

EILERS GRADUATE STUDENT FELLOWSHIP FINAL REPORT

EILERS FELLOW:	Andrew Schranck
FACULTY ADVISOR:	Dr. Kyle Doudrick
REPORT PERIOD:	2018
PROJECT TITLE:	Urea electrolysis cells for producing hydrogen fuel
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	<input checked="" type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS:

List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Investigate various electrode substrates for NiCo ₂ O ₄ as a urea electrooxidation catalyst	NiCo ₂ O ₄ outperformed Ni and Co catalysts. Carbon paper outperformed fluorine doped tin oxide and stainless-steel mesh substrates for NiCo ₂ O ₄ (Figures 1 and 2).	100
Use cyclic voltammetry to reveal the effects of urine components and propose next steps in addressing barriers of theoretical vs. experimental energy required to achieve urea electrooxidation and hydrogen production	Cyclic voltammograms showed phosphate, creatinine, and gelatin had significant inhibitory effects on urea electrooxidation (i.e., decreased current density) while ammonium chloride improved current density (Figure 3).	100
Elucidate the impacts of synthetic urine components on urea oxidation onset potential, peak urea oxidation current density, diffusion coefficients, and the kinetics related to urea to hydrogen transformation efficiency.	Urea oxidation onset potential and peak urea oxidation current density were evaluated for each component as seen in Figure 3 and Table 1. Diffusion coefficients, kinetics, and hydrogen production efficiency were not produced during the study period.	75
Identify mechanism of urea oxidation inhibition by electrolyte salts and organics in urine	Attenuated Total Reflectance (ATR) Fourier Transform Infrared (FTIR) Spectroscopy was used to identify the binding mechanisms between NiCo ₂ O ₄ and urea, phosphate, and creatinine (Figures 4, 5, and 6, Table 2). Urea and phosphate weakly bind to NiCo ₂ O ₄ through hydrogen bonding or long-range forces, whereas creatinine interacts strongly, forming deactivating inner-sphere complexes. Phosphate is presumed to disrupt the interaction between urea and NiCo ₂ O ₄ by serving as a hydrogen-bond acceptor in place of catalyst sites. The weak binding of urea supports the hypothesis that it is oxidized through an indirect electron transfer.	100
Compare diffusion coefficients and kinetic rate constants for urea electrooxidation at nickel electrodes compared to hydrogen evolution at platinum electrodes to evaluate this technology against water electrolysis methods employed elsewhere.	Due to increase in scope for materials synthesis and analysis at the beginning of the project, diffusion coefficients and kinetic rate constants were not obtained during this project. Greater understanding of the hydrogen production potential of this system is planned for future work. Maximum hydrogen achievable based on theoretical and experimental data so far projects a maximum hydrogen potential of 18.65 mM-H ₂ h ⁻¹ .	0

RESEARCH OUTPUT:

Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount) Fulbright, Urea Electrochemical Cells for Sustainable Treatment of Source Separated Urine, Kyle Doudrick and Emmanuel Mousset, 10/4/17, ?
EXTERNAL AWARDS	(Sponsor, Project Title, PIs, Award Date, Award Amount)
JOURNAL ARTICLES	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s) ES&T, Effect of Urine Compounds on the Electrochemical Oxidation of Urea Using a Nickel Cobaltite Catalyst: An Electroanalytical and Spectroscopic Investigation, Andrew Schranck, Randal Marks, Elon Yates, Kyle Doudrick, April 2018, June 2018, 52, 8638-8648
BOOKS AND CHAPTERS	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s)

PUBLIC PRESENTATIONS, SEMINARS, LECTURES	(Event, Presentation Title, Presentation Date, Location) Colleges of Science and Engineering Joint Annual Meeting, Teasing Apart Urine to Improve Advanced Wastewater Treatment and Resource Recovery, December 8, 2017, Notre Dame, IN. ND Energy Research Symposium, An investigation of the effect of urine compounds on electrochemical oxidation of urea using a nanostructured nickel cobaltite catalyst, April 18, 2018, Notre Dame, IN.
AWARDS, PRIZES, RECOGNITIONS	(Purpose, Title, Date Received)
INTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation)
EXTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation)
WEBSITE(S) FEATURING RESEARCH PROJECT	(URL)
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail)

