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Reactions of Atomic Hydrogen with Isotopes of Nitric Oxide in Solid Parahydrogen

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Abstract

Recent experiments in the Anderson group have shown that the reaction of hydrogen atoms (H) with nitric oxide (NO) at extreme low temperatures (<5 K) can produce both HNO and NOH. This is surprising because the reaction to form HNO is barrierless, whereas the reaction that forms NOH has a significant barrier. The fact that NOH is produced in these low temperature reactions is due to quantum mechanical tunneling effects and the fact that the NO molecule is freely rotating. I am helping analyze the Fourier Transform Infrared (FTIR) spectra that are used to follow the kinetics (how fast reactions occur) of these reactions, but specifically in the region where the NO molecule absorbs. I am also analyzing the FTIR spectra of different isotopes of nitric oxide (^{14}NO and ^{15}NO) to better characterize the rotational dynamics of the NO reagent. In the Born-Oppenheimer approximation, both of these isotopes of NO should react similarly at low temperature and based on my research it appears that this is true.

Introduction

Cold chemistry is becoming a hot area of research as a way to test fundamental principles about chemical reactions governed by quantum mechanics. Typically chemists think of molecules with ball and stick models, but at extremely low temperatures molecules can start to behave like waves. Molecules at very low temperatures (2-4 K) do not have much energy with which to react. Classically, at these low temperatures, only reactions with no barrier to reaction should take place. In this work we study the chemical reactions that occur between a hydrogen atom (H) and nitric oxide (NO). The reaction H + NO → HNO is barrierless, but the reaction

H + NO → NOH has a significant barrier (Ruzi, et al.). Even at room temperature, there is not enough available energy for NOH to be formed classically, that is, by going over the potential barrier between reactants and products. The chemical reaction only occurs through quantum mechanical tunneling, so HNO is formed much more readily than NOH at room temperature. Surprisingly, in recent low temperature reaction experiments, where the HNO product should be favored even more heavily than at room temperature, both HNO and NOH are formed in almost equal numbers (Ruzi, et al.). This does not make much sense because of the energy drought occurring at these low temperatures, so I was tasked with helping to determine why this is. I must tell you that the studied reaction (H + NO → HNO/NOH) is occurring in crystalline solids of para-hydrogen (made up of H_2 molecules all in their *para* nuclear spin state). Our first hypothesis was that the NO could be rotating in the para-hydrogen crystals because other similar species like carbon monoxide (CO) rotate in solid para-hydrogen (Paulson, et al). This could explain why both HNO and NOH were formed.

Nitrogen comes in two stable isotopes, so-called ^{14}N and ^{15}N. ^{14}N is, by far, the more common of the two, comprising 99.636% of all nitrogen (*Isotopes of Nitrogen*). ^{14}N has an atomic mass of fourteen and consists of seven protons, seven neutrons, and seven electrons. ^{15}N has seven protons, eight neutrons, and seven electrons. The mass comes mostly from the protons and neutrons. Because the two isotopes have the same number of protons and electrons, they react almost identically, but they have some different physical traits. In this work we used two different isotopomers of NO in the reactions. Within the Born-Oppenheimer approximation, both ^{14}NO and ^{15}NO have the same chemical bond strength. However, ^{15}NO is a bit heavier so it vibrates a little slower than ^{14}NO. This means, for an infrared (IR) absorption spectrum, the ^{15}NO

absorption peaks come at a lower energy than [14]NO. The two isotopes also have slightly different rotational constants. This was very important in my research.

