ChemE 2200 - Physical Chemistry II for Engineers

Quiz 3 - February 12, 2025

Name: *Solution*

Half the quizzes asked for information on the electronic *ground* state.

(A) The dissociation energy of AZ in its electronic ground state can be estimated from the emission spectrum. The high energy peak at 4.0 eV represents transitions from v' = 0 to v = 0. The low energy peak at 1.2 eV represents transitions from v' = 0 to the vibrational level at the top of the ground state potential. Thus the ground state well has a depth of about 4.0 – 1.2 = 2.8 eV.

(C) The first two peaks in the emission spectrum correspond to transitions from v' = 0 to v = 0 and transitions from v' = 0 to v = 1. So the energy separation between these two peaks is the difference between v = 0 and v = 1, which is the vibrational constant for harmonic potentials (a good approximation for the actual anharmonic potentials). If we ignore any anharmonicity correction, the difference is just the vibrational constant, $\tilde{\nu}$. The first peak is at 4.0 eV and the second peak is at 3.7 eV, so the vibrational constant is about 0.3 eV = 2400 cm^{-1}.

Half the quizzes asked for information on the first electronic *excited* state.

(B) The dissociation energy of AZ in its first electronic excited state can be estimated from the absorption spectrum. The lowest energy peak at 4.0 eV represents transitions from v = 0 to v' = 0. The highest energy peak at 6.4 eV represents transitions from v = 0 to the vibrational level at the top of the excited state potential. Thus the first electronic excited state well has a depth of about 6.4 – 4.0 = 2.4 eV.

(D) The first two peaks in the absorption spectrum correspond to transitions from v = 0 to v' = 0 and transitions from v = 0 to v' = 1. So the energy separation between these two peaks is the difference between v' = 0 and v' = 1, which is approximately the vibrational constant *v*. If we ignore the anharmonicity correction, the difference is just the excited state vibrational constant, $\tilde{\nu}'$. The first peak is at 4.0 eV and the second peak is at 4.2 eV, so the vibrational constant is about 0.2 eV = 1600 cm^{-1}.

