Calculations of Benzene Vibrational Temperature Upon S1→S0 Internal Conversion, the Corresponding Vibrational Modes, and the First Order Photolytic Rate Constant Between 170-179nm

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Abstract:

We firstly attempt to describe the relationship between the average kinetic energy of a molecule with its temperature using the equipartition theorem of energy distribution and a theoretical specific heat capacity calculated for Benzene. Following this, a similar calculation is performed using empirical specific heat data. These values are considered as local molecular vibration temperatures, and are used to estimate the wavenumber of the corresponding vibrational mode. Due to the difference in theoretical and empirical specific heat capacity (≈ 56.8%), a spectrum of vibrational temperatures can be calculated as ≈2500-5100K. This range implies vibrational wavenumbers of ≈1700-3500 cm^{-1}, the lower end of which corresponds to an e2g C=C ring stretch mode. There is also a characteristic C-H stretch mode (b1u & e2g) at ≈3200 cm^{-1}. Finally, a theoretical first order rate constant is calculated from a linear interpolation of absorption cross section data and a photon flux calculated from the advertised power density of the light source used in the experiment.

Introduction:

The photolysis mechanism of Benzene is regarded to be either a one or two photon absorption process whereby excited electronic states decay via radationless internal conversion to S0. This produces a vibrationally active "hot" Benzene and stipulates that all photo-reactants are produced from the ground state potential energy surface. A conical intersection between S1 and S0 has been shown to exist in the Benzene molecule which allows a non-adiabatic electronic transition to take place due to a breakdown of the Born-Oppenheimer approximation and vibronic coupling. DFT calculations predict that one photon absorption stimulates molecular Hydrogen loss with an exit barrier of ≈507 kJ/mol, and that the two photon absorption mechanism first produces a methylene-bridge intermediate with a ≈374 kJ/mol barrier followed by either molecular or atomic Hydrogen emission again at ≈507 kJ/mol. It is suggested in this work that the internal conversion of electronic excited states to "hot" Benzene stimulates vibrational modes corresponding to C-H stretches, and that it is the volatility of these vibrations which are responsible for C-H homolysis.

Calculation of Theoretical Specific Heat Capacity

(1) Let the total number of degrees of freedom (DOF) of a non-linear molecule with N atoms be equal to 3N for N>2. In Euclidian space, there are 3 translational DOF's and 3 rotational DOF's for sufficiently massive molecules. Therefore, the number of normal vibrational modes must equal the the total number of DOF's minus the possible translational and rotational directions. Considering a Benzene molecule (C_6H_6), the following is true;

$$\beta_{Tot} = 3N : N > 2$$
$$\beta_{Tra} = \beta_{Rot} = 3$$
$$\beta_{Vib} = \beta_{Tot} - \beta_{Tra} - \beta_{Rot} = 30$$

(2) In accordance with the equipartition theorem, let each non-vibrational DOF contribute the energy of one-half Boltzmann constant's times the temperature of the system. Further, let the total energy of the system equal the sum of translation, rotational, and vibrational contributions;

$$dE_{Tra} = \frac{\beta_{Tra} k_b}{2} dT$$
$$dE_{Rot} = \frac{\beta_{Rot} k_b}{2} dT$$
$$dE_{Vib} = \beta_{Vib} k_b dT$$

$$dE_{Tot} = \sum dE_i$$

(3) Therefore, the total energy of the system is equal to the following, and further, the theoretical specific heat capacity of Benzene, c_{Theory}, can be estimated as;

$$dE_{Tot} = \left[\frac{\beta_{Tra} k_b}{2} + \frac{\beta_{Rot} k_b}{2} + \beta_{Vib} k_b \right] dT$$

$$dE_{Tot} = \left[\frac{3k_b}{2} + \frac{3k_b}{2} + 30k_b\right]dT = 33k_b dT$$

$$c_{Theory} \approx 33k_b N_A \approx 274.2\frac{J}{molK}$$

(4) Assume that the transfer of energy between an incident photon and molecule is modeled elastically such that;