MAJOR GOALS AND ACCOMPLISHMENTS
(Additional Details, Technical Results, Charts and Graphics)

In this study, we investigated the effect of major urine compounds on the urea electro-oxidation activity for nano-structured nickel-based catalysts. The catalysts were synthesized on various electrode substrates, and the electrochemical performance (i.e., potential and current) was investigated using cyclic voltammetry for urea-only and synthetic-urine solutions. The molecular-scale sorption behavior of select deleterious urine compounds on the catalyst was investigated using in situ attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The outcomes provide support for using electrolysis to remove nitrogen from urine to improve wastewater treatment processes but also provide a valuable opportunity to produce low cost hydrogen for fuel cell applications. The project set out to go from analyzing materials for urea oxidation on the front end to producing hydrogen on the back end. Analysis of the urea oxidation process is still being analyzed. With preliminary understanding of urea oxidation at the anode, kinetics analysis will be used to better understand oxidation efficiency and subsequently hydrogen production at the cathode. The next step is looking at separating the electrode reactions with a two-cell reactor that prevents back reactions and competing reactions that limit the efficiency of single cell reactors. With a modest current of 0.1 A, a maximum hydrogen production possible would be 18.65 mM-H₂ h⁻¹.

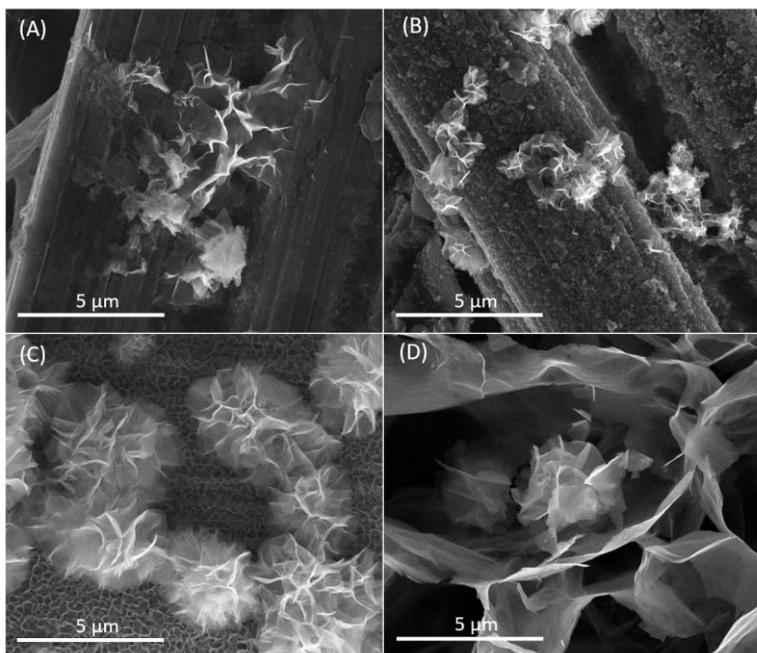


Figure 1. SEM micrographs of (A) NiO on carbon paper, (B) NiCo₂O₄ on carbon paper, (C) NiCo₂O₄ on stainless steel, and (D) NiCo₂O₄ on fluorine doped tin oxide.

