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# Infrared Absorption Spectra of *t*-HNOH Radicals Generated on VUV Irradiation of NO in Solid Hydrogen

Yu-Jong Wu, Meng-Yeh Lin, Sheng-Chuan Hsu, and Bing-Ming Cheng<sup>\*[a]</sup>

Irradiation of solid H<sub>2</sub> near 3 K containing NO with vacuum-ultraviolet light from a synchrotron yields new infrared absorption lines at 1241.7, 1063.6 and 726.2 cm<sup>-1</sup>. The structures of four possible structural isomers: H<sub>2</sub>NO, *t*-HNOH, *c*-HNOH and NOH<sub>2</sub>, their vibrational wavenumbers, IR intensities and D-isotopic shifts are calculated with density-functional theory according to B3LYP and PW91PW91/aug-cc-pVTZ methods. Based

on the results of those calculations and of experiments with deuterium labeling, we assign the new lines to  $\nu_4$  (cis bending),  $\nu_5$  (N=O stretching) and  $\nu_6$  (out-of-plane deformation) modes, respectively, of *t*-HNOH. This photoproduct is formed through reaction of electronically excited NO with neighboring H<sub>2</sub> in the solid sample.

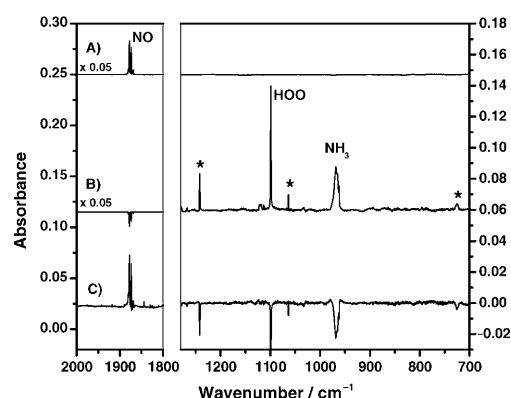
## 1. Introduction

Photochemical and photophysical processes in condensed phases attract interest because information from these experiments yields detailed knowledge about chemical transformations in extraterrestrial environments, insight into internal energy transfer and molecular dynamics, and new spectral data for transient species. The availability of powerful lasers operating in the ultraviolet and visible ranges has stimulated rapid development in these fields. In order to extend the range of photoexcitation into the vacuum-ultraviolet (VUV) region, we have set up an apparatus that consists of an infrared spectrometer and a refrigerator operating at 3 K coupled to an undulator of a synchrotron. This undulator beam line that delivers pseudo-continuous VUV light with photon flux  $\sim 10^{16}$  photons s<sup>-1</sup> (2% bandwidth) thus provides a possibility to investigate the photochemistry of molecules and materials in the VUV region. We have thereby recorded spectra of radicals C<sub>2</sub>H and C<sub>2</sub>H<sub>3</sub> trapped in solid Ne through VUV photolysis of precursors C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>.<sup>[1,2]</sup> The high performance of this experimental system provides an opportunity to study also photochemically induced reactions in the solid state. Here we report the reaction of NO with solid H<sub>2</sub> induced with VUV light.

Reaction of NO with hydrogen might form intermediate H<sub>2</sub>NO. Fushitani and Momose applied an ArF excimer laser for photolysis of NO in solid *para*-hydrogen (*p*-H<sub>2</sub>) and observed products HNO, H<sub>2</sub>O and NH<sub>3</sub>,<sup>[3]</sup> but they reported no other species generated. H<sub>2</sub>NO plays an important role in combustion chemistry<sup>[4–7]</sup> and in the destruction of ozone,<sup>[8,9]</sup> and serves as a key intermediate in several other processes.<sup>[10–12]</sup> It is also commonly used in spin-labeling experiments with electron-paramagnetic-resonance (EPR) detection.<sup>[13]</sup> Experimental data for H<sub>2</sub>NO are available mostly from EPR spectra,<sup>[14,15]</sup> and for H<sub>2</sub>NO (<sup>2</sup>B<sub>1</sub>) only a microwave spectrum<sup>[16]</sup> is reported. No isomer of H<sub>2</sub>NO has been characterized with infrared spectra; thus, it is interesting to study the intermediate of H<sub>2</sub>NO generated by VUV photon-induced reaction and identified by IR spectroscopy.

