Fourier Transform Spectroscopy in Flavor Analysis. V. Infrared Spectra of Vapors[1]

Manfred J. D. Low,* Howard Mark, and Shie H. Chan

A 3-m, single-pass cell coupled with a Fourier transform spectrometer was used to record infrared spectra at room temperature of the vapors of liquids and solids having low vapor pressure at room temperature. The sample vapor was at ~0.04 atm cm, much lower than is generally used, indicating that the measurements were at least an order of magnitude more sensitive than conventional gas spectra measurements. The technique should be useful for studying heat-sensitive materials and for detecting vapors present at low concentrations.

In recording the infrared (ir) spectrum of a substance which is liquid or solid at room temperature, it is general practice to examine the sample in its condensed state. Vapor ir spectra have seldom been recorded, although with the increased use of combined gas chromatography (gc)–ir techniques, the use of vapor spectra is increasing. Vapor spectra are of obvious utility for the characterization of gc effluents but, as pointed out by Willis (1970), the examination of relatively complex materials in the vapor phase is a most interesting study in its own right which is both of theoretical interest and of practical importance to the industrial spectroscopist.

Ir spectra of the vapors of many high boiling materials can be obtained by placing a liquid or solid in a conventional gas cell and then heating the cell to a temperature which is high enough to raise the vapor pressure of the material to a sufficient extent that a spectrum can be recorded. An alternative approach is to use gc–ir techniques; i.e., the material is vaporized by heating it, eluted from a gas chromatograph, and examined at elevated temperature. However, some low vapor pressure materials are thermally unstable at temperatures needed to produce appreciable vapor pressures. Consequently, if adequate heating is not permitted, the vapor pressure and partial pressure, P, remain low and a dilute sample results. The sample concentration ($\equiv P$) and the amount of sample, PL, where L is the length of the cell, are relatively small. The equivalent condition arises if the vapor of a small quantity of substance—which might be an air pollutant, a perfume, or a sex attractant—is dispersed in a large volume of air. The sample is again dilute, and procedures by which such dilute samples may be concentrated are frequently impractical or not at all feasible because a very small amount of material would have to be removed from a very large volume of air. Thus, PL is again small if conventional gas cells are used. In either of the two cases, P is very small and remains fixed, so that exceedingly great demands would be placed on instrumentation if conventional gas cells were used to examine dilute samples. The obvious way to circumvent this difficulty is to increase PL; because P is fixed, L is increased, and this is done by using a long-path gas cell. The measurement of ir spectra of dilute samples then becomes easier. As such measurements would be useful for a variety of purposes, we have examined the utility of Fourier transform spectroscopy for recording ir spectra of the vapors of some solids and liquids having low vapor pressures at room temperature. Also, to avoid sample contamination, an all-glass cell capable of being evacuated to 10^{-6} Torr was constructed and used.

EXPERIMENTAL SECTION

The cell was a Pyrex tube, 6.0 cm in diameter and 302 cm long, fitted with Hg and oil monometers, as well as Pi-

Department of Chemistry, New York University, New York, New York 10003.
[1] Part IV: Low, 1971.

rani and discharge gauges; KBr windows were attached with epoxy. Two independent, high-volume Hg diffusion pumps, with associated traps and fore pump, produced a vacuum of 10^{-6} Torr. Radiation from a globar source was collimated by an off-axis paraboloid mirror, passed through the interferometer, and, after passing through the cell, was collected by another mirror and focused onto a detector. The regions between the cell ends and the interferometer and the detector were flushed with dry air.

Spectra were recorded with a modified (Low et al., 1972) Digilab, Inc. Model FTS-14 Fourier transform spectrometer system. Initially, a "background" spectrum was recorded, with the sample cell evacuated. That single-beam spectrum was stored in the computer's memory. A sample was then introduced and, after the pressure had been measured, a second single-beam spectrum was recorded and stored. The "background" and "sample" spectra were then ratioed by digital computation to produce a ratioed spectrum. Ordinate- and abscissa-scale expansions were produced by digital computation as required, using the stored spectra.

Most substances were of CP grade. The orange oil was a natural sample from Florida. ABCO (1-azabicyclo[2.2.2]octane), DABCO (1,4-diazabicyclo[2.2.2]octane), and ABCUD (azabicyclo[3.3.3]undecane) were pure solids supplied by Professor A. Halpern of Northeastern University.

