Electric-field Induced Vibrational Spectrum of Liquid Tetrachloroethylene

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Summary The activation by an electric field of a formally i.r.-inactive band (the symmetric C=C stretching mode of tetrachloroethylene) has been observed in the liquid phase; from the zero-field intensity of this band, the internal field of the liquid has been estimated as *ca.* 4×10^6 V cm^{-1}.

The effect of an electric field in inducing i.r. activity in symmetric Raman-active vibrational modes of a molecule has been theoretically predicted[1] and observed in the gas phase for hydrogen.[2] This effect has now been observed in a condensed phase for the first time.

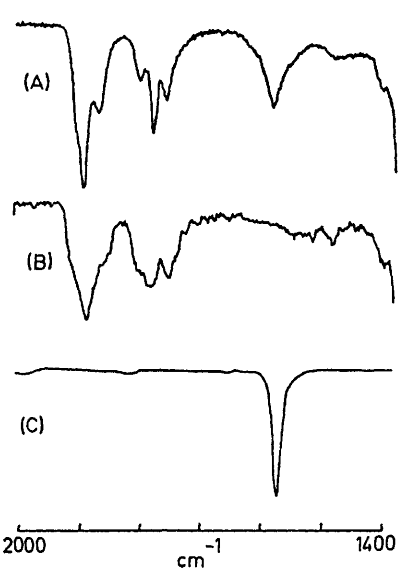

Figure. *Spectra of tetrachloroethylene.* (A) *I.r. spectrum of liquid* (0·3 *mm thickness*). (B) *I.r. spectrum of vapour* (10 *cm thickness,* ca. 400 *Torr*). (C) *Raman spectrum of liquid.*

The symmetric C=C stretching mode ν_1 of tetrachloroethylene occurs in the Raman spectrum of the liquid[3] as an intense band at 1574 cm^{-1}. It is formally forbidden in the i.r. spectrum, but in the pure liquid a very weak band is observed at 1577 cm^{-1} (ϵ_{max} 0·252). In the gas phase this band is very difficult to discern ($\epsilon_{max} <$ *ca.* 0·02) although other weak bands in this region persist with almost unchanged intensity (see Figure). This band is interpreted as ν_1, weakly i.r. allowed in the liquid by a small condensed phase effect.

I.r. cells and associated spectrometric equipment have been constructed to permit the examination of liquid specimens in high transverse electric fields.† In the case of tetrachloroethylene, a cell of 3 mm path-length was used, in which the volume traversed by the beam could be electrically stressed up to *ca.* 5×10^5 V cm^{-1}. With this apparatus, the variation in intensity of the 1577 cm^{-1} band with applied field could be measured (see Table). The results show that at the peak of the band the increase in extinction coefficient varies as the square of the applied field, as shown by the constancy of $(\Delta\epsilon_{max})/E^2$ and as required by the simple theory of the effect:[1] a dipole moment proportional to the field is induced across the molecule and the absorption intensity varies as its square. The induced absorption is not symmetrical about the peak and at 1557 cm^{-1} is negative. This may be due to a small shift of the peak to higher wavenumbers in the field, or by an alteration in band-contour. At present the form of the field-modified band-contour has not been measured accurately, but the increase of the peak wavenumber cannot be more than *ca.* 0·01 cm^{-1} at $3{\cdot}7 \times 10^5$ V cm^{-1}.

To confirm that the observed effect depends, like the Raman effect, on the change of molecular polarisability with normal co-ordinate of the vibrational mode, the neighbouring and comparably weak band at 1766 cm^{-1} was also examined for field-induced intensification. Within the limits of the measurements, no effect was observed; and this is consistent with the fact that this band (which has been identified[3] as the combination band $\nu_1 + \nu_{10}$) is not observed in the Raman spectrum of tetrachloroethylene (see Figure).

Since the 1577 cm^{-1} band, absent from the gas phase spectrum, appears in the liquid spectrum, and is sensitive to an electric field, it is worth considering whether this band can owe its liquid-phase activity entirely to induction by the liquid's own internal field. It is well known that each molecule in a liquid exists in the fluctuating field due to the bond-dipoles of its neighbours. The correlation-time for these fluctuations is long compared to the time for a vibrational transition;[4] and the time-averaged square of the induced dipole, which determines the resulting absorption-intensity, will be non-zero.

Extinction coefficients (ϵ) *in liquid tetrachloroethylene, and changes of extinction coefficient* ($\Delta\epsilon$) *in an electric field* E

Freq. (cm^{-1})	1557	1567	1577 (max)	1587	1597	
ϵ (±0·005)	0·107	0·164	0·252	0·158	0·088	
Field E (V cm^{-1})			$10^4\Delta\epsilon$ at each frequency			$10^{15}\Delta\epsilon_{max}/E^2$
$2{\cdot}7 \times 10^5$			4 ± 0·5			5·5
$3{\cdot}7 \times 10^5$	−6 ± 1	3·5 ± 1	8 ± 0·5	1·5 ± 1	0 ± 1	5·8
$5{\cdot}1 \times 10^5$			14 ± 0·5			5·4

Assuming for simplicity that the component of the r.m.s. internal field acting along the C=C axis of each molecule is

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† A paper describing the apparatus and technique is being prepared, and will be submitted to *J. C. S. Faraday II.*

effectively a constant E_{int}, and that the molecular polarisability in that direction is α, then in the presence of an applied field with which the molecule makes an angle θ, the square of the induced dipole will be:

$$D^2 = \alpha^2(E_{\text{int}} + E_{\text{ext}} \cos \theta)^2$$

By integrating over all molecular orientations, the mean extinction coefficient due to these dipoles is found for this simple model to be proportional to $E_{\text{int}}{}^2$ (zero-field term) + $(E_{\text{ext}}{}^2)/3$ (applied field term). Hence,

$$E_{\text{int}} = (\epsilon/3\Delta\epsilon)^{\frac{1}{2}} \times E_{\text{ext}}$$

Assuming that the zero-field extinction coefficient ϵ_{max} of the 1577 cm^{-1} band in tetrachloroethylene arises from this internal field effect, then the data of the Tabel allow E_{int} to be calculated from the above expression as *ca.* 3·7 × 10^6 V cm^{-1}. A molecule in an electrically stressed dielectric does not, however, experience exactly the applied external field. Using the Onsager expression[5] for the effective applied field in a liquid of dielectric constant 2·4, then E_{int} becomes 4·6 × 10^6 V cm^{-1}. If additional factors (*e.g.* slight reduction of molecular symmetry in the liquid environment) also contribute to the intensity of the band, then this figure represents an upper limit to the effective field along the C=C axis. But since internal fields in liquids are commonly of about this magnitude,[6] it is reasonable that the formally i.r. forbidden band ν_1 of tetrachloroethylene at 1577 cm^{-1} owes its weak activity in the spectrum of the liquid entirely to the internal field.

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