## 2. Results and Discussion

To investigate the possible isomers of H<sub>2</sub>NO from the reaction of NO with H<sub>2</sub>, we excited NO in solid hydrogen with VUV radiation from synchrotron source and analyzed the photoproducts by means of their IR absorption spectra. Figure 1A pres-



**Figure 1.** Partial IR absorption spectrum of a NO in solid H<sub>2</sub> (1/1000) before irradiation (A), difference spectrum after irradiation at 167 nm for 1 h (B), difference spectrum after further irradiation of the matrix at 121 nm for 10 min (C). New lines are marked with \*.

ents a partial IR absorption spectrum of a sample of NO in H<sub>2</sub> (molar ratio 1/1000) after deposition at 3 K; multiple lines near 1878 cm<sup>-1</sup> are characteristic of NO. Irradiation of this matrix sample with VUV light from the synchrotron produced many additional absorption lines due to photoproducts. For instance, irradiation of this sample at 167 nm for 1 h caused the intensities of lines of NO to decrease by  $\sim 44\%$ ; new IR absorption lines appear, most of which are readily identifiable as photo-

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**Table 1.** Products observed and wavenumbers of their absorption lines following irradiation of NO in solid H<sub>2</sub> or D<sub>2</sub>.

NO/H <sub>2</sub> Species	Wavenumber [cm <sup>-1</sup> ]	NO/D <sub>2</sub> Species	Wavenumber [cm <sup>-1</sup> ]
OH	3567.5 ( $\nu_1$ )	—	—
HO <sub>2</sub>	1099.0 ( $\nu_3$ )	DO <sub>2</sub>	914.0 ( $\nu_3$ )
HNO	2697.7 ( $\nu_1$ ), 1503.3 ( $\nu_2$ ), 1563.8 ( $\nu_3$ )	DNO	1150.4 ( $\nu_2$ ), 1547.7 ( $\nu_3$ )
H <sub>2</sub> O	3644.4 ( $\nu_1$ ), 1597.2 ( $\nu_2$ ), 3765.1 ( $\nu_3$ )	D <sub>2</sub> O	2661.5 ( $\nu_1$ ), 1178.2 ( $\nu_2$ ), 2773.0 ( $\nu_3$ )
NH <sub>2</sub>	1501.7 ( $\nu_2$ )?	ND <sub>2</sub>	1109.1 ( $\nu_2$ )
<i>t</i> -HONO	1690.0 ( $\nu_2$ ), 1267.3 ( $\nu_3$ ), 797.0 ( $\nu_4$ )	<i>t</i> -DONO	1684.3 ( $\nu_2$ ), 1013.3 ( $\nu_3$ ), 735.8 ( $\nu_4$ )
<i>c</i> -HONO	853.4 ( $\nu_4$ )	<i>c</i> -DONO	819.5 ( $\nu_4$ )
<i>t</i> -HNOH	1241.7 ( $\nu_4$ ), 1063.6 ( $\nu_5$ ), 726.2 ( $\nu_6$ )	<i>t</i> -DNOD	1072.0 ( $\nu_4$ ), 888.3 ( $\nu_5$ ), 530.8 ( $\nu_6$ )
H <sub>2</sub> O <sub>2</sub>	1280.6 ( $\nu_6$ )	D <sub>2</sub> O <sub>2</sub>	873.9 ( $\nu_3$ )
NH <sub>3</sub>	968.3 ( $\nu_2$ ), 3441.0 ( $\nu_3$ ), 1634.3 ( $\nu_4$ )	ND <sub>3</sub>	762.5 ( $\nu_2$ ), 2567.7 ( $\nu_3$ ), 1192.7 ( $\nu_4$ )

products HNO,<sup>[17]</sup> HO<sub>2</sub>,<sup>[18]</sup> H<sub>2</sub>O,<sup>[3]</sup> HONO,<sup>[19]</sup> H<sub>2</sub>O<sub>2</sub>,<sup>[20]</sup> NH<sub>2</sub>,<sup>[21]</sup> and NH<sub>3</sub>.<sup>[3]</sup> Table 1 summarizes these observed photoproducts at their line wavenumbers. Among the newly recorded IR lines, three new lines in the spectral range 700–1300 cm<sup>-1</sup> (marked \*, 1241.7, 1063.6 and 726.2 cm<sup>-1</sup>) are shown on the right side of the difference absorption spectrum in Figure 1B. This difference absorption spectrum was derived on subtracting the spectrum recorded after irradiation from the preceding deposition spectrum; a negative feature indicates destruction, whereas a positive feature indicates production.

