This literature discussion is in honor of the work of Gary J. Schrobilgen, winner of the 2025 M. Frederick Hawthorne Award in Main Group Inorganic Chemistry for “advances in the synthetic chemistries of Group 13–18 elements that encompass strong oxidizers; hypervalent, high-oxidation-state species; and ring, cage, and cluster polyatomic anions” (<https://cen.acs.org/articles/103/i1/2025-ACS-National-Award-winners-Part-V.html> accessed 1/22/2025). While there are many possible papers to choose from, we will be looking at a paper in which he reports several adducts of XeO3 (*Chem. Eur. J.* **2019**, *25*, 12357).

1. Let’s begin by reading the first paragraph of the introduction. This might be one of the first times you have encountered a compound containing a noble gas. Yes, they do exist. Let’s start by drawing all of the possible resonance structures of XeO3. Be sure to indicate the formal charge on each atom and the molecular geometry.
2. Look up the electronegativity values for oxygen and xenon. Based on these values, describe the polarity in the Xe-O bonds.
3. Using the electronegativity values, estimate the percent ionic character in these bonds.
4. Which resonance structure(s) in question 1 do you like the best? Why?
5. The authors state that “solid XeO3 readily detonates when subjected to mild mechanical or thermal shock, decomposing to Xe and O2 gases with the liberation of 402 + 8 kJ mol-1 of energy”. Write a balanced chemical equation for this decomposition reaction. The ΔHf for XeO3 was determined to be -402 kJ mol-1. The O=O bond energy is 494 kJ mol-1. Estimate the Xe-O bond energy in XeO3.
6. Reread the first paragraph of the introduction and read the first three sentences of the second paragraph of the introduction. The authors state that XeO3 forms a network structure in the solid state. In your own words, how this network is forming.
7. Read through the synthesis portion of the results and discussion section. You may notice many terms that indicate how challenging this chemistry was to perform. For now, we will focus on the [(CH3)2CO]3XeO3 compound which is compound **1** in the paper. This is formed by the slow evaporation of an acetone solution of XeO3. Draw the structure of (CH3)2CO and suggest how it might interact with the Xe atom to form compound **1**.
8. The crystal structure of compound **1** was determined and can be seen below. Determined the point group of compound **1**.

[insert Figure 1 compound **1** here]

1. The authors examine the Raman spectra of their compounds. Raman spectroscopy is often seen as being complementary to IR spectroscopy as both investigate vibrations within a molecule. In some cases, vibrations can be active in both IR and Raman spectroscopy, but many times, vibrations are only active in one or the other. In general, IR-active vibrations result in a net change in the dipole of the molecule whereas Raman-active vibration results in a change in the polarizability of the molecule. To get a slightly better feel for this, let’s consider the atmospheric pollutant CO2. It is linear and would have D∞h symmetry, but for this example we can treat it as D2h. Shown below is the D2h character table. Determine the irreducible representations for the IR-active (linear functions of x, y and/or z) and Raman-active (quadratic functions with combinations of x, y and z) vibrations in CO2.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| D2h | E | C2 z | C2 y | C2 x | i | σxy | σxz | σyz | linear | quad |
| Ag | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  | x2, y2, z2 |
| B1g | 1 | 1 | -1 | -1 | 1 | 1 | -1 | -1 |  | xy |
| B2g | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 |  | xz |
| B3g | 1 | -1 | -1 | 1 | 1 | -1 | -1 | 1 |  | yz |
| Au | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 |  |  |
| B1u | 1 | 1 | -1 | -1 | -1 | -1 | 1 | 1 | z |  |
| B2u | 1 | -1 | 1 | -1 | -1 | 1 | -1 | 1 | y |  |
| B3u | 1 | -1 | -1 | 1 | -1 | 1 | 1 | -1 | x |  |
| G | 2 | 2 | 0 | 0 | 0 | 0 | 2 | 2 |  |  |

