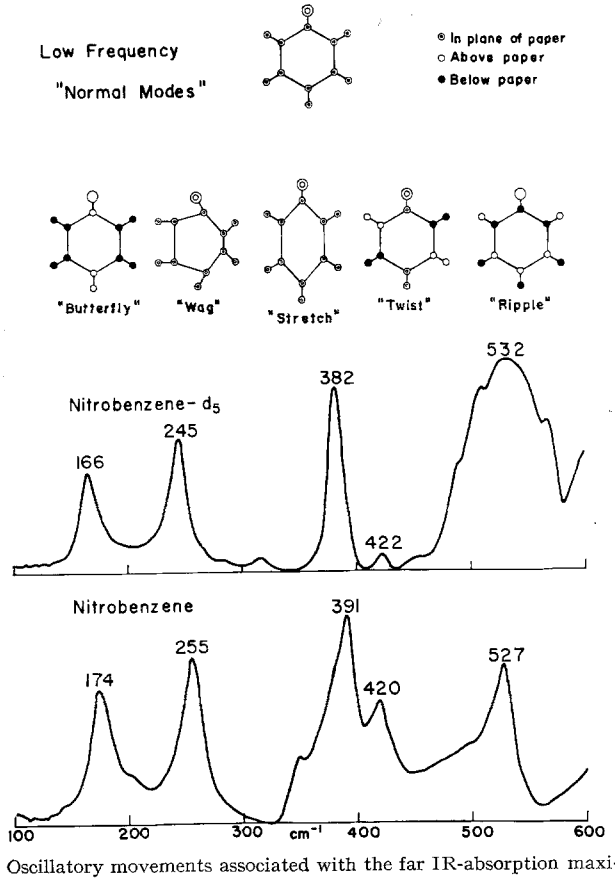
Odor and Molecular Vibration: Response to Nitrobenzene-d_5 of Honey Bees (*Apis mellifera* L.) Conditioned with Nitrobenzene

BARKER et al.[1] showed that honey bees, *Apis mellifera* L., conditioned to benzaldehyde would also respond, but less strongly, to nitrobenzene. This was taken to indicate that they recognized a similarity but not an identity in the quality of the odor. When bees conditioned to nitrobenzene, $C_6H_5NO_2$, were exposed to the fully deuterated compound, $C_6D_5NO_2$, (nitrobenzene-D_5), the response was the same as to ordinary nitrobenzene. Since deuteration would alter the molecular vibration frequencies but not the molecular shape, the bees' inability to discriminate between the deuterated and normal compounds led these authors to infer that 'electronic structure and force fields are involved in odor discrimination' and that vibration frequencies are not.

This inference would be valid if the effect on the vibration frequencies were sufficiently large, but Barker et al.[1] did not record frequencies below about 500 cm^{-1} which, on quantum grounds, are the only ones likely to be associated with olfactory stimulation[2].

Dr. BARKER was kind enough to send the writer the nitrobenzene-D_5 left after his tests so that the low-frequency absorption maxima could be compared with those of ordinary nitrobenzene. The spectra were recorded using a Perkin-Elmer Model 301 Far Infrared Spectrophotometer with the samples dissolved in *n*-heptane and mounted in polyethylene cells. The results are shown in the Figure.



Oscillatory movements associated with the far IR-absorption maxima.

It is evident that deuteration did not change the frequencies by more than 10 cm^{-1} or at most about 4% which is scarcely enough to be osmically significant. The Figure shows that the oscillatory movements or 'normal modes' associated with the far IR-absorption maxima have a 'whole molecule' character that makes them relatively insensitive to deuteration. For example, the stretching mode near 390 cm^{-1} can be pictured to a first approximation as an upper block of 2 C–H groups plus a C–NO_2 group vibrating against a lower block of 3 C–H groups. The masses of the 2 groups are, respectively, 84 and 39. For a simple harmonic motion, the frequency, ν, is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where k is the restoring force constant and μ is the 'reduced mass' of the system:

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

For the stretching mode of ordinary nitrobenzene the reduced mass is approximately 26.6 and for the fully deuterated compound the value becomes 28.2. The difference in their square roots is 0.15 or about 2.9%. The observed shift in the frequency is 9 cm^{-1}, or about 2.3%.

In some earlier experiments, DOOLITTLE et al.[3] found that deuterating 4-(*p*-hydroxyphenyl)-2-butanone acetate ('cue lure') did not affect its ability to attract the melon fly, *Dacus curcurbitae* Coq.; and the far IR-spectra they recorded also showed relatively small frequency shifts, e.g., from 199 to 192 cm^{-1}.

In general, therefore, isotopic substitution does not usually affect the osmically significant frequencies enough to modify the odor, though it may do so in a few cases such as that of naphthalene where there does seem to be a perceptible difference in the smell and the frequencies are shifted by complete deuteration from 363 and 183 to 331 and 169 cm^{-1} [4].

It can be concluded that the failure of deuteration to modify the insects' olfactory responses in no way conflicts with the vibration theory of olfactory specificity, a theory with a so-far unrivalled record of predictive successes[5].

Zusammenfassung. Nachweis, dass die molekulare Vibrationsfrequenz von voll deuteriumiertem Nitrobenzol im Bereich unterhalb 500 cm^{-1} sich höchstens um 4% von jener des normalen Nitrobenzols unterscheidet. Das Unvermögen von Bienen, die beiden Substanzen olfaktorisch zu unterscheiden, spricht daher offenbar nicht gegen die Vibrationstheorie einer geruchlichen Wahrnehmung.

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