We further irradiated this matrix sample at 121 nm for 10 min and scanned its IR spectrum; we then subtracted this IR absorption spectrum from the preceding spectrum after photolysis at 167 nm to obtain the resulting difference spectrum presented in Figure 1C. These three unknown lines diminished substantially along with regeneration of precursor NO and photoproducts OH and HNO. The ratios of the decreased intensities of these three new lines remain constant indicating that these three lines belong to the same carrier.

As in the case of NO in solid H<sub>2</sub>, VUV photolysis of NO in solid D<sub>2</sub> generates several photoproducts. Using the same irradiation conditions as a basis for comparison, photolysis of NO/D<sub>2</sub> (1/1000) at 167 nm for 1 h caused the intensities of NO lines to decrease by about 40%, similar to the value in solid hydrogen. Table 1 lists the photoproducts identified, and the corresponding wavenumbers of new IR lines observed, after VUV photolysis of NO in solid D<sub>2</sub>. Figure 2 displays a difference absorption spectrum in the range 500–1100 cm<sup>-1</sup> for the sample NO/D<sub>2</sub> (1/1000) upon irradiation with 167 nm for 1 h; photoproducts of known species in this spectral region, identified as DO<sub>2</sub>, D<sub>2</sub>O<sub>2</sub>, DONO and ND<sub>3</sub>, are marked in the figure. Three lines at 1241.7, 1063.5 and 726.2 cm<sup>-1</sup> in the spectrum recorded for NO in H<sub>2</sub> were not observed for NO in D<sub>2</sub>, indicating that the carrier of these lines contain H. The corresponding photoproduct generated in the deuterium sample might then contain D, which would cause a displacement of the IR absorptions associated with vibrational motions involving D atoms.

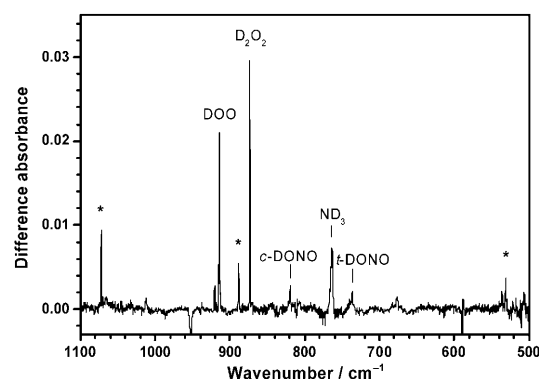
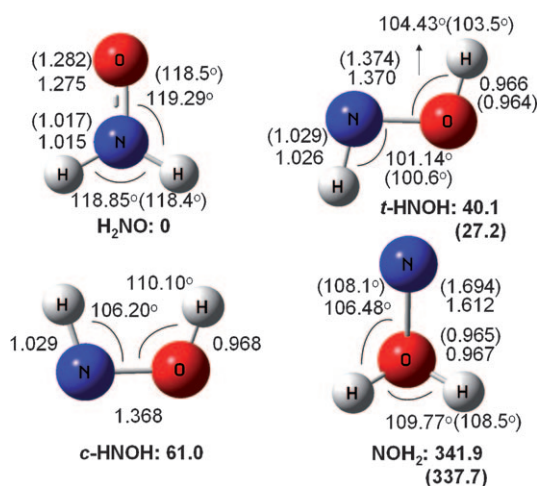
**Figure 2.** Partial difference IR absorption spectra of lines from NO/D<sub>2</sub> (1/1000) after irradiation at 167 nm for 1 h. New lines are marked with \*.

Figure 2 shows four new lines at 1072.0, 920.9, 888.3 and 530.8 cm<sup>-1</sup>, which may belong to the D isotopic variant of the new species formed in H<sub>2</sub>. For the line at 1241.7 cm<sup>-1</sup> for the H<sub>2</sub> sample, a shift to 1072.0 cm<sup>-1</sup> for the D<sub>2</sub> sample corresponds to a D-isotopic ratio 0.8633. The line at 1063.5 cm<sup>-1</sup> for the H<sub>2</sub> sample shifts to 920.9 or 888.3 cm<sup>-1</sup> in the D<sub>2</sub> matrix; based on the relative intensities, we chose the pertinent D-line to be 888.3 cm<sup>-1</sup>, which yields an isotopic ratio 0.8352. The broad feature at 726.2 cm<sup>-1</sup> observed in the H<sub>2</sub> experiments shifts to 530.8 cm<sup>-1</sup> and becomes a doublet; this shift yields an isotopic ratio 0.7309.

