CC/NUMBER 4
JANUARY 25, 1993

This Week's Citation Classic®

Whiffen D H. Vibrational frequencies and thermodynamic properties of fluoro-, chloro-, bromo-, and iodo-benzene. *J. Chem. Soc.* 1956:1350-6.
[Chemistry Department, The University, Edgbaston, Birmingham, England]

This paper brings together all 30 vibrational frequencies of each of the mono-halogenated benzenes from the literature of the Raman and infrared spectroscopy. This enables the gaseous values of the enthalpy, entropy, and specific heat of these compounds to be derived. [The *SCI*® indicates that this paper has been cited in more than 655 publications.]

Characteristic Frequencies

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During the years 1940-1955, interest in characteristic infrared frequencies was considerable as, prior to nuclear magnetic resonance, infrared spectroscopy was the major physical method of identifying organic groupings in chemicals of uncertain structure. I had participated in such work as part of my doctorate under Harold Thompson. Tables of such frequencies were widely collected and updated, and the authoritative book[1] by a great friend, Lionel J. Bellamy, cites the paper under discussion in its second edition of 1958.

At Birmingham, I continued an interest in the characteristic frequencies of aromatic compounds, and the work[2] of my first research student, Rex R. Randle, was funded by the National Coal Board in view of the interest in the relationship between coal and graphite. During the summer vacation of 1955, I was short of active research and thought that a complete set of frequencies of the monohalogenated benzenes might by then be assembled. Some of the infrared frequencies were not very characteristic. And the Raman spectra had been measured by the Austrian group under K.W.F. Kohlrausch, which was able to continue such measurements throughout the 1939-1945 war.[3] The paper assigns all 30 fundamental frequencies for each compound. Their values are seen to vary smoothly and monotonically with halogen mass; this gives confidence that the assignments are correct. Idealized pictures indicate simplified forms of the normal modes.

Just to have recorded these values seemed rather light for a publication and so the thermodynamic tables were calculated and added as a makeweight. Although today such calculations would be trivial, in 1955 only hand-operated calculators were available. However, useful tabulations such as those reproduced by K.S. Pitzer[4] greatly diminished the effort required.

It was a great surprise to me when ISI said this was deemed to be a most-cited publication. It may be that there has been no updating of the thermodynamic values, as the chief inaccuracy was the use of liquid-state frequencies instead of gas-phase values: and gaseous Raman spectra of fairly involatile materials are not yet common. Since the field of characteristic infrared frequencies was worn out by the early 1960s, and thermodynamics was never one of my interests, I have not followed subsequent work, if any exists, which improves this paper.

I can only add that this work was without novel ideas and caused no difficulty in execution. It did not lead to any prize or even a lecture invitation; nor did it merit such reward. This is a case where the citation index is not reliable in evaluating merit.

1. **Bellamy L J.** *The infra-red spectra of complex molecules* London: Methuen, 1958. 425 p. (Cited 840 times.)
2. **Randle R R & Whiffen D H.** The characteristic vibration frequencies of substituted benzenes. (Sell G. ed.) *Molecular spectroscopy, report of a conference*, 28-29 October 1954, London, England. London: Institute of Petroleum, 1955. p. 111-28.
3. **Kohlrausch K W F & Wittek H.** Studien zum Raman-Effekt. Mitteilung 131: Benzolderivate XVI (Benzol und monosubstituierte Benzole) [Studies on the Raman effect. Communication 131: benzene derivatives XVI (benzene and monosubstituted benzenes)]. *Monat. Chem.* 74:1-24, 1943.
4. **Pitzer K S.** *Quantum chemistry.* London: Constable, 1953. 529 p. (Cited 130 times.)

Received August 28, 1991