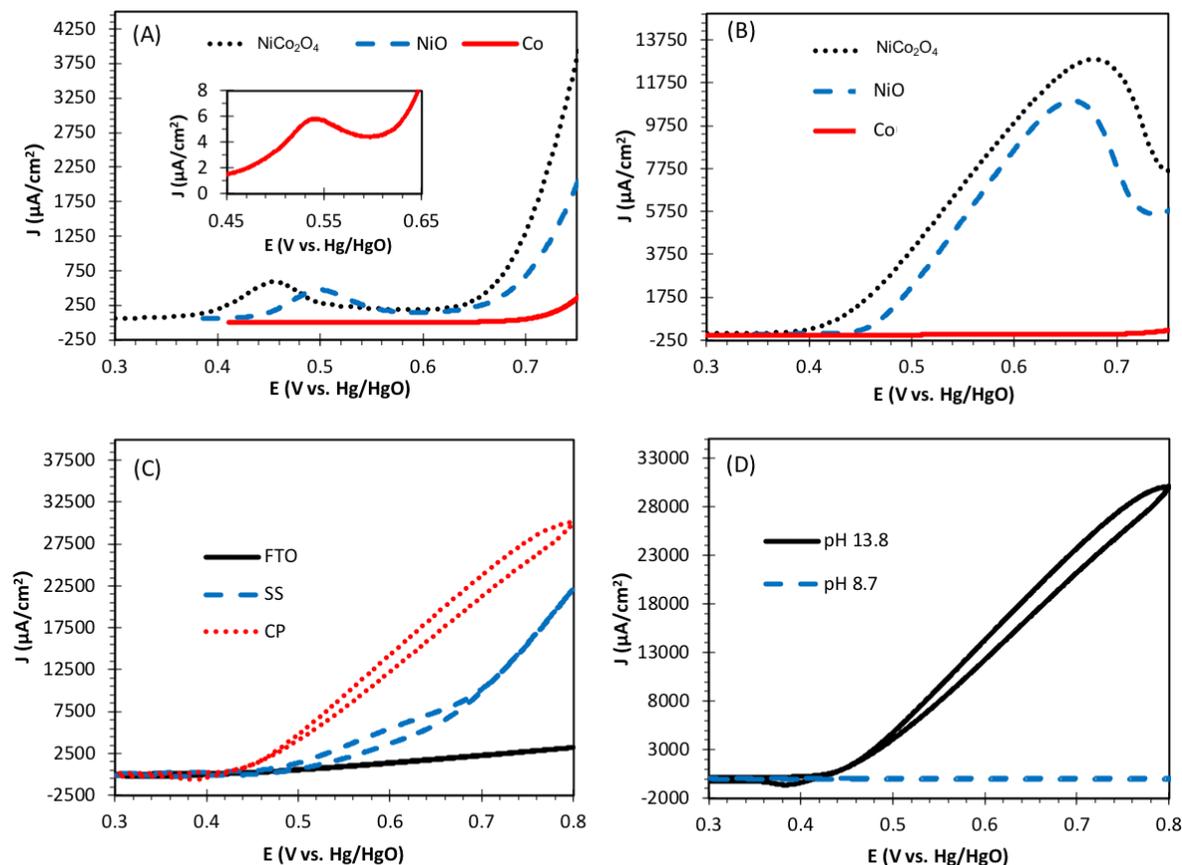


Figure 2. CVs for NiCo₂O₄, NiO, and Co_xO_y in 1 M KOH and the (A) absence or (B) presence of 0.33 M urea; (C) FTO, SS, and CP substrates loaded with NiCo₂O₄ in 1 M KOH with 0.33 M urea; and (D) NiCo₂O₄ on CP in 1 M KOH (pH = 13.8) and 1 M NaClO₄ (pH = 8.7) and 0.33 M urea. The inset in (A) highlights the Co region between 0.45–0.65 V.