Comparison of results for photochemical tests on NO in H<sub>2</sub> and D<sub>2</sub> indicates from the isotopic shifts that the new species contains at least one H atom. According to the number of the new lines, we deduce also that the carrier contains at least three atoms. As an additional consideration, when we irradiated the NO/H<sub>2</sub> sample, first at 167 nm and then at 121 nm, lines at 1241.7, 1063.5 and 726.2 cm<sup>-1</sup> decreased whereas lines due to NO, HNO and OH increased slightly. This observation infers that the new species contains atomic constituents of NO, HNO and OH and could thus be H<sub>2</sub>NO. Several structural isomers exist for H<sub>2</sub>NO, therefore the carrier cannot be unambiguously identified from only these experimental results; for this reason we undertook quantum-chemical calculations.

The energies, equilibrium structures, vibrational wavenumbers and corresponding IR intensities of H<sub>2</sub>NO in various isomers were calculated with the Gaussian 03 program.<sup>[22]</sup> We used density-functional theory (DFT) for calculations of two types: the B3LYP method uses Becke's three-parameter hybrid exchange functionals,<sup>[23]</sup> and a correlation functional of Lee, Yang, and Parr, with both local and non-local terms,<sup>[24]</sup> PW91PW91 method uses exchange and correlation functionals of Perdew and Wang.<sup>[25]</sup> Dunning's correlation-consistent polarized valence triplet-zeta basis set,<sup>[26]</sup> augmented with s, p, d, and f functions (aug-cc-pVTZ), was used in both cases. By this means, four stable isomers of H<sub>2</sub>NO were obtained on utilization of analytic first derivatives at each stationary point. Figure 3 shows the geometries and relative energies predicted for species H<sub>2</sub>NO, *t*-HNOH, *c*-HNOH, and NOH<sub>2</sub>. H<sub>2</sub>NO is characterized with a short N–O bond (length 1.28 Å) similar to a double bond of NO. The N–O bond lengths of *t*-HNOH and *c*-HNOH are almost identical, about 1.37 Å. NOH<sub>2</sub> shows the



**Figure 3.** Geometries and relative energies/ $\text{kJ mol}^{-1}$  of isomers of  $\text{H}_2\text{NO}$  calculated with the B3LYP/aug-cc-pVTZ method; these energies are corrected with zero-point energies. The unit of bond length is Å. Results from CCSD(T)/6-311++G\*\* in ref. [29] are listed in parentheses.

longest N–O bond (1.61 Å) but an O–H bond of length between those of  $t\text{-HNOH}$  and  $c\text{-HNOH}$ .

The most stable isomer is  $\text{H}_2\text{NO}$ , but  $t\text{-HNOH}$  and  $c\text{-HNOH}$  have energies greater by only 44.5 and 61  $\text{kJ mol}^{-1}$ , respectively. Isomer  $\text{NOH}_2$ , lying  $\sim 342 \text{ kJ mol}^{-1}$  above  $\text{H}_2\text{NO}$ , has the greatest energy. From the point of view of energy, the structure  $\text{NOH}_2$  is the least likely candidate for the observed carrier.

The complete calculated results of vibrational modes and infrared intensities for various isomers  $\text{H}_2\text{NO}$  are listed in Table 2. For vibrational modes of  $t\text{-HNOH}$  predicted with B3LYP, the three most intense modes are designated  $\nu_4$  (*cis* bending) at 1266.6,  $\nu_5$  (NO stretching) at 1097.8 and  $\nu_6$  (out-of-plane deformation) at 736.1  $\text{cm}^{-1}$ ; these values are near observed values 1241.7, 1063.6 and 726.2  $\text{cm}^{-1}$  of the unknown carrier in  $\text{H}_2$ . The wavenumbers of the three most intense vibrational modes predicted for other isomers differ markedly from the values observed. For instance, although the lines for  $\nu_4$  and  $\nu_5$  of *cis*-HNOH are also near the experimental values, the predicted values 566.9 and 568.4  $\text{cm}^{-1}$  of mode  $\nu_6$  are smaller than the experimental value 726.2  $\text{cm}^{-1}$  by more than 22%. According to these theoretical calculations, we suggest that the newly recorded lines belong to  $t\text{-HNOH}$ . The ratios of integrated intensities observed for lines at 1241.7, 1063.6 and 726.2  $\text{cm}^{-1}$  are

0.7:0.4:1 agreeing satisfactorily with the relative intensities  $\sim 0.6:0.4:1$ , predicted for  $\nu_4$ ,  $\nu_5$  and  $\nu_6$  modes of  $t\text{-HNOH}$  with the B3LYP method, again consistent with our suggestion.

