

Teaching Molecular Applications of the Particle-in-a-Ring Model Using Azulene

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Background

Although crude, the particle-in-a-box model is widely used for pedagogical purposes. Its simplicity makes it valuable to bridge theoretical and experimental fields in introductory physical chemistry courses. Reports of particle-in-a-box experiments in this *Journal* date back to the 1960s (1–14) and include interesting cases of unconventional geometries (4–6). Cyanine dyes are common molecular applications for one-dimensional boxes, although some experimental uncertainties about the box limits are hard to overcome (1, 10, 11); linear polyenes can also be used (14). The H atom (8) and C₆₀ (15, 16) are reasonable three-dimensional boxes.

Two-dimensional boxes, including a meaningful circular geometry, have been overlooked for pedagogy. Benzene, the “classical” model ring molecule, is unsafe for use in a teaching laboratory. Moreover, its intense electronic absorption spectrum occurs at wavelength ca. 200 nm, at which problems due to interference of contaminants, oxygen, and solvents cannot be easily solved. 1,3,5,7-Cyclooctatetraene is not a feasible alternative owing to its nonplanar “tub” or “boat” conformation with alternating single and double bonds (17); as its planes of adjacent double bonds are almost orthogonal, there is little conjugative interaction between those bonds. Naphthalene and other cata-condensed polycyclic aromatics (those that have no carbon atom belonging to more than two rings), were studied by Platt in the context of the particle-in-a-ring model and important theoretical work was developed (18), but a nonsignificant π -electron density over the bond common to both rings had to be assumed; this assumption has no physical counterpart.

Azulene and the Particle-in-a-Ring Model

In this paper, azulene (Fig. 1) is proposed as a model compound for an application of the particle-in-a-ring (i.e., 2-D circular) model, and work performed by undergraduate students in physical chemistry at the University of Lisbon, Portugal, is described. The ten π electrons of azulene are delocalized around the periphery; in many respects the molecule can be regarded as a cyclodecapentaene with a transannular valence bridge (18). Because neither Kekulé-type structure that can be written involves a double bond common to the two rings, the perimeter model is appropriate for azulene (Fig. 1). Although π electrons of azulene are concentrated more in the five-membered ring than in the seven-membered ring (18), this physical detail has fortuitously little effect in deviating the theoretical expectation from the experimental data, despite an assumption of constant potential energy throughout the box being violated.

Azulene was purchased from Fisher Scientific/Acros Organics (Hampton, NH). Solutions were prepared in heptane;

a stock solution (0.22 mM) was subsequently diluted ten times. Reference spectra are found in a UV spectral atlas (e.g., ref 19). A weak band, responsible for the purple/blue color of azulene, is discernible in the red region of the spectrum. A band with moderately strong oscillator strength occurs at 310–350 nm (maximum at 341 nm [Fig. 2]).

The clear and pedagogical paper by Alan Vincent (13) on the energy levels of the *particle-in-a-ring* system was used for theoretical background. The wave functions of the particle-in-the-box model become alternately forbidden and allowed when converted to the particle-in-a-ring model, only those functions corresponding to an even quantum number being allowed. The allowed energy levels for the particle in a ring are formulated in eq 1.

$$E = \frac{2n^2\hbar^2}{8m\ell^2} = \frac{n^2\hbar^2}{2m\ell^2} \quad (n = 0, 1, 2, 3, \dots) \quad (1)$$

where n is the quantum number of the level having energy E .

Most practical applications of particle in a box pertain to one-dimensional boxes (i.e., linear molecules) and most pedagogical papers on one-dimensional boxes include equa-

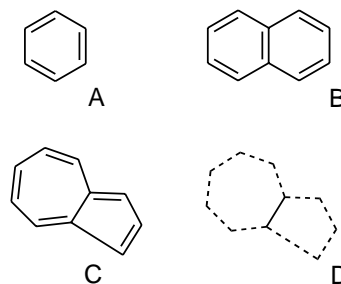


Figure 1. Molecules for which a model of the particle in a ring has been applied: A, benzene; B, naphthalene; C, azulene; D, azulene periphery.