$$dE_{Tot} = E_p = \frac{hc}{\lambda_p}$$

$$\frac{hc}{\lambda_p} = 33k_b dT$$

$$dT = \frac{hc}{33k_b\lambda_p}$$

(5) Letting the wavelength of the incident photon be equal to 173 nm, the following temperature of a Benzene molecule is estimated;

$$dT_{173nm} \approx 2500K$$

Calculation of Vibrational Temperature from Empirical Specific Heat Capacity

(6) Using the empirical specific heat capacity of Benzene in the liquid phase, c_{Emp}, and its definition, the following relationship is determined, where n is equal to number of moles;

$$c_{Emp} = \frac{dQ}{ndT} \approx 134.8\frac{J}{molK}$$

(7) And for a single molecule;

$$\frac{c_{Emp}}{N_A} = \frac{dQ}{dT}$$

(8) Once again assuming the exchange of photon/molecule energy is elastic, the change in energy of the system can be set equal to the energy of an incident photon;

$$dQ = E_p = \frac{hc}{\lambda_p}$$

$$\frac{c_{Emp}}{N_A} = \frac{hc}{\lambda_p dT}$$

$$dT = \frac{hcN_A}{\lambda_p c_{Emp}}$$

(9) Once again letting the wavelength of the incident photon be equal to 173 nm, the following temperature of a Benzene molecule is estimated;

$$dT_{173nm} \approx 5100K$$

Estimating Vibrational Wavenumbers from Vibrational Temperature

(10) Finally, these temperatures are used as vibrational temperatures, θ_{vib}, to calculate the wavenumber of vibrational modes where ν is mode frequency;

$$\theta_{vib} = \frac{h\nu}{k_b}$$

(11) With the relationship between wavenumber, wavelength, and frequency, an equation in terms of wavenumber can be established;

$$\tilde{\nu} = \frac{1}{\lambda} \rightarrow \lambda\nu = c \rightarrow \nu = c\tilde{\nu}$$
$$\theta_{vib} = \frac{hc\tilde{\nu}}{k_b} \rightarrow \tilde{\nu} = \frac{\theta_{vib}k_b}{hc}$$

(12) Therefore, the wavenumber of the mode associated with the previously calculated vibrational temperatures are;

$$\tilde{\nu}_{2500K} \approx 1737cm^{-1}$$
$$\tilde{\nu}_{5100K} \approx 3544cm^{-1}$$

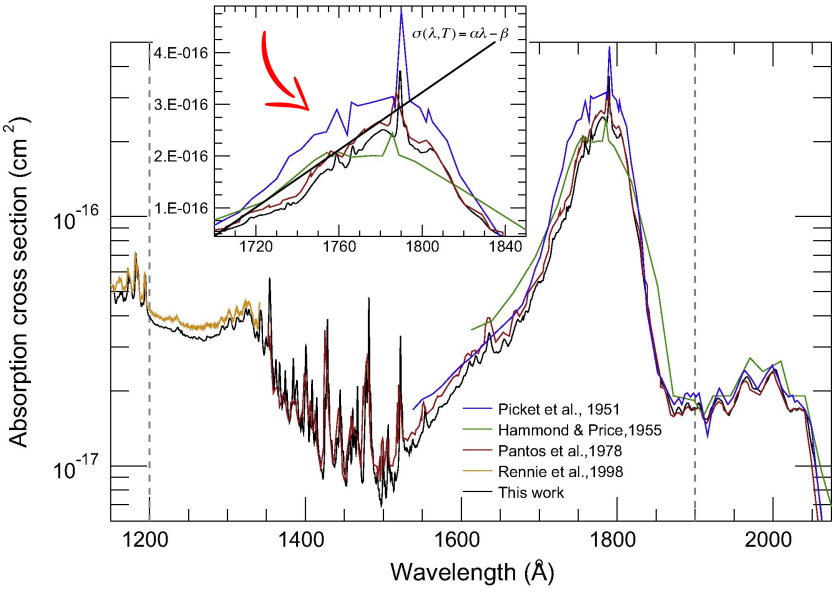
Calculating the Benzene Photolytic Rate Constant

