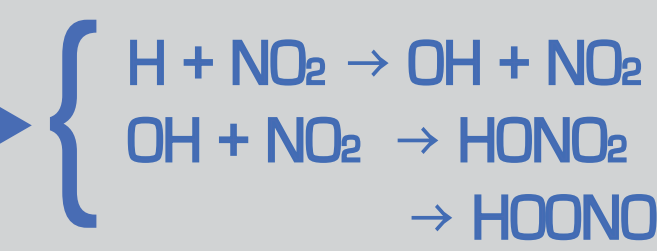
Abstract

HOONO is a weakly-bound isomer of nitric acid produced in the OH + NO₂ reaction. The OH + NO₂ reaction is the major sink of both HOx (OH + HO₂) and NOx (NO + NO₂) families of radicals, the most important reactants in polluted air. The short thermal lifetime of HOONO makes it a temporary reservoir of OH and NO₂ rather than a permanent sink. Thus, understanding the extent and kinetics of HOONO formation, and studying the spectroscopy so that HOONO may be searched for in the atmosphere, are crucial to evaluating the OH + NO₂ reaction and the atmospheric concentrations of OH and NO₂. In our lab, the spectroscopy and kinetics of HOONO are studied in a flow cell reactor using the technique of action spectroscopy, or vibrational predissociation spectroscopy in the first OH overtone (2ν₁) region. Two conformers of HOONO are distinguished based on their differing time and temperature behavior, and assigned as cis-cis and trans-perp HOONO based on ab initio vibrational frequencies and reasoning about the interactions of vibrational modes in the hydrogen-bonded cis-cis conformer versus the trans-perp conformer of HOONO. Using the kinetics flow cell, the isomerization from the less stable trans-perp HOONO to cis-cis HOONO can be observed directly in the range 223 - 238 K to determine the isomerization barrier of 33 ± 12 kJ/mol. Calculations to predict this isomerization barrier in a master equation model yield 42 kJ/mol, consistent with the experimental measurement. Ab initio calculations have been performed to predict the relative transition strengths of the two conformers. Based on these calculations, we estimate the atmospheric impact of HOONO.

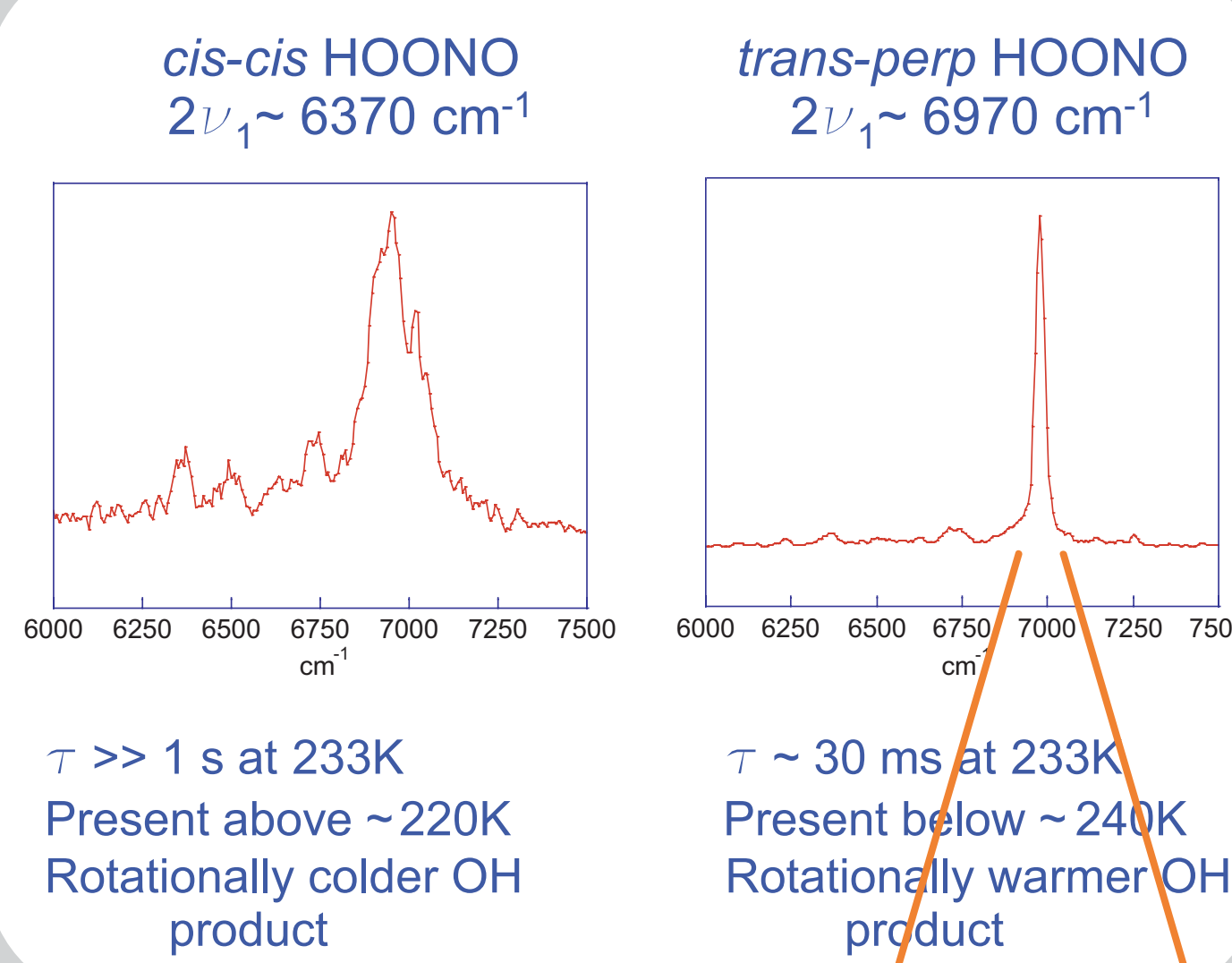
Action spectroscopy and kinetics flow cell