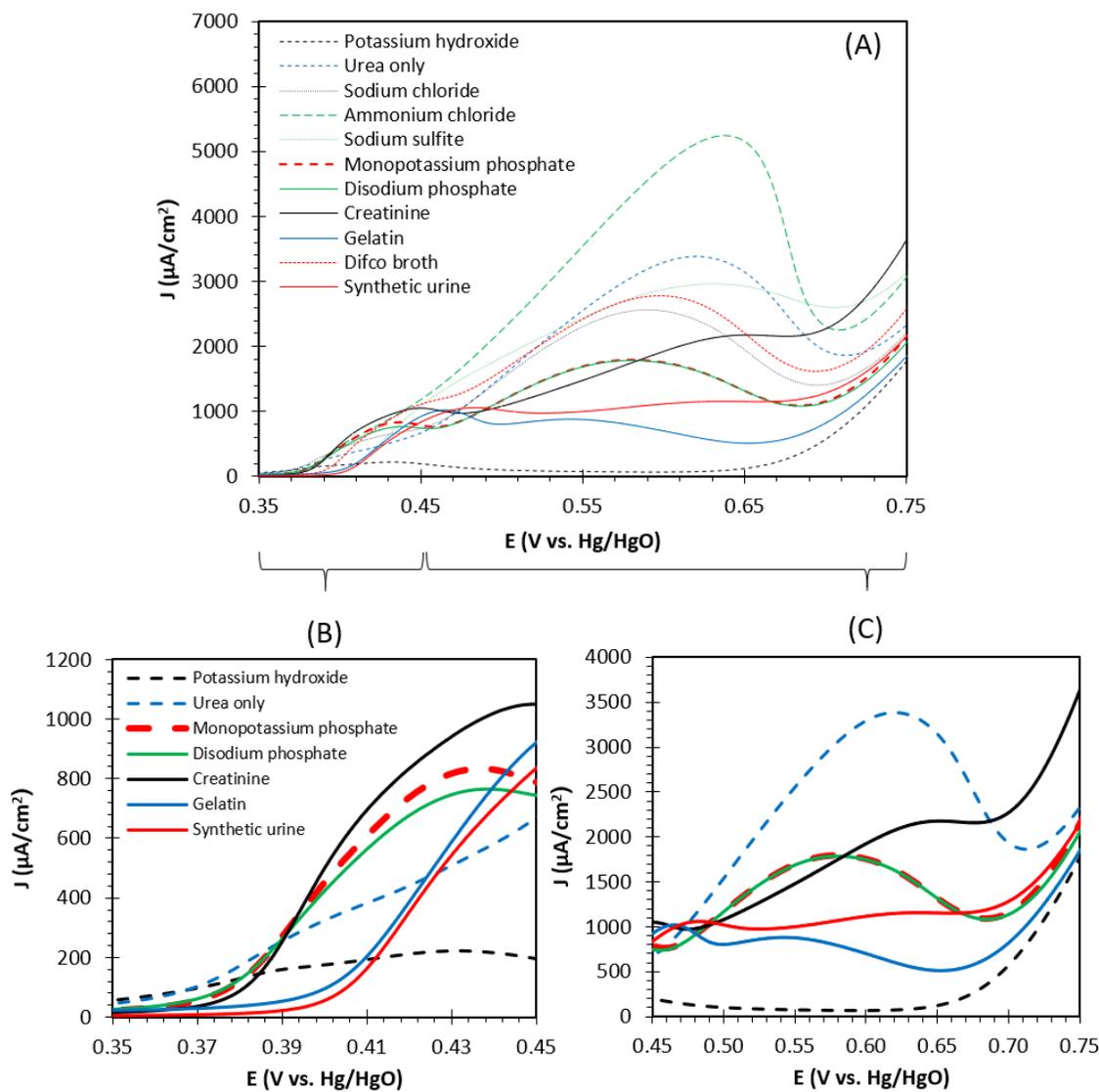


Figure 3. CV anodic sweeps of (A) synthetic urine compounds and highlighted regions detailing (B) E_{500} and (C) $J_{0.65}$ values for select urine compounds. All solutions contained 1 M KOH. The potassium hydroxide curve represents “no urea” control, and all other solutions contained 0.33 M urea. All experiments were conducted with NiCo_2O_4 loaded onto carbon paper.

Table 1. Synthetic urine compound concentrations and their $J_{0.65}$ for NiCo_2O_4 on CP. All solutions contained 1 M KOH. All solutions contained 0.33 M urea.