Both B3LYP and PW91PW91 methods predict nearly identical isotopic ratios for all isomers; D-isotopic ratios of four isomers predicted with B3LYP are listed in Table 3. The predicted isotopic ratios for modes  $\nu_4$  and  $\nu_6$  of  $t\text{-HNOH}$  are nearly the same as those determined experimentally (deviations  $< 0.0018$ ); even a slightly greater deviation ( $\sim 0.0038$ ) of mode  $\nu_5$  is still reasonable, but isotopic ratios predicted for other isomers fit less well with the experimental results. Further supported by these D-isotopic shifts, we thus conclude that new absorption lines at 1241.7, 1063.6 and 726.2  $\text{cm}^{-1}$  are associated with vibrational modes  $\nu_4$ ,  $\nu_5$  and  $\nu_6$  of  $t\text{-HNOH}$  dispersed in solid  $\text{H}_2$ .

For photoexcitation of NO dispersed in solid  $\text{H}_2$ , we irradiated the samples with light from the synchrotron tuned to wavelengths 210, 190, 167, 150 and 130 nm. Although the yields of photoproducts varied, the species of photoproducts generated

**Table 2.** Vibrational modes [ $\text{cm}^{-1}$ ] and infrared intensities [ $\text{km mol}^{-1}$  in parentheses] of various isomers  $\text{H}_2\text{NO}$  from quantum-chemical calculations.

Species	Vibrational mode	B3LYP/aug-cc-pVTZ	PW91PW91/aug-cc-pVTZ	Experiment $\text{H}_2$ matrix <sup>[a]</sup>
$t\text{-HNOH}$	$\nu_1$ , OH stretch	3758.8 (69)	3643.5 (55)	
	$\nu_2$ , NH stretch	3369.6 (4)	3268.3 (8)	
	$\nu_3$ , trans bend	1569.1 (2)	1531.5 (1)	
	$\nu_4$ , cis bend	1266.6 (103)	1231.2 (91)	1241.7 (75)
	$\nu_5$ , NO stretch	1097.8 (65)	1060.1 (57)	1063.6 (44)
	$\nu_6$ , oop bend	736.1 (178)	723.7 (165)	726.2 (100)
$c\text{-HNOH}$	$\nu_1$ , OH stretch	3703.8 (25)	3580.5 (15)	
	$\nu_2$ , NH stretch	3313.7 (17)	3211.1 (23)	
	$\nu_3$ , trans bend	1506.5 (45)	1463.7 (39)	
	$\nu_4$ , cis bend	1320.3 (4)	1281.8 (3)	
	$\nu_5$ , NO stretch	1084.8 (59)	1039.1 (46)	
	$\nu_6$ , oop bend	566.9 (5)	568.4 (5)	
$\text{H}_2\text{NO}$	$\nu_1$ , NH sym. stretch	3408.2 (0.1)	3304.6 (5)	
	$\nu_2$ , in-plane bend	1660.9 (12)	1611.1 (7)	
	$\nu_3$ , NO mixed stretch	1369.9 (11)	1340.0 (20)	
	$\nu_4$ , rock	1268.4 (1)	1229.5 (2)	
	$\nu_5$ , NH asym. stretch	3536.2 (6)	3416.4 (1)	
	$\nu_6$ , wag	336.8 (169)	318.7 (152)	
$\text{NOH}_2$	$\nu_1$ , OH sym. stretch	3707.0 (57)	3577.6 (35)	
	$\nu_2$ , OH <sub>2</sub> scissor	1575.9 (88)	1523.4 (77)	
	$\nu_3$ , OH <sub>2</sub> wag	716.0 (65)	754.8 (37)	
	$\nu_4$ , NO mixed stretch	483.0 (160)	449.2 (132)	
	$\nu_5$ , OH asym. stretch	3805.3 (201)	3654.7 (205)	
	$\nu_6$ , twist	753.3 (0.2)	700.0 (0)	

[a] Relative IR intensities are listed in parentheses.