(13) The photolysis rate constant is defined as the following where $\sigma(\lambda,T)$ is the absorption cross section as a function of incident wavelength and temperature, $\phi(\lambda)$ is the quantum yield, $F(\lambda,T)$ is photon flux, and the upper and lower limits of integration define the domain over which the integrand is valid;

$$J = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda,T)\phi(\lambda,T)F(\lambda,\theta)d\lambda$$

(14) Using data taken from the following graph, the absorption cross section of Benzene is modelled linearly as the following where α & β are constants;

$$\sigma(\lambda,T) = \alpha\lambda - \beta$$



Data courtesy of;

Capalbo, Fernando J, et al. “New Benzene Absorption Cross Sections in the VUV, Relevance for Titan's Upper Atmosphere.” *Icarus*, vol. 265, Feb. 2016, pp. 95–109.

(15) The quantum yield is a piecewise function of λ corresponding to either a one or two photon absorption photolysis mechanism;

$$\phi(\lambda,T)=\begin{cases}1, \lambda>193nm\\ \frac{1}{2}, \lambda<193nm\end{cases}$$

(16) And the photon flux is estimated from the documented power density of the plasma lamp used in the experiment (≈15 mW/cm^2). Here, let the number of emitted photons per square centimeter, n, be related to power density, E, as follows;

$$\overline{E}=\frac{n_\rho hc}{\lambda}\rightarrow n_\rho=\frac{\overline{E}\lambda}{hc}$$

$$F(\lambda,\theta)=\overline{E}=\frac{\overline{E}\lambda}{hc}$$

(17) Therefore, the photolytic rate constant J is estimated as follows;

$$J = \int_{\lambda_1}^{\lambda_2} \frac{\overline{E}\phi\lambda}{hc}(\alpha\lambda - \beta)d\lambda = \frac{\overline{E}\phi}{hc}\left(\frac{\alpha\lambda^3}{3} - \frac{\beta\lambda^2}{2}\right)_{\lambda_1}^{\lambda_2}$$

(18) Assuming the following, J is equal to;

$$\lambda_1 = 170nm$$
$$\lambda_1 = 179nm$$
$$\alpha = 2.6 * 10^{-17}$$
$$\beta = 4.4 * 10^{-15}$$
$$\phi = 1$$

$$J \approx 1.64 * 10^{10} s^{-1}$$

(19) If a two photon absorption process is assumed such that ϕ=1/2, then the rate constant is;

$$J \approx 8.2 * 10^{9} s^{-1}$$

(20) Further, let the total number of Benzene molecules at time t with the following initial condition (where n_0 is the initial number of molecules present) be equal to;

$$\frac{dn}{dt} = -Jn \rightarrow \int \frac{dn}{n} = -\int J\,dt$$
$$\ln(n) = -Jt + c \rightarrow n = Ce^{-Jt} : n(0) = n_0$$
$$n = n_0 e^{-Jt} = n_0 e^{-t\frac{\overline{E}}{hc}\left(\frac{\alpha\lambda^3}{3} - \frac{\beta\lambda^2}{2}\right)_{\lambda_1}^{\lambda_2}}$$

(21) Manipulating this result algebraically, the following is shown;

$$t = -\frac{hc}{\overline{E}\left(\frac{\alpha\lambda^3}{3} - \frac{\beta\lambda^2}{2}\right)_{\lambda_1}^{\lambda_2}} \ln\left(\frac{n}{n_0}\right)$$

(22) Assuming an n photon absorption process, the time for dissociation of 99.9% of n0 is,

$$t_{n=1} \approx 4.2 * 10^{-10} \text{ sec}$$
$$t_{n=2} \approx 8.4 * 10^{-10} \text{ sec}$$