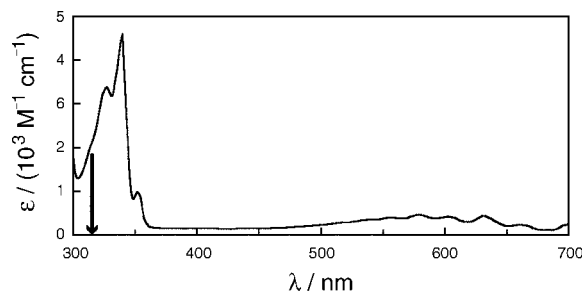


Figure 2. Electronic absorption spectra of azulene in heptane at room temperature. The wavelength for absorption predicted according to the particle-in-a-ring model is indicated with an arrow.

tions that relate the lowest energy transition wavelength (λ) to the total number of π electrons in the molecule (N). Therefore the homologous equations for circular boxes, assuming N even, were used (eqs 2–5). At this point, students should be reminded that spectral transitions take place between two states of a molecule; comparing spectral transitions to gaps between energy levels is an approximation. State diagrams should be used instead if more detailed models are considered.

$$n_{\text{gr}} = \text{trunc}(N/4) \quad (N \text{ even}) \quad (2)$$

$$n_{\text{ex}} = \text{trunc}(N/4) + 1 \quad (N \text{ even}) \quad (3)$$

$$\Delta E = \frac{[2\text{trunc}(N/4) + 1]h^2}{2m\ell^2} \quad (4)$$

$$\lambda = \frac{hc}{\Delta E} \quad (5)$$

where ΔE is the lowest energy gap between occupied and unoccupied energy levels, m is the electron mass, ℓ is the ring perimeter, c is the speed of light in vacuum, and h is Planck's constant; $\text{trunc}(N/4)$ is the truncation of $N/4$ to an integer by removing the decimal part and is related to the fact that all electronic levels, except the lowest energy level, are doubly degenerate; and n_{gr} and n_{ex} are the quantum numbers of the ground and first electronically excited energy levels, respectively.

I believe it is more appropriate for students to calculate the expected transition wavelength (eq 5) and compare this value with the absorption spectrum, than to use an experimental wavelength value to estimate the box dimension and then to compare this with the value calculated from a sum of individual bond lengths. The absorption spectrum defines a range of absorption wavelengths. A crude and oversimplified theory such as the one behind free-electron models cannot account for the fact that there is not a specific and well-defined transition wavelength. Comparison of box lengths forces a student to select a wavelength among those at which absorption occurs, despite the fact that this procedure causes conflict between theory and experimental data. This conflict raises doubts about what wavelength to choose—the intensity averaged wavelength? the wavelength for maximal absorption? the wavelength for the 0–0 (lowest-energy) vibrational band? There are several possible and reasonable answers to this question.

The perimeter of azulene was taken to be ten times the bond length between carbon atoms in benzene ($10 \times 138 \text{ pm} = 1380 \text{ pm}$), with $N = 10$. Equation 5 leads to $\lambda = 314 \text{ nm}$, unambiguously within the wavelength range of the absorption spectrum (Fig. 2). Nevertheless, it is advisable to caution the students. The moderately intense absorption spectrum observed for azulene ($f \cong 0.08$) and polyenes (17, 20) in the UV–vis region is the $S_2 \leftarrow S_0$ transition: $S_1 \leftarrow S_0$ is forbidden by symmetry in polyenes (18, 20) and is weak in azulene (Fig. 2; oscillator strength $f \cong 0.009$, $\lambda \cong 600 \text{ nm}$). In fact, as discussed by others and thoroughly illustrated with benzene, particle-in-a-box experiments can predict only the “center of mass” of transitions between singlets because electron correlation is not taken into account (17, 21).