EXPERIMENTS AND RESULTS

A variety of samples which were liquids and solids at room temperature and which had very low vapor pressures at room temperature was examined. A small quantity of the material was placed into a tube fitted with a Teflon stopcock and a ball joint. The sample tube was then attached to a small manifold adjoining the long-path cell, cooled with liquid nitrogen, evacuated to remove air, warmed to room temperature, and then opened to the cell so that the vapor of the material passed into the cell. The Teflon stopcock was then closed, and, after the pressure within the cell had been measured, a spectrum was recorded.

Some typical results are shown in Figures 1–7. In general, there was no difficulty in recording spectra of the vapors of pure liquids or solids; e.g., Figures 1–3 show spectra of chloroacetic acid, ABCUD, and ABCO vapor. As the spectral resolution could be readily varied (Low, 1969), spectra were frequently recorded at resolutions better than the 8-cm^{-1} resolution usually applied; this is illustrated by the spectra of ABCO and DABCO (Figures 3–6).

As anticipated, some difficulty was encountered when a complex mixture was examined. It would be expected that some fractionation would occur, and such an effect apparently occurred when an orange oil was examined. The upper trace of Figure 7 shows the spectrum of the vapor obtained from an orange oil. Comparison of that spectrum with the spectrum of the original liquid orange oil (the
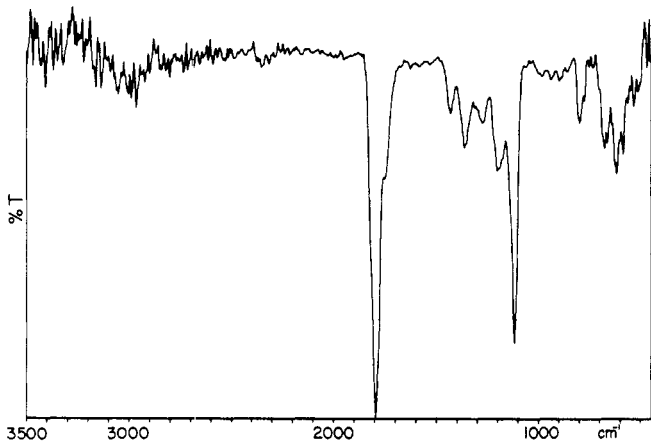
Figure 1. Chloroacetic acid vapor; 0.15 Torr; resolution, 8 cm^{-1}; 500 scans.
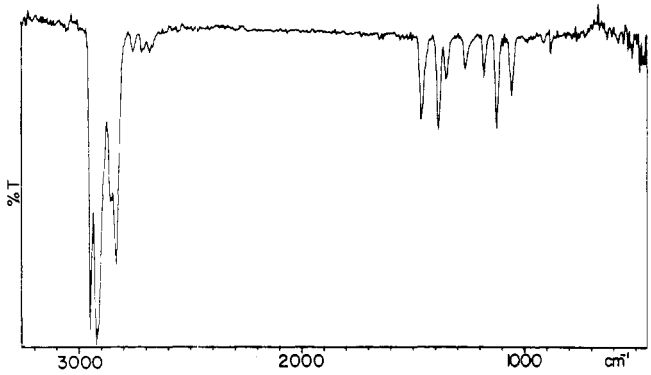

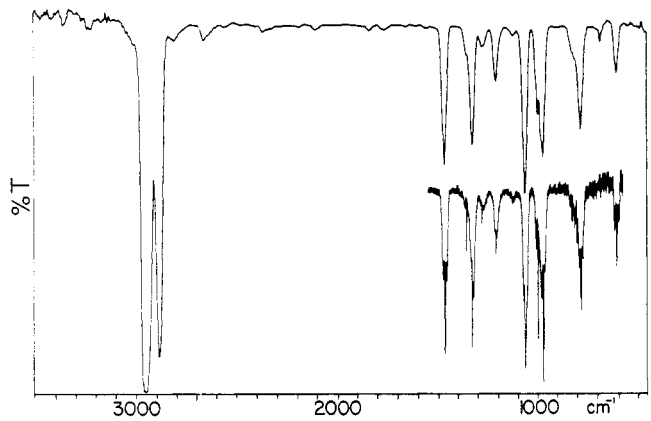**Figure 2.** ABCUD vapor; 0.068 Torr; resolution, 8 cm^{-1}; 500 scans.