**Table 3.** Experimental and calculated D-isotopic ratios<sup>[a]</sup> for four isomeric  $\text{H}_2\text{NO}$ .

Species	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$
Expt.				0.8633	0.8352	0.7309
$t\text{-DNOD}$	0.7284	0.7316	0.7522	0.8651	0.8390	0.7292
$c\text{-DNOD}$	0.7286	0.7320	0.7695	0.8249	0.8607	0.7507
$\text{D}_2\text{NO}$	0.7182	0.8341	0.8612	0.7830	0.7428	0.7707
$\text{NOD}_2$	0.7193	0.7338	0.7798	0.9106	0.7353	0.9106

[a] Defined as the ratio of vibrational wavenumbers of the D-isotopic variant to that of the corresponding H-species.

were all the same, as listed in Table 1, for these excitation wavelengths. Absorption into the first electronic excited state of H<sub>2</sub> that begins about 110 nm is inaccessible for these excitation wavelengths, whereas the electronic absorption<sup>[27]</sup> of NO overlaps strongly with these wavelengths. The bond energy of NO, 6.496 eV, corresponds to wavelength 190.9 nm. The observed photoproducts must originate from reactions of NO, in an electronically excited state, with hydrogen, as the photon energy at 210 nm is insufficient to break the N=O bond. In the previous investigation,<sup>[28]</sup> excitation of NO at 193 nm induced reaction with CO in Ne to form the ONCO radical, and excitation of NO with 193 nm in *p*-H<sub>2</sub> induced reactions with *p*-H<sub>2</sub> to form HNO, H<sub>2</sub>O and NH<sub>3</sub>,<sup>[3]</sup> which is confirmed in our own experiments. Production of *t*-HNOH on irradiation in our experiments is hence due to the reaction of H<sub>2</sub> with electronically excited NO.

### 3. Conclusions

In summary, we irradiated samples of NO in solid hydrogen near 3 K with VUV light from a synchrotron radiation and observed new IR absorption lines at 1241.7, 1063.6 and 726.2 cm<sup>-1</sup>. We attribute these features to *t*-HNOH in its *cis* bending ( $\nu_4$ ), NO stretching ( $\nu_3$ ) and out-of-plane deformation ( $\nu_6$ ) modes, respectively, based on observed D-isotopic shifts and theoretical predictions of line wavenumbers, infrared intensities and isotopic ratios for possible isomers of H<sub>2</sub>NO. The photoproduct *t*-HNOH is likely formed via reaction of electronically excited NO with neighboring hydrogen.

### Experimental Section

The experimental setup is similar to that described previously.<sup>[1,2]</sup> A CsI crystal cooled to ~3.0 K with a closed-cycle refrigerator (Janis RDK-415) served as a substrate for a matrix sample. The enclosure of this cryostat was evacuated with a turbomolecular pump backed with a scroll pump to less than  $5 \times 10^{-8}$  Torr. A gaseous mixture of 0.03 mol of NO/H<sub>2</sub> (NO/D<sub>2</sub>) at a molar ratio 1/1000 was deposited on the CsI crystal over 2 h before irradiation with VUV light. Which is tunable from the U9 undulator beam line at the National Synchrotron Radiation Research Center in Taiwan; this beam line provides pseudo-continuous VUV light with photon flux  $\sim 10^{16}$  photons s<sup>-1</sup> (2% bandwidth). The higher harmonics generated by the undulator were suppressed with an absorption filter filled with a noble gas Ne, Ar or Kr, depending on the desired wavelength. In this work, the desired photon wavelength was greater than 105 nm, a LiF window was added and installed downstream from the beamline to further remove photons in higher harmonics.

IR absorption spectra were recorded at various stages of experiments with an interferometric spectrometer (Bomem, DA8) equipped with a KBr beamsplitter and a Hg/Cd/Te detector (cooled to 77 K) to cover the spectral range 500–5000 cm<sup>-1</sup>. Spectra with 400 scans and resolution 0.5 cm<sup>-1</sup> were typically recorded at each stage.

NO (99.0%, MG industries), H<sub>2</sub> (99.999%, Matheson), and D<sub>2</sub> (isotopic purity ~99.7%, Matheson) were used without further purification.

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**Keywords:** condensed phase • density functional calculations • hydrogen • IR spectroscopy • vibrational modes

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