1. And now back to compound **1**. Consider acetone and compound **1**. How many Raman-active C-O vibrations would you expect to see in each of these compounds?
2. On page 12359 the authors describe the structure of compound **1** and a number of bond lengths and angles are presented in Table 2. The authors reports that there are “two cyrstallographically unique [(CH3)2CO]3XeO3 units”. What does this mean?
3. The average Xe-O (this is the oxygen that is not part of the acetone) for **1** is 1.766 Å whereas the average Xe---O (this is the oxygen that is part of the acetone) for **1** is 2.758 Å. Account for this difference in bond lengths.
4. The authors have also reported the structure of XeO3 in the solid state, although as mentioned previously, it forms a large network and three different solid-state structures were observed (*Inorg. Chem.* **2016**, *55*, 12975-12981, <http://dx.doi.org/10.1021/acs.inorgchem.6b02371>). In comparing distances to compound **1**, the shorter Xe-O distances are on average 1.768 Å and the longer Xe---O distances are 2.754 Å. Although these are very similar and one should be extremely careful to not read too much into it, what do these values suggest about the relative donor ability of another XeO3 unit relative to that of three acetone molecules? How can you account for this?
5. The authors also describe the synthesis of compound **2** which contains dimethylsulfoxide (DMSO) in place of acetone. Unlike the synthesis of compound **1**, the authors could not just dissolve XeO3 in DMSO as the XeO3 “detonates on contact with liquid dimethylsulfoxide (DMSO)”. Draw the structure of DMSO and suggest why the authors can dissolve XeO3 is acetone but not DMSO.
6. The average Xe-O (this is the oxygen that is not part of the DMSO) for **2** is 1.7683 Å (1.766 Å in **1**) whereas the average Xe---O (this is the oxygen that is part of the DMSO) for **2** is 2.7409 Å (2.758 Å in **1**). What does this suggest about the relative donor ability of DMSO compared to acetone? How can you account for this difference?
7. Table 3 presents some of the Raman data for these compounds. Reading through the text that begins on the previous page, the vibrations that the listed are Xe-O vibrations. Comparing the exptl values for compounds **1** and **2**, does this support your relative rankings of donor ability of acetone vs. DMSO in the previous question? Why or why not?
8. Draw the structure of C5H5NO and from this structure suggest why it might not be a surprise that the authors report “slow addition of an acetone solution of C5H5NO to solid XeO3 resulted in detonation”.
9. The authors do report the synthesis of a compound using C5H5NO (compound **3**) but it has a very different stoichiometry. Suggest why this makes such a different compound.
10. The authors attempted a reaction between triphenylphosphine (P(C6H5)3) and XeO3 but were unable to make an adduct. What products formed in this reaction? What might this suggest about relative bond strengths in comparing the reactants and the products? What other thermodynamic factor is also likely a significant driving force in this reaction?
11. The authors are eventually able to make an adduct (compound **4**) using (C6H5)3PO instead of (C6H5)3P. Again, the stoichiometry is quite different than what was observed for acetone or DMSO, account for this difference.
12. Given the potential for detonation, it is not surprising that the authors did not appear to attempt and NMR characterization of their products. Compound **4** would have been especially fun as both Xe-129 (26.4% abundant) and P-31 (100% abundant) are spin ½ NMR active nuclei. Had the authors obtained the 31P{1H} and 129Xe{1H} spectra what patterns would they have expected to see assuming there is P-Xe coupling?
13. According to NOAA ([https://www.noaa.gov/jetstream/atmosphere accessed 1/21/2025](https://www.noaa.gov/jetstream/atmosphere%20accessed%201/21/2025)) the earth’s atmosphere contains 0.934% Ar, 18.2 ppm Ne, 5.24 ppm He, 1.14 ppm Kr and 0.09 ppm Xe. Given the extremely low abundance of Xe in the atmosphere, why might the authors have chosen to work with this element.
14. Computational Chemistry can be used to estimate thermodynamic parameters, among other characteristics of a molecule. Rationalize the following thermodynamic observations (Data in Table 5, for reactions (1), (2), (4) and (6)):
    1. All ΔSrxn are negative:
    2. All Binding Energies are negative:
    3. The ΔGT of compounds **2-4­** are significantly more negative than for compound **1**:
    4. The experimental protonation enthalpies (ΔHi) for compounds **1** and **4** are consistent with their binding energies:
15. Computational Chemistry can also be used to estimate atomic charges using Natural population analysis (NPA). NPA calculates orbital populations of the molecular orbitals and uses this to provide atomic charges. It is the method most often used when some ionic character of the bond is suspected. Looking at the NPA atomic charges given in Table 4 for XeO3, which Lewis Structure drawn in question 1) does the calculation best support? Is that consistent with which resonance structure you preferred in Question 4)? Why might this calculation have not exactly matched any one Lewis Structure?