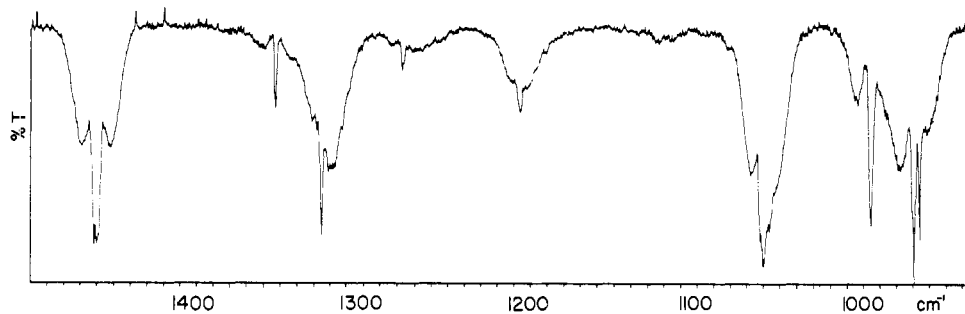**Figure 3.** ABCO vapor; 0.4 Torr; resolution, 8 cm^{-1}; 500 scans; insert: resolution, 0.5 cm^{-1}.
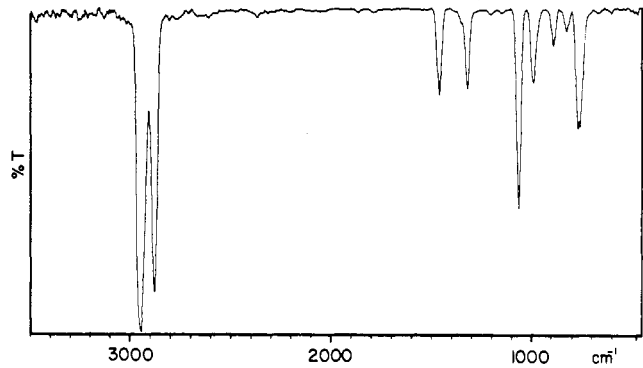

Figure 5. DABCO vapor; 0.3 Torr; resolution, 8 cm^{-1}; 500 scans.
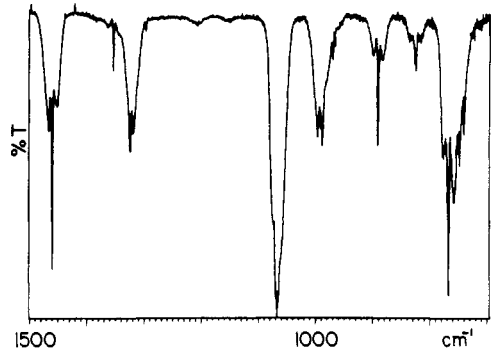

Figure 6. DABCO vapor; 0.3 Torr; resolution, 0.5 cm^{-1}; 2000 scans; abscissa scale expanded segment of spectrum.
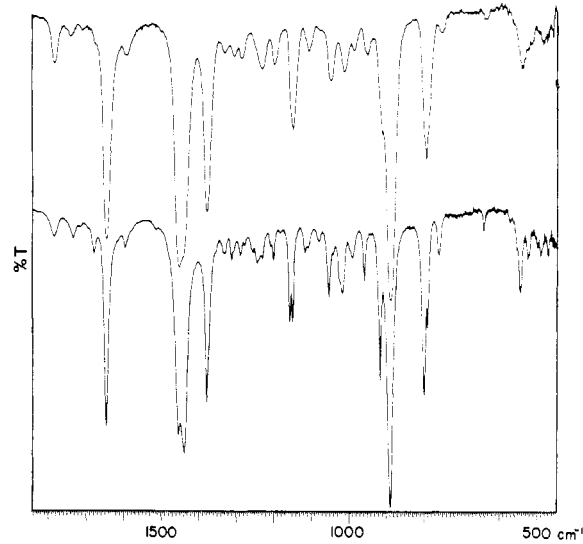

Figure 7. Orange oil: (A, upper) orange oil vapor; 1 Torr; resolution, 2 cm^{-1}; 1000 scans; (B, lower) orange oil liquid; film between KBr flats; resolution, 2 cm^{-1}; 256 scans.

Figure 4. ABCO vapor; 0.4 Torr; resolution, 0.5 cm^{-1}; 500 scans; abscissa scale expanded.

lower trace of Figure 7) shows that there are some significant differences between the spectra; *e.g.*, the intensity ratios of the overlapping bands near 1455 and 1437 cm^{-1} differ, and the small band near 1678 cm^{-1} of the spectrum of the liquid is barely discernible in the spectrum of the vapor. The spectrum of the residual liquid sample was similar to the lower trace of Figure 7; only a small fraction of the original sample had been vaporized.