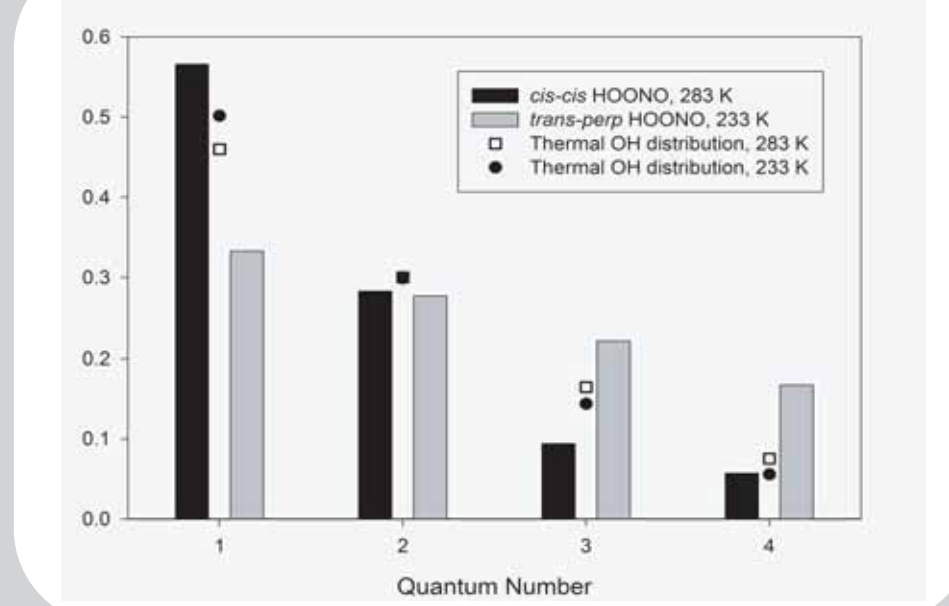
In the action spectroscopy technique, molecules are excited above or close to their dissociation threshold via direct overtone pumping (in this case, by the output of a 355 nm pumped OPO). Subsequent unimolecular decomposition results in products that are sensitively detected by laser induced fluorescence (LIF) either directly or after a chemical conversion. We employ the doubled output of a 532 nm pumped Rhodamine 6G dye laser. The kinetics flow cell allows precise control of the reaction temperature and mixing time prior to detection. The discharged H₂/He/Ar flow is injected into the NO₂/N₂ flow via a variable position injector. At our flow conditions, this allows spectroscopic detection of HOONO from 90 - 160 ms after mixing.