I performed these analyses using Fourier Transform Infrared (FTIR) spectroscopy. These same FTIR spectra showed us that both HNO and NOH were present in almost equal quantities in the reaction. IR spectroscopy is based on infrared radiation. IR radiation is lower in energy than light in the visible spectrum. It excites the molecules that it is analyzing in a way that promotes vibration and rotation, but it is not energetic enough to break their bonds. These vibrational and rotational excitations are then analyzed by a computer using Fourier transforms. They are then graphed based on the wavenumber at which they vibrate and their intensity.
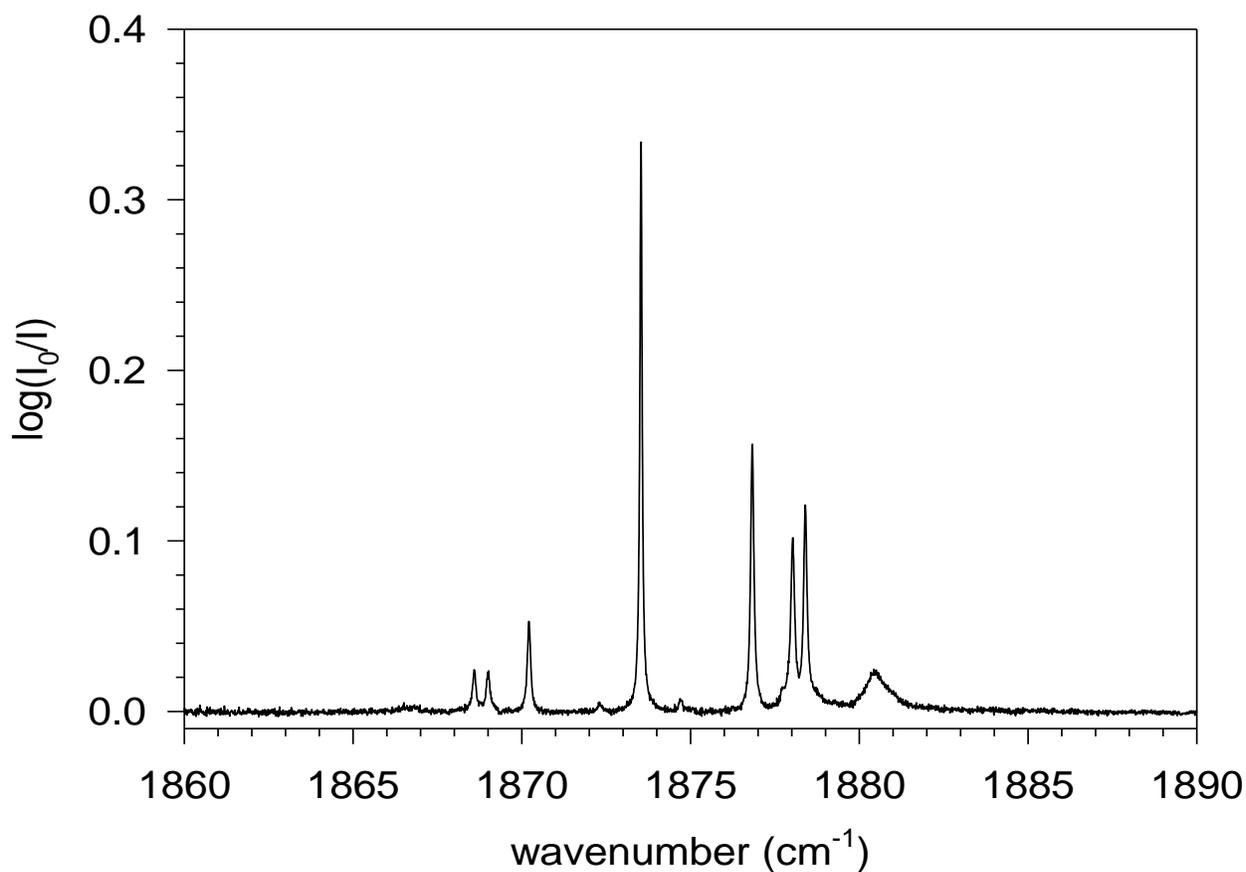

Figure 1: An FTIR spectrum of [14]NO trapped in solid para-hydrogen at 4.3 K.

These spectra show a plethora of important information about the molecules they are interrogating. Different functional groups vibrate at distinct wavenumbers, so this provides evidence about what molecules are present. The masses of certain atoms can be determined using IR spectroscopy. Most importantly for my research, the spectra can provide information about the rotational and vibrational nature of the molecules being analyzed.

Experimental

I did not do much in the way of lab work. I occasionally helped in the lab, but I did not help perform any experiments. My work consisted of analyzing the data from experiments that Dr. Anderson or one of his graduate students performed. I would look at the FTIR spectra that they gave me in the program OPUS. I would find the wavenumbers (energies) of several of the peak maxima, and I would put those into a Microsoft Excel spreadsheet. I would do this for several scans of a given sample. I then took the average and standard deviation of those peak wavenumbers from each scan. I would then find the energy difference of each peak from the center peak.

MEB01083MCT	MCT.0004	MCT.0003	MCT.0002	MCT.0001	MCT.0000	AVG	STD	DIFF
P(1.5)	1835.7508	1835.746	1835.7458	1835.7467	1835.7431	1835.74648	0.002776	-4.77422
P(1.5)	1836.0955	1836.0973	1836.1013	1836.1036	1836.1013	1836.0998	0.003305	-4.4209
P(1.5)	1837.2643	1837.2631	1837.2664	1837.2634	1837.261	1837.26364	0.00196	-3.25706
Q(1.5)	1839.3306	1839.3355	1839.334	1839.3355	1839.3154	1839.3302	0.008512	-1.1905
Q(0.5)	1840.5207	1840.5207	1840.5207	1840.5207	1840.5207	1840.5207	2.54E-13	0
Q(1.5)	1841.6456	1841.6623	1841.6456	1841.6459	1841.6745	1841.65478	0.013161	1.13408
R(0.5)	1843.7586	1843.7593	1843.7585	1843.7601	1843.7587	1843.75904	0.000669	3.23834
R(0.5)	1844.9089	1844.9075	1844.9117	1844.9093	1844.9132	1844.90935	0.001746	4.38865
R(0.5)	1845.2266	1845.2252	1845.2242	1845.2237	1845.2219	1845.22432	0.001748	4.70362
R(1.5)	1847.3025	1847.2109	1847.2683	1847.196	1847.2703	1847.2496	0.044574	6.7289

Table 1: Peak maxima (cm^{-1}) for several scans of one sample of ^{15}NO/para-hydrogen.

