Problem II.S ... optical molecule spectroscopy 10 points

1. *Attempt to interpret the simple spectrum of hydronium, or the hydroxonium* H_3O^+*. Based on the information from the series text, assign four specific peaks in the infrared and Raman spectra to the molecular vibrations determined by the quantum-chemical calculation program.*

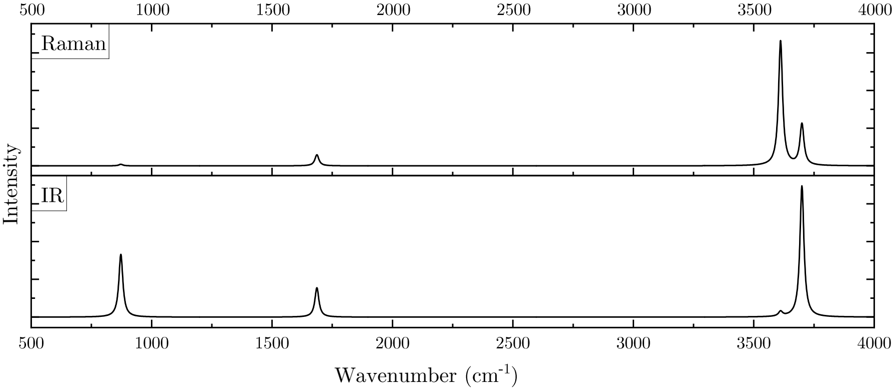

Figure 1: Simulated infrared and Raman spectrum of the hydronium.

The wavenumbers in the spectrum have intensity maxima estimated at $872\,\mathrm{cm^{-1}}$, $1\,686\,\mathrm{cm^{-1}}$, $3\,611\,\mathrm{cm^{-1}}$, *and* $3\,700\,\mathrm{cm^{-1}}$*. The second and fourth modes in this sequence are actually doubled due to the symmetry of the cation; however, this does not affect this problem. Assign the depicted vibrational modes in the figure below to the individual wavenumbers. Justify your answer as well as possible in terms of vibrational symmetry, charge displacement, i.e., changes in the dipole moment vector, and molecular orbitals. – 5 points*

Hint: *You can take inspiration from the spectrum of water, which has the same number of electrons as hydronium, and its interpretation can also be found on many online resources.*

2. *Using subproblem 1, determine the stiffness of the hypothetical "spring" corresponding to the vibration of the hydronium at the wavenumber* $3\,611\,\mathrm{cm^{-1}}$*. The equilibrium O—H bond length in the cation is* $98\,\mathrm{pm}$*. Neglect more complex effects, such as possible changes in the effective mass during the vibration. – 3 points.*

3. *Derive how the maximum mentioned in the previous subproblem shifts when the light hydrogen atoms* (^1H) *are replaced with deuterium* (^2H)*. Is this estimate reasonable if molecules of ordinary water are present in an acidic deuterated solution? Discuss what would actually be observed in aqueous solutions. – 2 points.*

   Hint: *Consider that solvation occurs in the solution, i.e., the substance is surrounded by the solvent. This is often a subject of modeling in quantum chemistry. The whole process is dynamic, involving clustering through hydrogen bonding and (de)protonation of water clusters.*

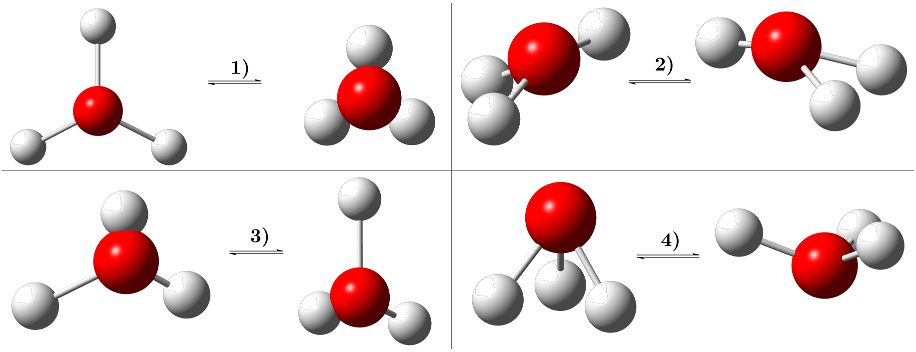

Figure 2: Oxonium vibration modes

Dan will try not to poison the well.

1. Let us start from the beginning. The figure
    (a) shows valence (bonding) vibrations representing so-called *symmetric stretching*, i.e., the stretching and shortening of multiple bonds simultaneously. This vibration does not change the dipole moment because the contributions from the partial positive charges of the three hydrogens add up to the same resultant. On the contrary, the LUMO is significantly stretched by this vibration and the HOMO/LUMO overlap is reduced. Thus, the willingness of electrons to delocalize between orbitals decreases dramatically, changing the polarizability tensor. The vibration is therefore strongly Raman and practically invisible in the IR; we assign it a peak at $3\,611\,\mathrm{cm^{-1}}$.

