

Comment on “Sublimation Energy of Benzene”

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(2) This last result disagrees even more strongly with experiment and indicates that the σ -electron contribution must be considerable. This will be the case even if Sen and Basu's statement that "the quadrupole moments of C-C and C-H sigma bonds are extremely small" is correct, since the C-H bond *dipole* moments must make a substantial contribution to the molecular quadrupole moment.

The expectation values relevant to a calculation of the benzene quadrupole moment, using all the valence electrons, have been calculated³ on the basis of wavefunctions expressed as linear combinations of Slater-type atomic orbitals. Using these results, we obtain the following values for the bond moments: $\Theta(\text{C}-\text{C})_{\sigma} = 4.86 \times 10^{-26}$ esu; $\Theta(\text{C}-\text{H})_{\sigma} = 3.23 \times 10^{-26}$ esu (relative to an origin at the center of gravity of the electron cloud, i.e., 0.0782 Å from the carbon atom); $\Theta(\pi) = -14.63 \times 10^{-26}$ esu; $\mu(\text{C}-\text{H}) = -2.30 \times 10^{-18}$ esu. The contributions from the nuclear charges are included in each case, and it is to be noted that the σ -bond quadrupole moments are of considerable magnitude. Combining these results leads to a calculated molecular quadrupole moment of -8.8×10^{-26} esu, which is of the same order of magnitude as the experimental result.⁵ Better agreement would not be expected unless a very sophisticated wavefunction were used, the quadrupole moment being a small difference between two large numbers [$\Theta(\text{electronic}) = 164.1$ esu; $\Theta(\text{nuclear}) = -172.9$ esu].

We conclude, therefore, that Sen and Basu's method of estimating the quadrupole moment is an extreme approximation which results in an estimated electrostatic contribution to the lattice energy which is nearly 2 orders of magnitude greater than that based on the experimental quadrupole moment.² Their conclusions on the importance of the quadrupole-quadrupole interaction are therefore unacceptable, and the agreement obtained with the experimental latent heat of sublimation is fortuitous.

Two comparatively minor (and probably typographic) errors in Sen and Basu's paper may be noted. Equation (1) for the free-electron wavefunction should read⁶:

$$\psi_{l=0,\pm 1} = N[(K)^{1/2}z] \exp(-Kz^2/2) [(C)^{1/2}\rho]^{\eta} \\ \times \exp(-C\rho^2/2) \exp(il\phi),$$

and the expression for Θ_{zz} should be:

$$\Theta_{zz} = 3e[(3/K) - (1/C)] - (e/C) \sum_{l=0,\pm 1} \eta$$

(because η is a function of l) with a corresponding expression for Θ_{xx} .

¹ P. Sen and S. Basu, *J. Chem. Phys.* **48**, 4075 (1968).

² D. P. Craig, P. A. Dobosh, R. Mason, and D. P. Santry, *Discussions Faraday Soc.* **40**, 110 (1965).

³ K. Bannerjee and L. Salem, *Mol. Phys.* **11**, 495, (1966).

⁴ A. I. M. Rae and R. Mason, *Proc. Roy. Soc. (London)* **A304**, 487 (1968).

⁵ R. M. Hill and W. V. Smith, *Phys. Rev.* **82**, 451 (1951).

⁶ P. Sen and S. Basu, *J. Chim. Phys.* **64**, 901 (1967).

Comment on "Sublimation Energy of Benzene"

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Using free-electron molecular orbital, Sen and Basu calculated the pi-quadrupole moment of benzene and arrived at the conclusion that the electrostatic interaction between pi-quadrupole moments is strong enough to account for the sublimation energy of benzene. Since Sen and Basu considered the exact agreement between theoretical and experimental sublimation energy to be purely accidental, it is evident that they did not consider the electrostatic force to be operative alone in benzene crystal. Rae and Mason calculated the quadrupole moment of benzene arising from the distribution of C-H dipoles and found it to be quite large. Consequently, in this model the electrostatic interaction is large in benzene crystal. Since De Boer in 1936 theoretically calculated the sublimation energy of benzene for the first time, various workers have calculated this quantity using different physical models. It is amazing that in all such calculations the agreement between calculated and experimental values has been quite good. Probably the last word about this problem has not yet been said.

Errata

Erratum: Electron Spin Relaxation in Solvated Manganese (II) Ion Solutions

[*J. Chem. Phys.* **44**, 890 (1966)]

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An algebraic error in Eq. (6) where a factor of 2 was omitted from the first term on the right, and a physical¹

incorrect treatment of the off-diagonal relaxation matrix elements in Eqs. (12)–(14), gave an incorrect set of relative linewidths in Eq. (15). In the separated line approximation which was used, off-diagonal relaxation matrix elements are small and only the diagonal terms $R_{\alpha, \alpha+1, \alpha, \alpha+1}$ in Eqs. (12)–(14) need be considered. Thus Eqs. (15) should read

$$[T_2^{-1}]_{3/2, 5/2} = [T_2^{-1}]_{-5/2, -3/2} = 2.143 Z(0), \quad (15a)$$

$$[T_2^{-1}]_{1/2, 3/2} = [T_2^{-1}]_{-3/2, -1/2} = 1.886 Z(0), \quad (15b)$$

$$[T_2^{-1}]_{-1/2, 1/2} = 1.543 Z(0). \quad (15c)$$

These corrections represent only a small narrowing (<4%) of the center resonance relative to the wing

lines as compared to the set of linewidths used in the study of line shapes. This would tend to give a better fit of theoretical to experimental lineshapes in Figs. 2 and 3. Thus none of the conclusions about either the relaxation mechanisms or the chemistry of manganese (II) solutions are altered by the above corrections. It should be noted, however, that exactly superimposed resonances would have a single relaxation time,¹ which would suggest that inhomogeneously broadened lines require an intermediate treatment. The line-shape studies indicate that the separated line approximation is adequate for manganese (II) solution spectra.

¹ B. B. Garrett, A. B. Denison, and S. W. Rabideau, *J. Phys. Chem.* **71**, 2606 (1962).