Spectroscopic assignment of two conformers of HOONO

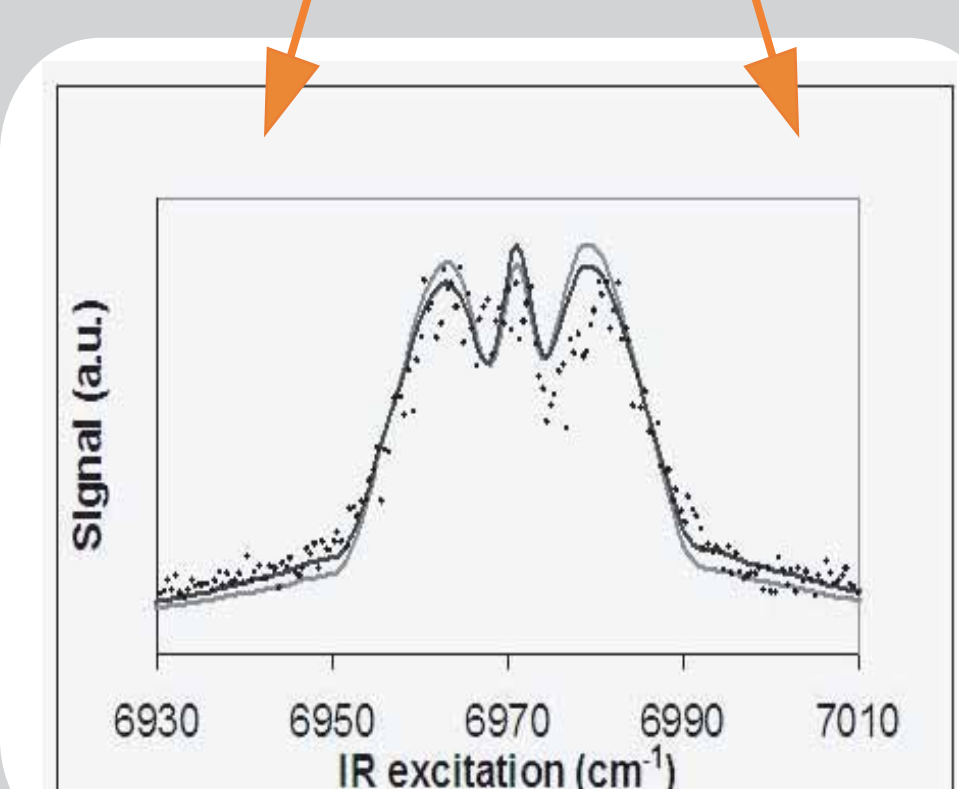


Two distinct conformers of HOONO, cis-cis and trans-perp are differentiated by their temperature and lifetime behavior. Trans-perp HOONO is only observed at low temperatures, and disappears with a lifetime of 30 ms at 233 K. The 2ν₁ bands are assigned based on predicted ab initio ν₁ frequencies: at the CCSD(T)/cc-pVTZ level, ν₁ (cis-cis) is 3521 cm⁻¹ and ν₁ (trans-perp) is 3780 cm⁻¹.



These assignments are corroborated by a study of the internal energy distribution in the OH photofragment. The LIF probe laser can be scanned over a series of rotational states of the OH product. This reveals that OH photofragments originating from cis-cis HOONO have much less internal rotational energy than photofragments from trans-perp HOONO, consistent with a larger energy release (hν-D₀) for trans-perp than for cis-cis HOONO.