Compound	Concentration (g/L)	$J_{0.65}$ ($\mu\text{A}/\text{cm}^2$)
Synthetic urine	-	1152
Urea	19.82	3145
Ammonium chloride	3	5154
Sodium sulfite	3	2926
Difco broth	1.6×10^{-4}	2205
Creatinine	2	2176
Sodium chloride	9	1950
Monopotassium phosphate	2.5	1318
Disodium phosphate	2.5	1316
Gelatin	1	512

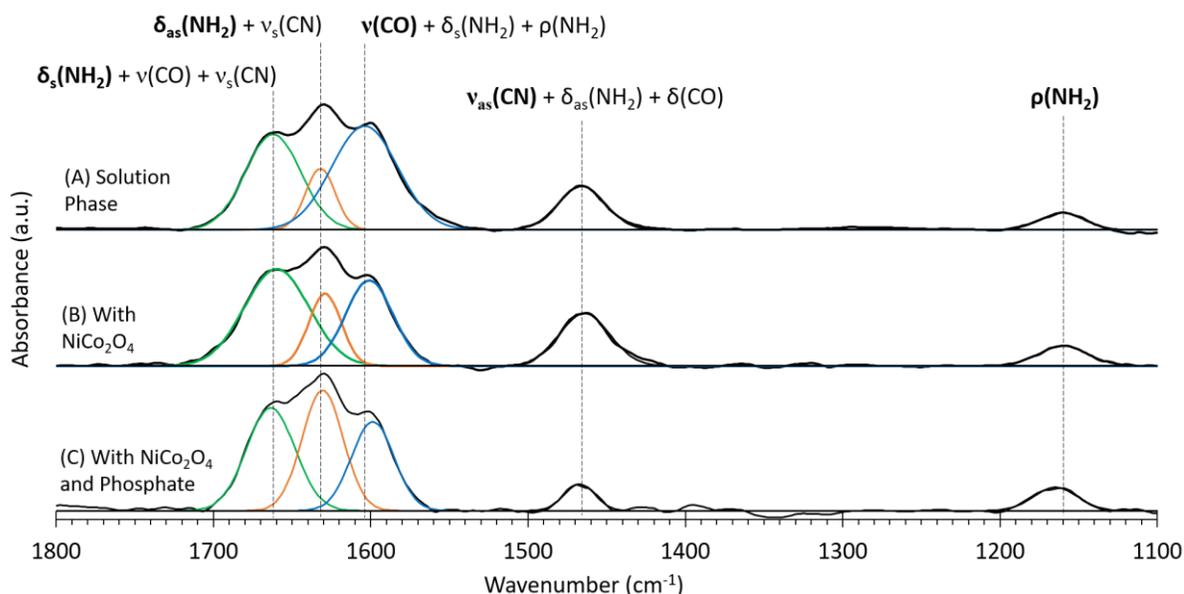


Figure 4. In-situ ATR-FTIR spectra of 40 mM urea (A) solution-phase, (B) in the presence of a NiCo₂O₄ particulate film, and (C) with NiCo₂O₄ and 40 mM of phosphate. All experiments were conducted with 1 M KOH to mimic electrochemical pH conditions. Spectra are offset for clarity.

Table 2. Urea peak locations (in cm⁻¹) observed in this study, and a comparison to those observed or calculated previously. The bold assignments represent the major vibration.

Peak Assignment ¹	Solution Phase	On NiCo ₂ O ₄	On NiCo ₂ O ₄ and with Phosphate	Reported Values ^{1, 2}
$\delta_s(\text{NH}_2) + v(\text{CO}) + v_s(\text{CN})$	1662	1660	1664	1663–1668
$\delta_{as}(\text{NH}_2) + v_s(\text{CN})$	1632	1629	1631	1629–1636
$v(\text{CO}) + \delta_s(\text{NH}_2) + \rho(\text{NH}_2)$	1604	1601	1599	1597–1602
$v_{as}(\text{CN}) + \delta_{as}(\text{NH}_2) + \delta(\text{CO})$	1466	1464	1467	1463–1473
$\rho(\text{NH}_2)$	1160	1160	1165	1155–1160