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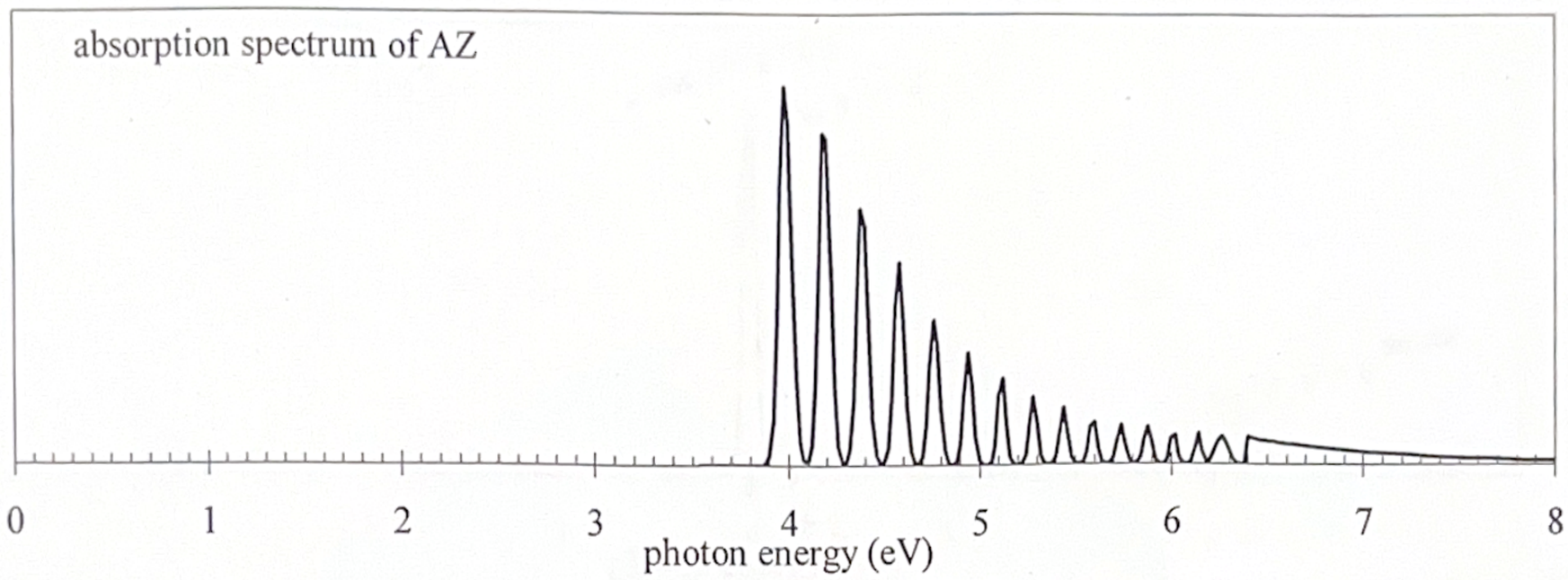
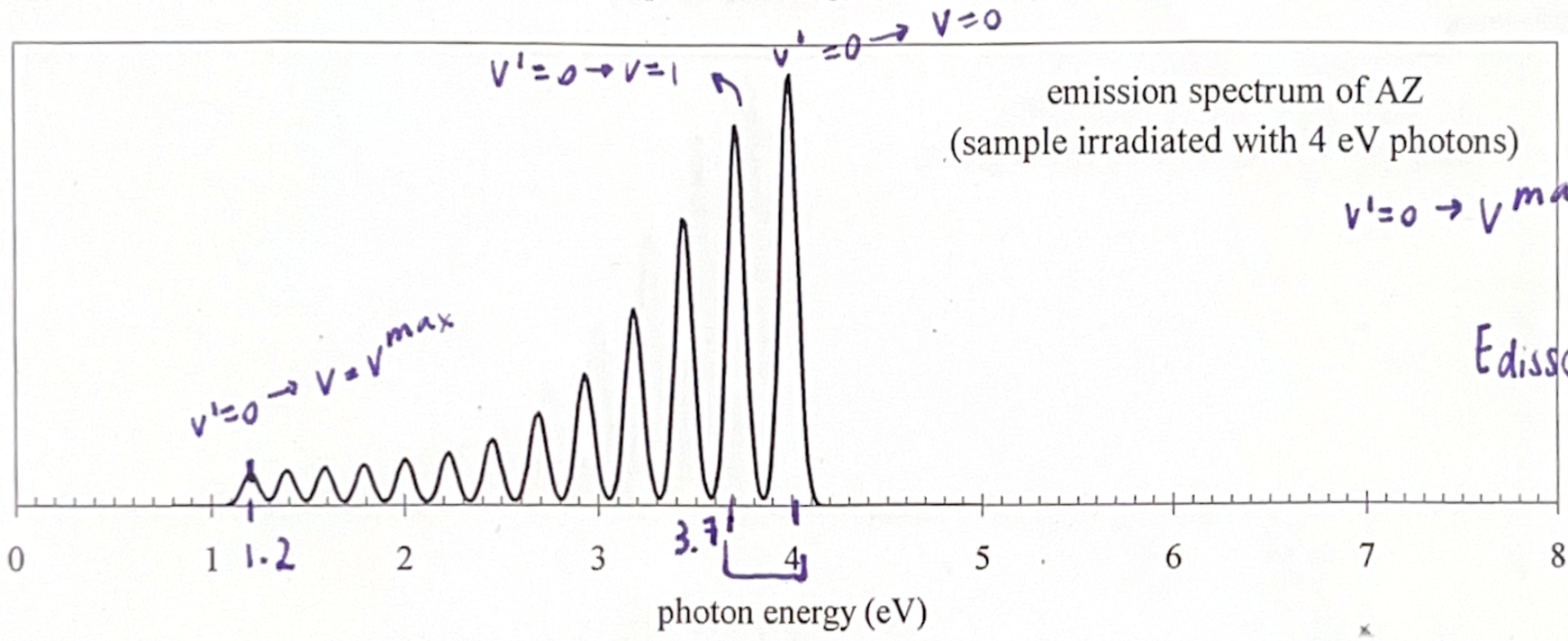
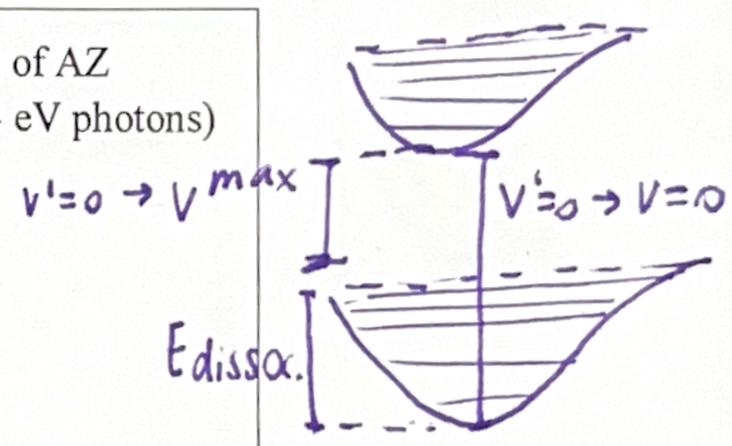
Name: Key: Ground State

Shown below are the UV/visible absorption spectrum and UV/visible emission spectrum of a gaseous substance AZ, a diatomic molecule. The pressure in the sample of AZ is high.