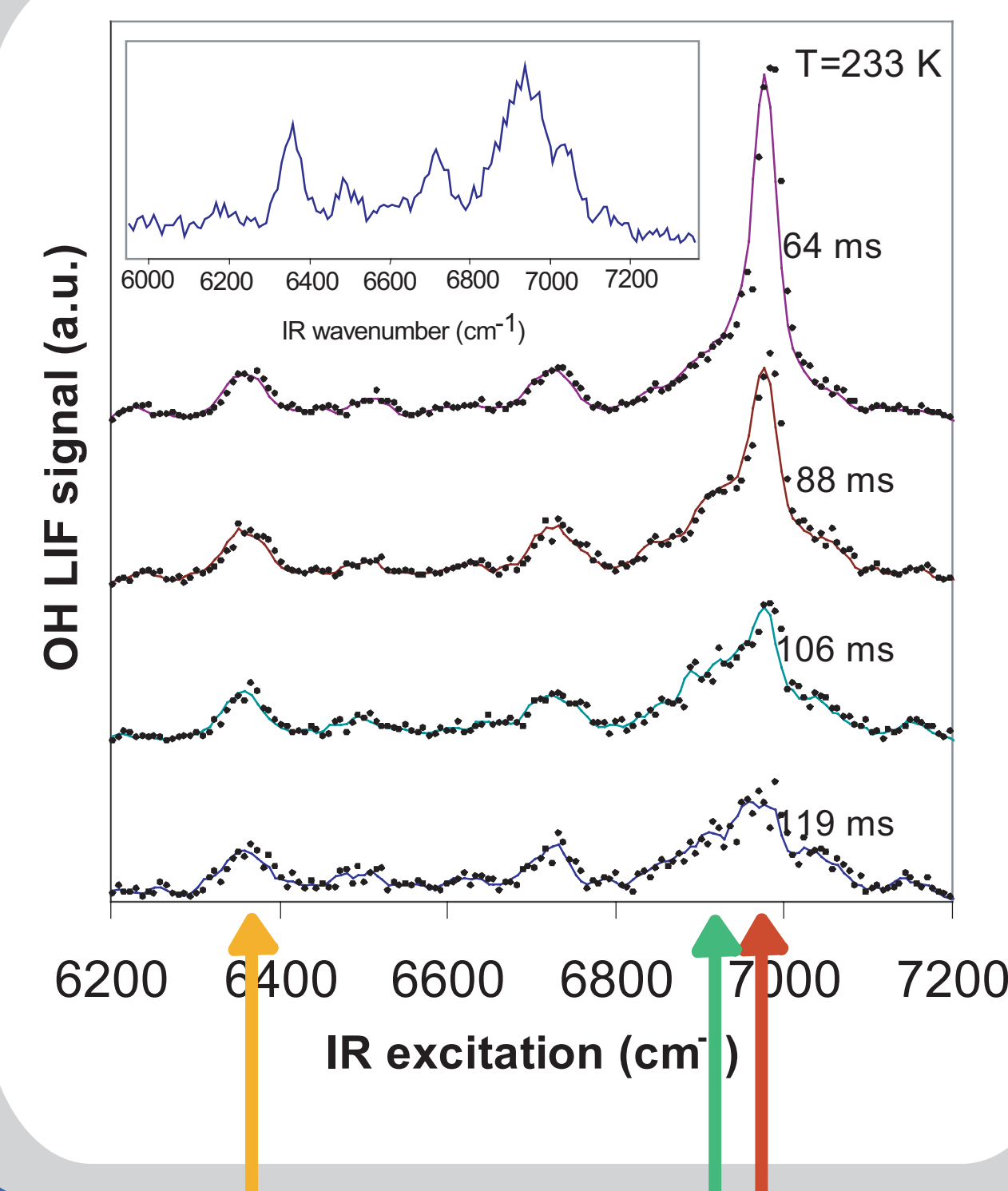
A 2 cm⁻¹ resolution scan of the trans-perp HOONO peak reveals rotational band structure that can be fit with the modeling program AsyRot. We predict a band contour of between 1.3 to 1 and 1.8 to 1 a-type to c-type (smooth lines in plot).



Predicted cis-cis HOONO (hν-D₀): -575 cm⁻¹: requires additional thermal energy to dissociate.
 Predicted trans-perp HOONO (hν-D₀): 1100 cm⁻¹: energy available for rotational excitation of OH fragment
 Consistent with observed energy distributions!

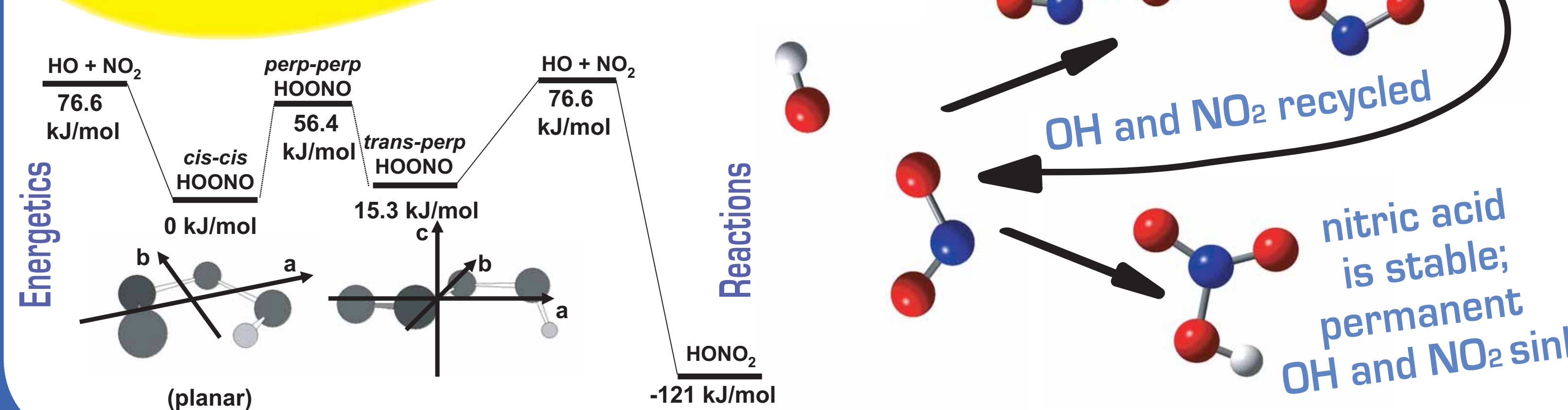
Measurement of cis-cis to trans-perp isomerization