Pedagogical work on the synthesis of azulene has been published (21–23). Practical work combining synthesis and spectral analysis of azulene is both possible and desirable. Students

should be challenged with the question “Why is the azulene fluorescence blue instead of red?” The $S_1 \leftarrow S_0$ transition occurs at approximately 600 nm, so at first glance fluorescence emission at 600–700 nm might be expected. Nevertheless, on placing azulene under UV light, even from an ordinary UV lamp such as the ones used in thin-layer chromatography, one sees a blue fluorescence, instead of red. The extremely unusual combination of a large energy gap $S_2 \leftarrow S_1$, a small energy gap $S_1 \leftarrow S_0$, and forbidden transitions $S_1 \leftarrow S_0$ and $S_2 \rightarrow S_1$ produces $S_2 \rightarrow S_0$ fluorescence. This experiment presents an optimal opportunity to introduce students to Einstein coefficients. Color is another property peculiar to azulene by comparison with other polycyclic hydrocarbons. The work can be extended into quantum chemistry if students are challenged to explain the color of azulene (18) and, by inference, its name.

Hazards

Azulene is irritating to eyes, respiratory system, and skin; therefore contact with skin and eyes should be avoided. Use of gloves and safety glasses is recommended, although azulene is presented as a powder easy to handle. A safety data sheet is available at the Internet site of the manufacturer (<http://www.catalogue.fisher.co.uk>).

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Literature Cited

- Gerkin, R. E. *J. Chem. Educ.* **1965**, *42*, 490.
- Padnos, N. J. *J. Chem. Educ.* **1965**, *42*, 600.
- Jinks, K. M. *J. Chem. Educ.* **1975**, *52*, 312.
- Miller, G. R. *J. Chem. Educ.* **1979**, *56*, 709.
- Knox, K. J. *J. Chem. Educ.* **1980**, *57*, 626.
- Castro, E. A.; Fernandez, F. M. *J. Chem. Educ.* **1983**, *60*, 378.
- Farrell, J. J. *J. Chem. Educ.* **1985**, *62*, 351.
- Varandas, A. J. C.; Martins, L. J. A. *J. Chem. Educ.* **1986**, *63*, 485.
- Breneman, G. L. *J. Chem. Educ.* **1990**, *67*, 866.
- Moog, R. S. *J. Chem. Educ.* **1991**, *68*, 506.
- Taubman, G. J. *J. Chem. Educ.* **1992**, *69*, 96.
- Liang, Y. Q.; Zhang, H.; Dardenne, Y. X. *J. Chem. Educ.* **1995**, *72*, 148.
- Vincent, A. *J. Chem. Educ.* **1996**, *73*, 1001.
- Anderson, B. D. *J. Chem. Educ.* **1997**, *74*, 985.
- Berberan-Santos, M. N. *Química Nova* **1994**, *17*, 293.
- Ball, D. W. *J. Chem. Educ.* **1994**, *71*, 463.
- Suzuki, H. *Electronic Absorption Spectra and Geometry of Organic Molecules*; Academic: New York, 1967; pp 160–162, 200–201, 362–363.
- Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley, New York, 1962; pp 242–247, 287–303, 337–344.
- Photoelectric Spectrometry Group and Institut für Spektrochemie und Angewandte Spektroskopie. *UV Atlas of Organic Compounds*; Verlag Chemie: Weinheim, 1966; p F1/1.
- Hudson, B.; Kohler, B. *Annu. Rev. Phys. Chem.* **1974**, *25*, 437.
- Lemal, D. M.; Goldman, G. D. *J. Chem. Educ.* **1988**, *65*, 923.
- Brieger, G. J. *J. Chem. Educ.* **1992**, *69*, A262.
- Salter, C.; Foresman, J. B. *J. Chem. Educ.* **1998**, *75*, 1341.