    (b) Here we mainly see a deformation of the O–H bond angle, which is a scissoring motion, known as . It will therefore be in a less energetic region. Because it causes significant asymmetry, the dipole moment changes. At the same time, however, there are shifts in electron density across the molecule. This is therefore a vibration visible in both spectra, and we assign it a peak at $1\,686\,\mathrm{cm^{-1}}$.

    (c) The situation is analogous to vibration (a), only this time the stretching is *asymmetric*. However, this means that the vibration will be weaker in the Raman spectrum and stronger in the IR spectrum because the dipole moment changes. In the valence region, a peak at $3\,700\,\mathrm{cm^{-1}}$ appears promising.

    (d) The figure shows a somewhat exaggerated example of a deformation vibration, aptly called *umbrella*. The vibration flips the entire molecule into a plane. However, the dipole moment will be zero in the plane, so the change is significant and the vibration will have a pronounced peak in the IR spectrum. On the other hand, the change in polarizability will be minimal because the bond lengths and orbital overlap (electron density) remain virtually the same. This leaves the peak at $872\,\mathrm{cm^{-1}}$.

2. From the previous subproblem, we know that the given vibration at $3\,611\,\mathrm{cm^{-1}}$ is symmetric. From the equations in the serial, it follows that the spring constant does not depend on the bond length (it is a constant), so we only need to calculate the reduced mass for

this system. For this, we will boldly assume that the three protons (H^+) oscillate equally and their masses can be added to a single "counterweight" of the central oxygen atom. The mass of a proton and hydrogen is almost identical, since the mass of an electron is negligible in this context. Then we can imagine that three connected weights are pulling on the oxygen at the same time, i.e.,

$$m' = \frac{3m_O m_H}{m_O + 3m_H} \approx 4.222 \cdot 10^{-27}\mathrm{kg}\,.$$

The stiffness of the imaginary triple spring is related to the frequency, which we will calculate next. We will therefore modify the formula:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m'}} \quad \Rightarrow \quad k = m'(2\pi\nu)^2\,.$$

We convert the wave number to frequency, paying attention to the units, because the wave number used in spectroscopy is not in SI base units. We must therefore convert either that or the speed of light

$$\nu = c\tilde{\nu} \approx 108.26\,\mathrm{THz}\,.$$

Interestingly, this energy corresponds to infrared radiation, which is related to the fact that we can measure molecular vibrations using IR absorption.

All that remains is to substitute everything we got so far and we get

$$k \approx 1.953.5\,\mathrm{N{\cdot}m^{-1}}\,.$$

We made several fundamental approximations in the calculation—we assumed that the vibration is completely symmetrical and that the formula for reduced mass will work (which is not generally guaranteed in the case of molecules where bonds extend outside the plane; here, the results are approximately valid due to the difference in mass between O—H).

3. If we replace the counteratom (hydrogen ^{1}H) with deuterium (^{2}H), the effective mass will change. This time, it comes out to $7.282 \cdot 10^{-27}$ kg. Then, after adjustments, we get approximately $\tilde{\nu} = 2\,750\mathrm{cm}^{-1}$. The qualitative estimate that a heavier atom vibrates more slowly is certainly correct; the quantitative determination is already up for discussion. Moreover, this whole consideration is only hypothetical, the calculation has two Achilles' heels. First, for this result to have at least some chance of holding up, we would need to have an almost fully deuterated solution. If even a little common (light) water were mixed in, the dynamic transfer of hydrogen ions would lead to the formation of HDO water and H_2DO^+, HD_2O^+ ions.

   Much more important, however, is the related fact that, due to molecular dynamics, the oxonium cation itself exists only in the gaseous phase for a long time. Its lifetime in aqueous solution is less than a picosecond. At room temperature, the speed is comparable to the interaction with photons itself. Here it is necessary to compare theoretical results with experiments. The actual measured spectrum does not contain sharp lines, but a much blurrier continuous signal across the entire width of the spectrum. If we wanted to obtain a cleaner spectrum, we would have to perform measurements at extremely low temperatures or in the most acidic solutions known. The spectra also experimentally proved (in acidic solutions) the existence of a whole mixture of ions, such as $H_5O_2{}^+$, $H_7O_3{}^+$, $H_9O_4{}^+$ and so on. These heavier so-called oxonium clusters with water form and disappear quickly due to strong hydrogen bonding (intermolecular interaction).

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FYKOS is organized by students of Faculty of Mathematics and Physics of Charles University. It's part of Media Communications and PR Office and is supported by Institute of Theoretical Physics of CUNI MFF, his employees and The Union of Czech Mathematicians and Physicists. The realization of this project was supported by Ministry of Education, Youth and Sports of the Czech Republic.