The HOONO spectrum changes with time in the flow cell: trans-perp HOONO disappears, while cis-cis HOONO does not. We assume that this change is due to isomerization from trans-perp to the more stable cis-cis HOONO, since the barriers to OH + NO₂ and to HONO₂ are high. The ability to monitor both conformers of HOONO over time in the flow cell and over a range of temperatures allows the direct measurement of cis-cis to trans-perp HOONO isomerization rate.

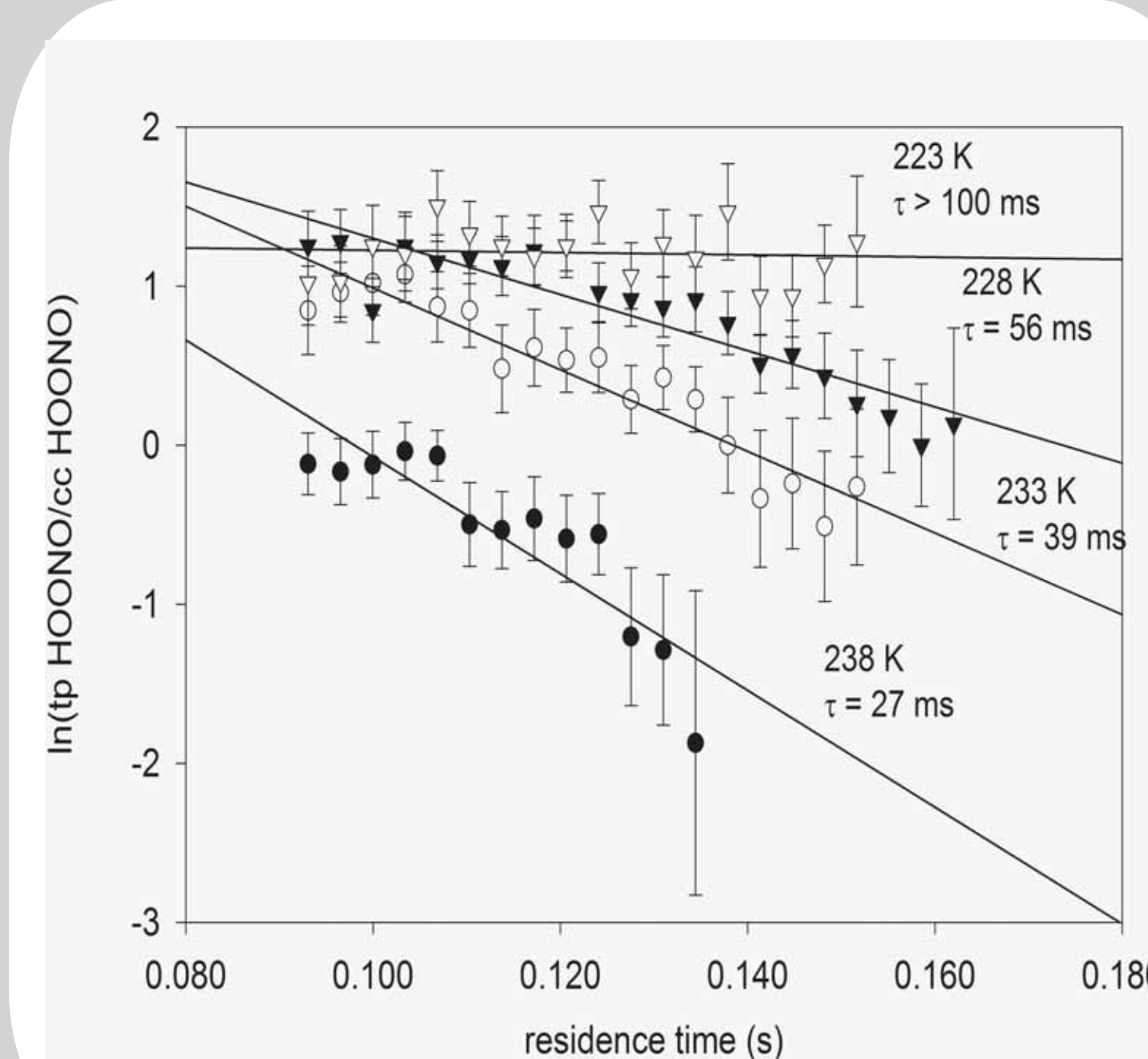


The ratio S₆₃₆₅/S₆₉₇₀ of trans-perp HOONO to cis-cis HOONO signal is monitored at a series of injector positions (residence times) in the flow tube at several temperatures by measurement of signal intensity at three wavelengths: one where both trans-perp and cis-cis HOONO absorb (6971 cm⁻¹), one which determines the baseline absorption by cis-cis HOONO underneath the 6971 cm⁻¹ signal (6950 cm⁻¹), and one where only cis-cis HOONO signal is present (6365 cm⁻¹).
 $S_{6365}/S_{6970} = (S(6971 \text{ cm}^{-1}) - S(6950 \text{ cm}^{-1})) / S(6365 \text{ cm}^{-1})$
 We use this ratio because we assume that both conformers of HOONO have the same wall and diffusive losses in the flow tube, so that this ratio will cancel the contribution of these losses to the lifetime. In addition, we