DISCUSSION

The present results show that good-quality ir spectra of the vapors of liquids and solids having low vapor pressures at room temperature could be readily obtained. The scanning periods were relatively short, so that spectra can be obtained efficiently in terms of both time and expense. (The total time required is the sum of the times needed for scanning, computing, and plotting. The scanning time needed is a function of the resolution and gas pressure, and the plotting time depends on the signal-to-noise ratio and on the width of the spectral region which is plotted out. The total time can thus vary appreciably. Typical periods would be on the order of 10 min for an 8-cm^{-1} spectrum and 70 min for a 0.5-cm^{-1} spectrum.) The question of "sensitivity" then arises. That, however, should be considered from the points of view of sample concentration, the sample amount PL, and the total sample volume (*i.e.*, the total amount of sample present in the gas cell, connecting tubing, gauges, etc.).

With conventional measurements, the conditions which are frequently encountered involve the use of a 10-cm long cell and gas pressures of a few tens to several hundreds of Torr. Welti (1970), for example, in preparing his extensive collection of ir vapor spectra, used a 9.2-cm cell of 25-ml volume with various amounts of sample (frequently 2 μl $\simeq$ 2 mg) at various temperatures up to 200°, so that the partial pressure was ~100 Torr. Such conditions must be compared with the present ones.

In terms of P, the present measurements were carried out at concentrations about three orders of magnitude lower than those conventionally employed. That comparison, however, must be tempered by the realization that the cell length had been increased 30-fold. In terms of PL, conventional measurements are carried out under conditions (*e.g.*, 10-cm cell, $P \simeq 100$ Torr) such that $PL \simeq 1.3$ atm cm. In contrast, in the present work (*e.g.*, 3-m cell, $P \simeq 0.1$ Torr) $PL \simeq 0.04$ atm cm. The sample size expressed as PL was thus appreciably lower, so that the "sensitivity" of the present measurements is at least an order of magnitude better than that of conventional measurements.

A partial pressure of 0.1 Torr is ~100 ppm. It is obvious that the effective path length can be increased by using a multiple-reflection cell so that the gas pressure can be further reduced. At a gas pressure of 10^{-3} Torr, the usable concentration would be near 1 ppm. (This estimate is realistic; we have observed the fundamental band of CO at 4 × 10^{-3} Torr at 0.5-cm^{-1} resolution using the described system.) Further improvements should be obtainable through the use of a cooled detector. The concentrations or amounts detectable will, of course, vary with the extinction coefficients of the substances examined.

The effect of total sample volume is difficult to assess because the shapes of the cell and the ir beam determine how much of the gas present actually interacts with the beam. In the present case, the cell was cylindrical to match the shape of the roughly cylindrical beam, but the latter was ~50 mm in diameter, so that about one-third of the gas present was not examined. Conventional gas cells may be cylindrical, but frequently are shaped into truncated rectangular pyramids to match the beams of dispersion instruments, and again some fraction of the gas within the cell is not examined. With P a fraction of a Torr in the present case, or several tens of Torr with conventional cells, a total sample of about 10^{-5}–10^{-4} mol is needed. The total sample quantity is thus relatively large, and this may lead to some difficulties if only very small amounts of sample are available. It is, however, possible to reduce the cell volume, and consequently the total sample size, by "folding" the ir beam, as is done in commercial multiple-reflection cells.

It thus seems that the present techniques should be useful for examining the vapors of low-volatility materials, particularly heat-sensitive ones, *e.g.*, lactic acid, pyruvic acid, or primary amines, and for detecting and examining gases and vapors present at quite low concentrations. Also, as the measurements can be carried out relatively quickly with suitable sampling optics it should be possible to follow changes in the composition of vapor mixtures, *e.g.*, changes occurring during the vaporization of a complex flavor or perfume mixture.

In general, the use of high resolution for the examination of gases is confined to small molecules; as a rule, the vapor spectra of large molecules are similar to normal liquid or solution spectra and do not exhibit the well-resolved rotational lines found in the spectra of small molecules. The use of resolutions of 8, 4, or 2 cm^{-1} is thus adequate. However, in some cases, the use of better resolution can bring out much more spectral detail (compare Figures 3 and 4, and Figures 5 and 6) which can aid in studying materials having similar structures. The use of high resolutions may thus be advantageous in some cases.

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