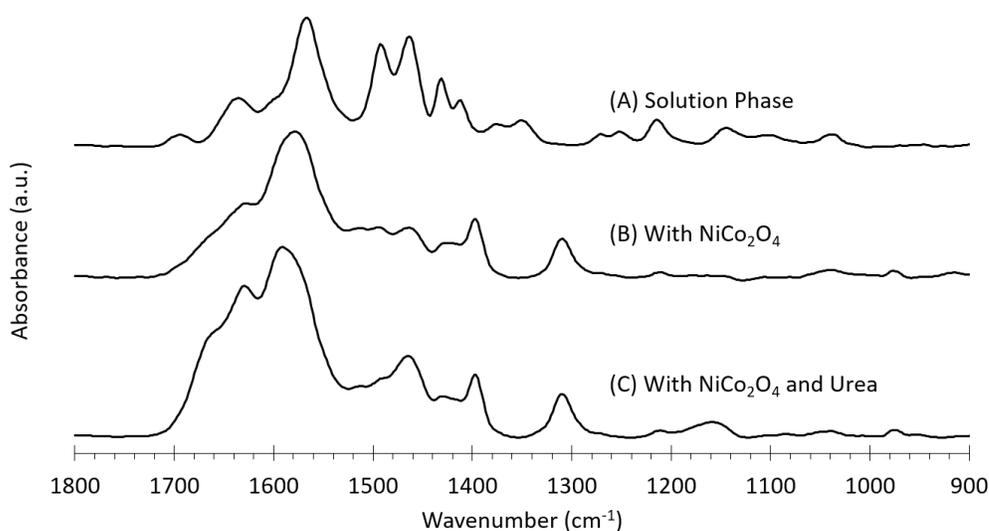


Figure 5. In-situ ATR-FTIR spectra of 40 mM creatinine (A) solution-phase, (B) on NiCo₂O₄, and (C) on NiCo₂O₄ and with 40 mM urea. All experiments conducted in 1 M KOH to mimic electrochemical pH conditions. Spectra are offset for clarity. See Table S5 for peak identification.

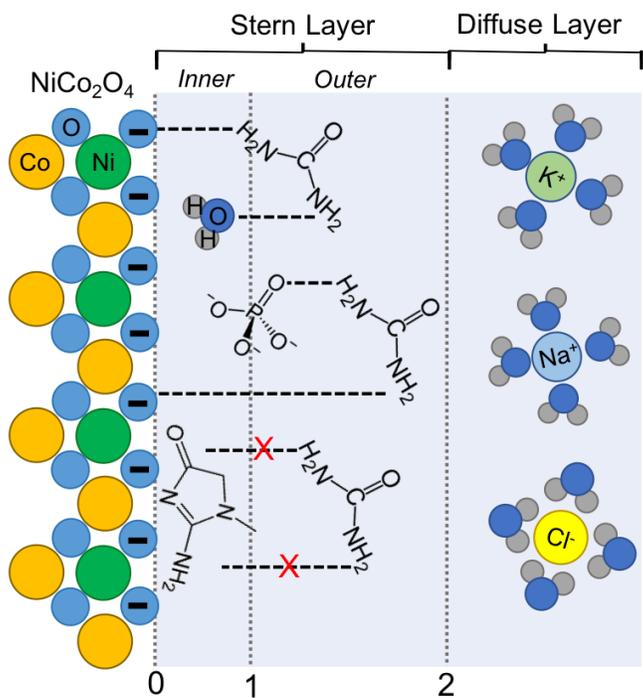


Figure 6. Conceptual schematic of the solid-solution interface, including interactions between NiCo_2O_4 , urea, phosphate, and creatinine. The 0, 1, and 2 indicate the Stern plane numbers.

References

1. Grdadolnik, J.; Marechal, Y., Urea and urea-water solutions-an infrared study. *Journal of Molecular Structure* **2002**, *615*, (1-3), 177-189.
2. Keuleers, A.; Desseyn, H. O.; Rousseau, B.; Van Alsenoy, C., Vibrational analysis of urea. *Journal of Physical Chemistry A* **1999**, *103*, (24), 4621-4630.