assume that the increase in cis-cis HOONO signal due to the isomerization is negligible, since the number density of trans-perp HOONO is significantly lower than that of cis-cis HOONO, and since the spectrum is spread over a broad 1000 cm⁻¹ wavelength range compared to the spectrally narrow 30 cm⁻¹ trans-perp peak.

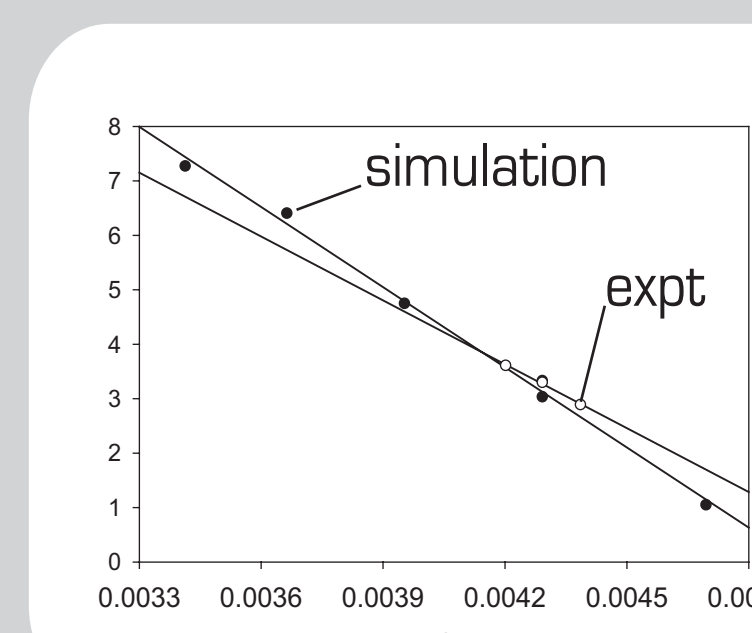
the OH + NO₂ system



Isomerization barrier: experiment and theory



A plot of log(S₆₃₆₅/S₆₉₇₀) versus residence time has a slope that is the unimolecular rate of trans-perp to cis-cis HOONO isomerization. Temperature-dependent isomerization rates are shown here, in the range 223 K < T < 238 K. The lifetime of trans-perp HOONO at 238 K, 233 K, 228 K, and 223 K, is 27 ± 4 ms, 39 ± 3 ms, 56 ± 6 ms, and > 100 ms, respectively, in 13 hPa of Ar. The Arrhenius ln(k) vs. 1/T relationship gives an activation energy for isomerization of E_a = 33 ± 12 kJ/mole. The narrow temperature range of the data causes the high error limits on this determination of E_a.



This system can also be simulated using a master equation statistical model. We use the MultiWell suite of programs developed by John Barker, and determine a barrier of 42 kJ/mole with a strong collision model (average energy transferred per collision = 600 cm⁻¹).

