Theoretical Analysis of the UV Photolysis of Pyrazine to Form Hydrogen Isocyanide

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INTRODUCTION

The over-abundance of hydrogen isocyanide (HNC) relative to hydrogen cyanide (HCN) in the interstellar medium (ISM) has been an anomaly in the astrochemical community since its discovery in comets Lee and Hale-Bopp in 2001 [1]. While initially HCN:HNC ratio is on the order of 10^4-1, studies of comets Lee and Hale-Bopp have shown HCN:HNC ratios on the order of 10:1 and as low as 1.1. In the incredibly diffuse ISM, with few intermolecular collisions, a non-equilibrium ratio produced from a possible photolysis mechanism can be prolonged indefinitely [2]. These ratios were also shown to decrease with increasing temperature, contrary to standard astrochemical models.

One possible source for the anomaly, and the partial focus of this study, is photolytic reactions including larger cyano-containing hydrocarbons [3]. In theory, as the cometary approach stars they are hit with more photons that have the potential to cause unimolecular reactions that produce more HCN and HNC. If one or more of these precursors is found to have a dominant channel leading to HNC over HCN, we can increase our understanding of cometary reactions and explain, in part, the relative abundance anomaly [4].

In this study, we focus on the nitrogen heterocycle, 1,4-diazabenzene, also known as pyrazine. Pyrazine is one of many cyano-containing hydrocarbons that are confirmed to exist in the ISM [5]. By performing calculations simulating the ultraviolet-visible and infrared spectra of pyrazine and comparing them to experimental values, we can find the accuracy of these calculations and use them to map the potential energy surface (PES) of pyrazine to find possible reaction channels leading to HNC and HCN. It is possible for pyrazine and other hydrocarbons to provide available channels to form HNC and HCN, and collectively, these reactions with increased photons from the sun could be a source for the ratio imbalance and a source for the anomaly.

EXPERIMENTAL

The gas phase ultraviolet-visible (UV-Vis) and infrared (IR) spectrum of pyrazine was recorded using a JASCO V-630 spectrometer, and a JASCO FT/IR 47000 respectively. The spectra were taken using a homemade reaction cell, consisting of a 10 cm long and 4.4 cm inner diameter metal cylindrical tube with two sapphire windows and two potassium bromide lenses for the UV-Vis and IR spectra respectively. A background of the empty cell was collected and used as baseline. At room temperature, pyrazine is a crystalline solid (325 K). Roughly 0.1 g of pyrazine was added to the cell, which was then sealed and heated to 383 K using heat tape. At this temperature, we estimate the pressure of pyrazine to be 50 torr.

CALCULATIONS

Calculations of possible transition states of pyrazine were carried out with ab initio and semi-empirical calculations for molecular energy using the Post Hartree-Fock method carried out at the CCSD(T)/6-311G(d,p) level with Gaussian 09 program. In addition to theoretical transition states, we found it necessary to provide a reference of theoretical IR emission spectra to compare experimental spectra from highly excited molecules. It is crucial to provide evidence of the validity of our calculations through comparison to accepted experimental values, if the simulated spectra match accepted values, then can be confident in our calculations as an accurate reference with which we can compare our own future experimental results. Calculations of simulated IR absorption spectra for pyrazine were carried out with ab initio and semi-empirical calculations for vibrational frequencies and IR intensities using the Hartree-Fock method at the 6-31G(d,p) level with Dalton 2017. Calculated vibrational frequencies were scaled by a factor of 0.9300 as suggested in a previous study for (193 nm Photon)

Discussion

Comparison of calculated and experimental spectra is a valuable tool to measure the accuracy of the calculation used. Represented in this work is the process of using increasingly higher level calculation to obtain more accurate data; calculations involving smaller basis sets are easier and cheaper to obtain, while those of higher level are more expensive but are costly in either time or money. Overall, our calculations show a high degree of agreement with experimental results, indicating that our calculation methods are a valid estimation tool. This is useful in calculating possible reaction pathways to predict products of photolytic reactions and in estimating spectra of possible photolytic products. In future experiments, we can predict photolytic products of reactions involving pyrazine and other cyano-containing hydrocarbons and their respective spectra. Predicting products and their IR spectra gives a reference to which we can compare experimental results, either affirming or disaffirming our predictions. Of particular interest is photoproduts that lead to, or are associated with, production of HNC; Holistically this process can lead us to understanding the HCN/HNC anomaly and shed light on the astrochemical environment as a whole.

REFERENCES


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