(A) Estimate the dissociation energy of AZ in its electronic ground state. → look @ emission

$E_{dissoc.} = 4.0\ eV - 1.2\ eV = 2.8\ eV$

(C) Estimate the vibrational constant, $\tilde{\nu}$, of AZ in its electronic ground state.

$$\tilde{\nu} \equiv \left| \begin{matrix}\text{energy of} \\ v'=0 \rightarrow v=0\end{matrix} - \begin{matrix}\text{energy of} \\ v'=0 \rightarrow v=1\end{matrix} \right| = 4.0\ eV - 3.7\ eV = 0.3\ eV$$

$$= 2400\ cm^{-1}$$

either OK

Rubric

(A) 5 points
- correct reasoning + answer → +5
- math error/wrong readings, otherwise correct → +4
- correct reasoning but looked at wrong spectra → +3
- some correct work, incorrect answer → +2

(C) 5 points
- correct reasoning + answer → +5
- math error/wrong readings, otherwise correct → +4
- correct reasoning but looked at wrong spectra → +3
- some correct work, incorrect answer → +2

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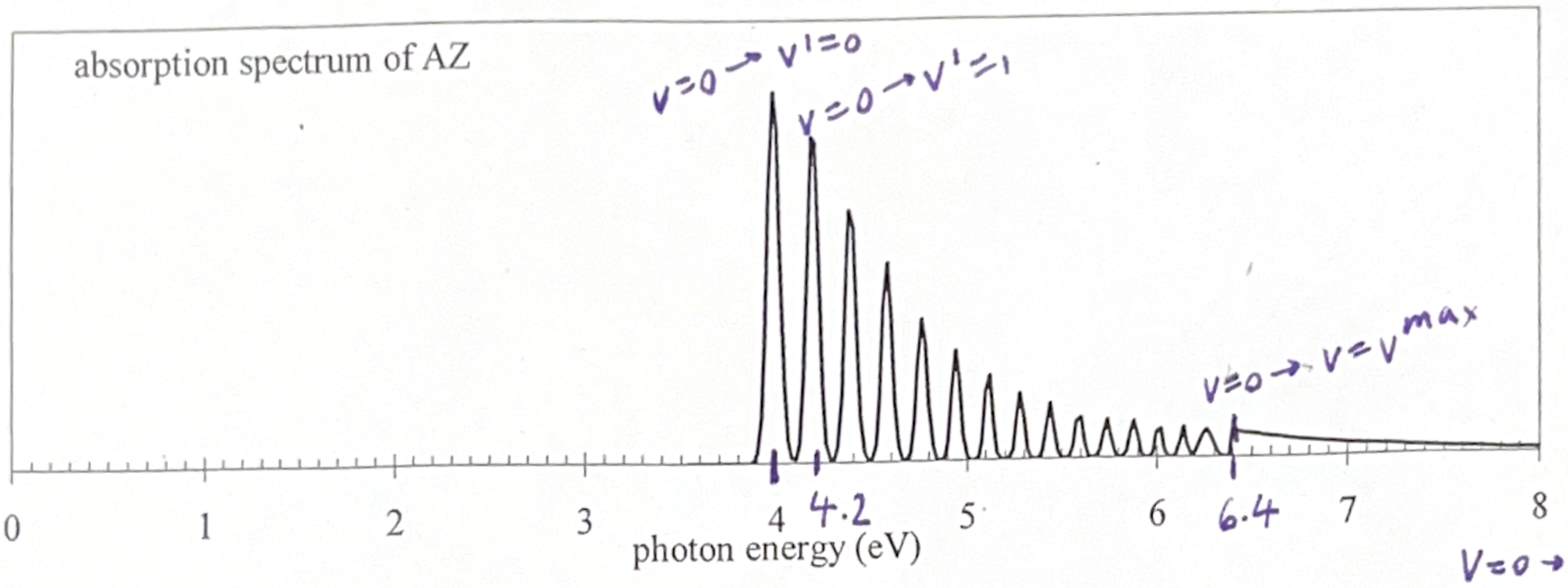
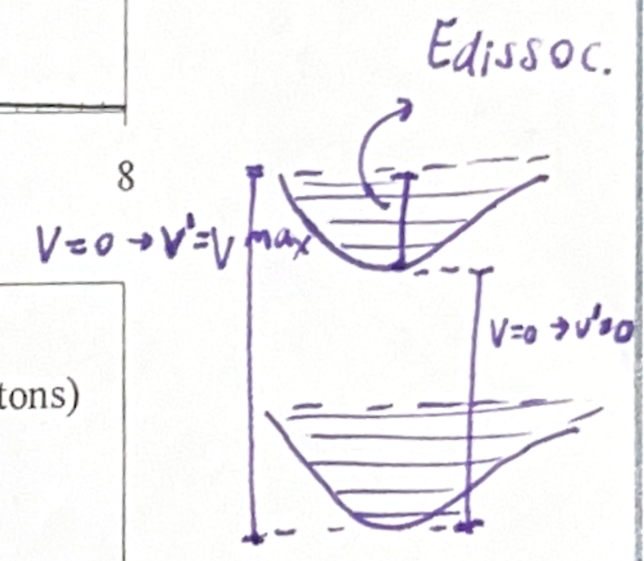
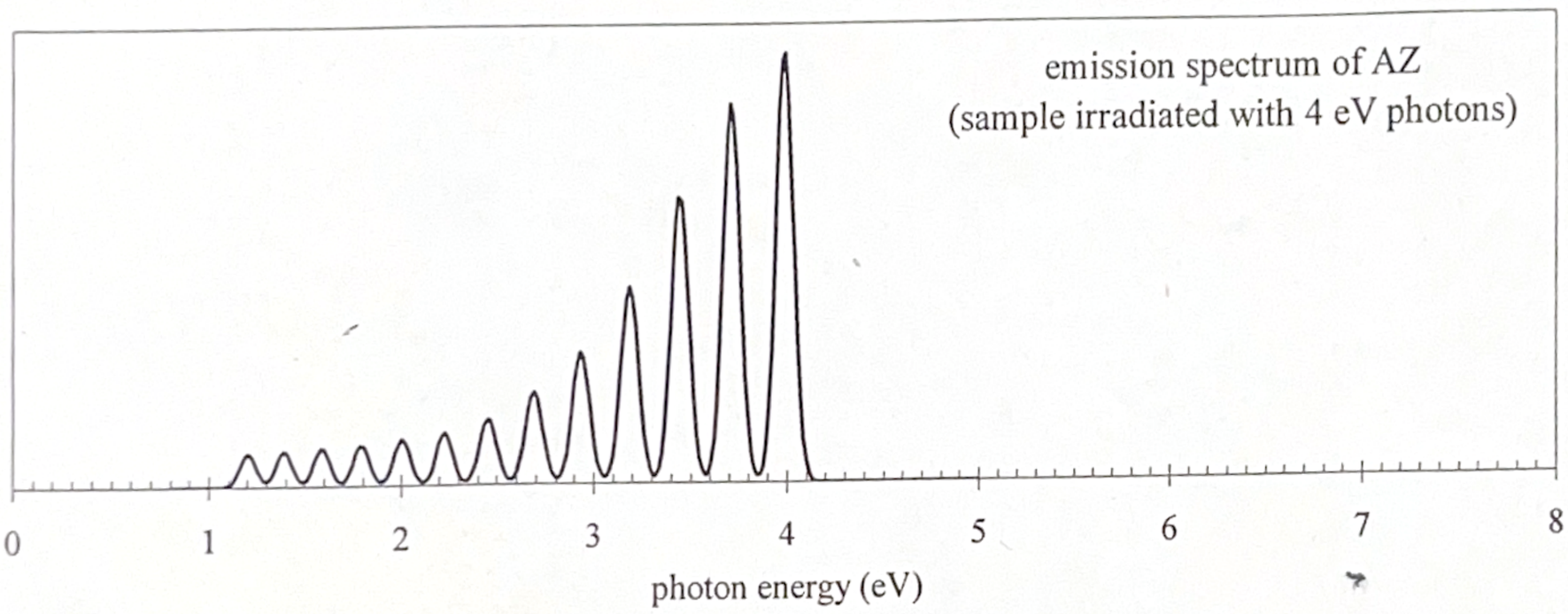
Quiz 3 - February 12, 2025

Name: key: 1st excited state

Shown below are the UV/visible absorption spectrum and UV/visible emission spectrum of a gaseous substance AZ, a diatomic molecule. The pressure in the sample of AZ is high.







(B) Estimate the dissociation energy of AZ in its first electronic excited state. → look @ absorption

$E_{dissoc.} = 6.4\ eV - 4.0\ eV = 2.4\ eV$

(D) Estimate the vibrational constant, $\tilde{\nu}$, of AZ in its first electronic excited state.

$\tilde{\nu}' = \left|\text{energy of } v=0 \to v'=0 - \text{energy of } v=0 \to v'=1\right| = 4.2\ eV - 4.0\ eV = 0.2\ eV$

$= 1600\ cm^{-1}$

either ok

Rubric

(B) 5 points
- correct reasoning + answer → +5
- math error/wrong readings, otherwise correct → +4
- correct reasoning but looked at wrong spectra → +3
- some correct work, incorrect answer → +2

(D) 5 points
- correct reasoning + answer → +5
- math error/wrong readings, otherwise correct → +4
- correct reasoning but looked at wrong spectra → +3
- some correct work, incorrect answer → +2