Calculation of cis-cis and trans-perp HOONO overtone transition strengths

In order to estimate the relative concentrations of the cis-cis and trans-perp HOONO from the observed band intensities, we perform semi-empirical calculations to compute transition strengths for the overtone bands of both isomers. The oscillator strength for a given vibrational transition is given by

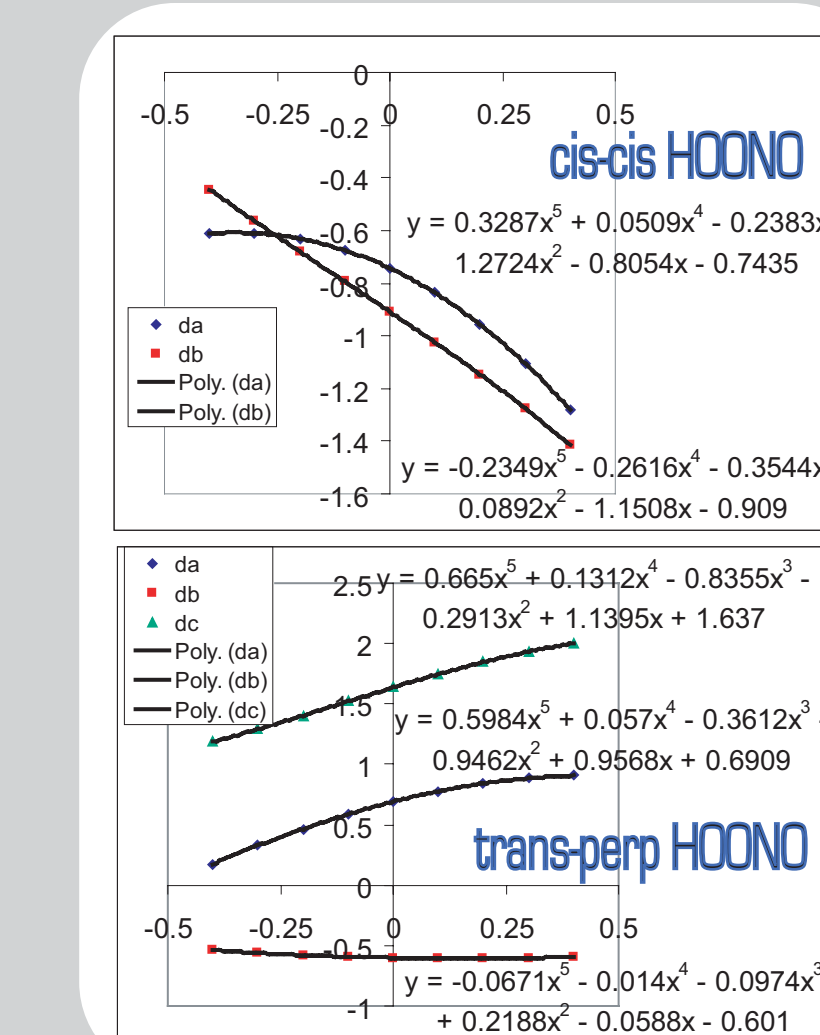
$$f_{if} = \frac{4\pi m_e}{3e^2 \hbar} \nu_{if}^2 \sum_{i,a,b,c} |M_{i,a,b,c}|^2$$

where ν is the frequency of the transition and M_i are the matrix elements of the transition dipole moment between the ground and excited vibrational states:

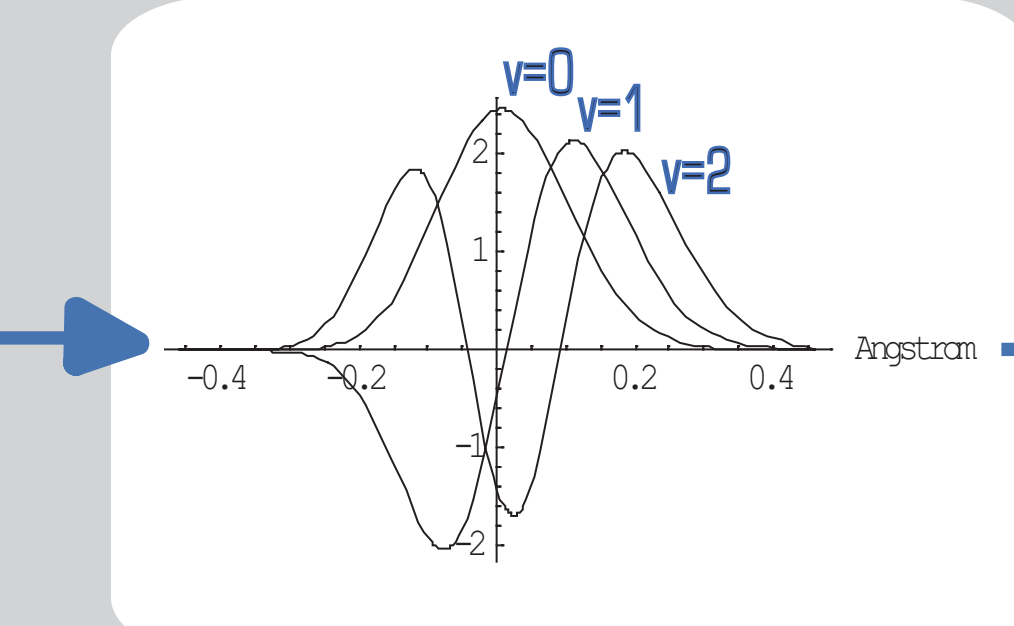
$$M_i = \langle f | \mu_i | i \rangle$$

The values of the matrix elements M_i for the 2ν₁ overtone transitions are obtained by first computing ab initio dipole moment functions along one dimension, the normal mode q₁ (essentially the OH stretch). The vibrational matrix elements are then calculated using an anharmonic oscillator model with a single cubic perturbation, where the parameters are fit using observed vibrational energies. The results shown here were computed at the MP3/AUG-cc-pVDZ level of theory.

Dipole moment functions



Anharmonic wavefunctions



Oscillator strengths

cis-cis	trans-perp	tp/cc
1.55 × 10 ⁷	5.34 × 10 ⁷	3.4

Atmospheric Importance of HOONO

Isomerization of trans-perp to cis-cis HOONO occurs in milliseconds, even at low pressure. As a result, only the cis-cis conformer of HOONO will have appreciable concentration in Earth's atmosphere. Our study suggests an upper limit for the cis-cis HOONO lifetime in Earth's atmosphere of 1.4 × 10⁵ s (less than 40 daylight hours). Excitation of 2ν₁ and companion bands will be an efficient loss mechanism for HOONO. The average solar radiance at 1.4 μm is 4.90 × 10¹³ photons cm⁻² s⁻¹ cm. The predicted oscillator strength of 1.6 × 10⁷ gives an integrated band intensity for cis-cis HOONO of 1.4 × 10¹⁹ cm² molecule cm⁻¹. Assuming unit quantum yield for photodissociation, the resulting photolysis rate of HOONO in the atmosphere due only to IR excitation will be ca. 7 × 10⁶ s⁻¹. Other losses will shorten this lifetime further. The polar lower stratosphere in summer is a region and time characterized by fast gas-phase formation of HNO₃ and temperatures that are cold enough to yield a long HOONO thermal lifetime. At 20 km altitude, where [OH] concentrations are 2 × 10⁹ molecules cm⁻³ (1 pptv), the reaction of OH with NO₂ proceeds at a rate of 1 × 10⁴ molecules cm⁻³ s⁻¹. Assuming a 10% yield of HOONO in this reaction and the maximum HOONO lifetime (1.4 × 10⁵ s), the upper limit for the concentration of HOONO is 70 pptv. UV photolysis, reaction with OH, and thermal decomposition will certainly lead to lower abundances. Thus, unless other major sources of HOONO exist, it is unlikely to play a major role in the atmospheric photochemistry.

Conclusions

The two stable conformational conformers of HOONO have been distinguished via action spectroscopy, leading to a new understanding of earlier tentative spectral assignments. Trans-perp HOONO quickly isomerizes to the more stable cis-cis conformer, with an isomerization lifetime of 29 ms at 233 K. Isomerization data over the temperature range 223 - 238 K give an estimate of the activation energy for trans-perp to cis-cis HOONO isomerization of 33 ± 12 kJ/mole, consistent with a strong collision model. Semi-empirical ab initio transition strength calculations show that the 2ν₁ band of trans-perp HOONO absorbs more strongly than the 2ν₁ band of cis-cis HOONO, with a relative strength of 3.4 to 1. The more stable cis-cis HOONO is predicted to exist in the atmosphere at maximum concentrations of only 70 pptv, and therefore, will be of limited importance in photochemical processes. For atmospheric chemistry, the most important impact of the formation of the short-lived HOONO reservoir is that radical loss via OH + NO₂ is not unity.