I did this for several samples of both ^{14}NO and isotopically enriched ^{15}NO. I then took the

average of each sample and put them in a master table, keeping the two isotopes separate.

^{15}NO Data					
$^{15}B_{V=0}$	State	AVG	STD	DIFF	DIFF/B
1.6361951	P(1.5)	1835.7195	0.059021	-4.8048	-2.93658
$^{15}B_{V=1}$	P(1.5)	1836.1186	0.040584	-4.4057	-2.69265
1.6195494	P(1.5)	1837.2575	0.005131	-3.2668	-1.9966
	Q(1.5)	1839.3334	0.004469	-1.1909	
	Q(0.5)	1840.5243	0.00574	0.0000	
	Q(1.5)	1841.6546	0.000283	1.1303	
	R(0.5)	1843.7637	0.009232	3.2394	2.000173
	R(0.5)	1844.8950	0.021137	4.3707	2.698714
	R(0.5)	1845.2305	0.011235	4.7062	2.905847
	R(1.5)	1847.2198	0.017068	6.6955	

Table 2: Average of each sample of ^{15}NO.

I then divided each energy difference from the center peak by the corresponding rotational

constant because the two isotopes have different rotational constants (Amiot, et al)(Hinz, et al).

During my analysis of all the data the Anderson group provided me, I had to throw out some data

that were "outliers." This is a part of any spectral analysis where, to be successful, I had to

measure precisely very small energy differences. Dr. Anderson did not tell me in advance that

some of the data was not appropriate for my analysis. I came to this conclusion by myself. Later,

after I had excluded certain data, Dr. Anderson told me this was right because some of the

provided data was recorded at the wrong optimum temperature, or contained experimental

artifacts.

Results and Discussion

We found that the displacements of each isotope divided by the appropriate *B* rotational constants were almost equal to each other.

State	^{15}DIFF/B	^{14}DIFF/B	Difference
P(0.5)	-2.936583	-2.91011	-0.0264732
P(0.5)	-2.692652	-2.66909	-0.0235629
P(0.5)	-1.996604	-1.95647	-0.0401304
R(0.5)	2.000173	1.966383	0.0337908
R(0.5)	2.698714	2.668159	0.0305549
R(0.5)	2.905847	2.902852	0.0029949

Table 3: The displacements from the center peak divided by their rotational constants, and the difference between each isotope.

This strongly suggests that the NO is rotating in the solid para-hydrogen, because the energy difference is scaling with the respective *B* rotational constant. If instead this fine structure (multiple peaks) was caused by different solvation environments (sites), this would not be true. More evidence that suggests that the NO is rotating comes from the values of the first and last displacements divided by the rotational constants for both isotopes. They are very close to three. This makes sense because the energy difference of a freely rotating NO molecules is 3*B*, three times the rotational constant (Ruzi, et al). Thus, by carefully analyzing the relative peak positions of both isotopomers of NO, we can determine that the NO molecule is freely rotating in the para-hydrogen crystal. Now this free rotation is not completely unhindered, because the spectral patter does not match exactly the gas phase spectrum, but it is relatively close. Further analysis of the details of this rotational motion goes beyond the scope of this project, and would require solving the Schrödinger equation for rotation in the presence of potential barriers.

Because the NO is rotating, it will not behave classically. To use a classical analogy, it is spinning (rotating) so rapidly compared to the translational motion of the attacking hydrogen atom, that the NO would appear like a sphere where it is equally likely that a nitrogen or oxygen atom is pointed in any direction (like an s-orbital in the H atom). Since the hydrogen atom has to approach at a specific angle to move along the barrierless reaction pathway (Ruzi, et al), this quantum mechanical behavior makes it almost impossible for the NO to be oriented correctly to form the barrierless reaction. This causes an "effective barrier" for the reaction that forms the HNO product under these low temperature reaction conditions. The only way either product can be formed is through quantum mechanical tunneling through this reaction barrier. It then becomes simply a matter of probability which product will be formed, with about equal chances of forming HNO or NOH.

Conclusion

Based on the experimental data and my analyses, it was determined that NO freely rotates in solid para-hydrogen. This helps rationalize why both HNO and NOH were formed in the chemical reaction under these conditions. This finding is contrary to conventional wisdom that would say only the barrierless reaction should readily occur at these low temperatures. This finding helps to better understand how chemical reactions occur at very low temperatures in solid para-hydrogen. The key realization is that the NO molecule freely rotates in the para-hydrogen crystal and is required by quantum mechanics to be evenly distributed in space in the ground rotational state. This requirement is related to Heisenberg's uncertainty principle in terms of the angular momentum of the rotating NO molecule. Typically, molecules do not freely rotate in crystalline solids at these low temperatures, but the special properties of solid para-hydrogen

allow this to occur. My research also helps the Anderson research group plan future experiments related to the H + NO reaction, by helping explain the production of NOH in the low temperature reaction they can hopefully devise new experiments to test my claim that the reactivity is due to freely rotating NO.

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