INFRARED MICROSPECTROMETRY OF CAPILLARY GAS CHROMATOGRAPHY EFFLUENTS AND OF GAS-PHASE FREE RADICALS

S. BEHRENDT* AND H. RICHTERING

Institut für Physikalische Chemie, Universität Göttingen, Göttingen (Germany)

(Received December 28th, 1965)

The most useful single method of analysis of a volatile covalent substance is by infrared spectrometry. Due to the weakness of the interaction between molecules and infrared quanta, however, the absorption of a measurable fraction of the incident radiation requires sizable samples[1,2]. Samples as small as the vapor bands eluted from capillary columns, or free radicals produced in gases, could, however, be monitored by a microspectrometer which obtains their infrared spectra instead by measuring the effect of infrared radiation on molecular beams of such samples.

DIFFERENTIAL INFRARED MICROSPECTROMETER

A molecular-beam electric-resonance apparatus permits the observation of rotational spectra of polar molecules[3-8]. The spectrum is obtained by plotting the wavelength of the microwave radiation against the resulting molecular-beam intensity at the detector. The substitution of infrared radiation should likewise yield rotation–vibration spectra, since, according to the selection rules, the capture of vibrational energy by a molecule is likely to be accompanied by a rotational transition. A differential infrared microspectrometer, based on this principle, has been discussed[9]. Its sensitivity is limited by the precision with which the intensity of the molecular beam can be measured and by the intensity of the available infrared radiation. An electron bombardment detector can measure an attenuation of 10^{-4} of a molecular beam[10]. Very intense infrared radiation of continuously variable wavelength is emitted continuously by junction diode lasers. Alternatively, thermal radiation combined with a monochromator can be used; the following calculation offers an example involving a minimum emittance required from the radiant heater.

MATHEMATICAL TREATMENT OF INFRARED ABSORPTION BY A BEAM OF HCl MOLECULES

For HCl, the absorption intensities of the separate lines of the fundamental infrared band have been determined experimentally[11]. The following mathematical treatment, which is due to one of us (H.R.), is restricted to the case of diatomic molecules such as HCl.

After the molecular beam passed through the velocity selector and the rotational state selector, all the HCl molecules remaining in it are assumed to have a

---

velocity w and to be in the quantum state with vibrational number $v'' = 0$ and rotational number $J'' = 1$. If infrared radiation from a thermal source is perpendicularly directed at a longitudinal length l of the HCl beam, then the exposure time (τ) of the molecules is given by $\tau = w/l$. Let the wave numbers of the allowed transitions from $v'' = 0$; $J'' = 1$ to $v' = 1$; $J' = 2$ and to $v' = 1$; $J' = 0$ be $\nu_{1,2}$ and $\nu_{1,0}$, respectively. The mean absorption cross-sections $\bar{\sigma}_{1,2}(\Delta\nu)$ and $\bar{\sigma}_{1,0}(\Delta\nu)$ for these transitions are assumed to be constant over an arbitrary width $\Delta\nu$ around both $\nu_{1,2}$ and $\nu_{1,0}$. If $Z(\nu_{1,2}; \Delta\nu)$ and $Z(\nu_{1,0}; \Delta\nu)$ are defined as the numbers of photons, within the same widths $\Delta\nu$ around $\nu_{1,2}$ and $\nu_{1,0}$, which traverse the length l of the molecular beam during the time τ, then the fraction $\Delta n/n$ of irradiated molecules which experience vibrational and thus rotational transitions is:

$$\Delta n/n = Z(\nu_{1,2}; \Delta\nu)\cdot\bar{\sigma}_{1,2}(\Delta\nu) + Z(\nu_{1,0}; \Delta\nu)\cdot\bar{\sigma}_{1,0}(\Delta\nu) \tag{1}$$

Calculation of the numbers of photons $Z(\nu_i; \Delta\nu)$

The following arbitrary numerical values meet the minimum radiation requirement of the differential infrared microspectrometer. Thermal radiation corresponding to the emittance of a surface area of $1\ cm^2$ of a black body at an absolute temperature T is focused on a 2-cm long section of the molecular beam. For HCl molecules with a velocity $w = 500$ m/sec, the exposure time then is $\tau = 4 \times 10^{-5}$ sec. The numbers of photons $Z(\nu_i; \Delta\nu)$ within a width $\Delta\nu = 0.1\ cm^{-1}$ by which the molecules are thus irradiated during the exposure time τ can be evaluated by Planck's radiation laws. Some numerical values resulting for these conditions are listed and specified in Table I.

TABLE I

NUMBERS OF PHOTONS $Z(\nu_i; \Delta\nu)$

Radiation		Black body temperature (°K)		
Wave length (μ)	Wave number (cm^{-1})	2000	3000	4000
3	3333	$92\cdot10^{10}$	$235\cdot10^{10}$	$480\cdot10^{10}$
5	2000	$93\cdot10^{10}$	$186\cdot10^{10}$	$285\cdot10^{10}$
10	1000	$71\cdot10^{10}$	$122\cdot10^{10}$	$174\cdot10^{10}$

Derivation of the absorption cross-sections $\bar{\sigma}_{1,2}(\Delta\nu)$

Let $I^\circ(\nu_{1,2})$ and $I(\nu_{1,2})$ be the radiation intensities at wave number $\nu_{1,2}$ before and after traversing a layer of x centimeters of the absorbing gas. In this gas, let the number of molecules in the quantum state $v'' = 0$; $J'' = 1$ be N_1 per cm^3. Then the absorption cross-section $\sigma_{1,2}$ for the transition from $v'' = 0$; $J'' = 1$ to $v' = 1$; $J' = 2$ is defined by:

$$I(\nu) = I^\circ(\nu)\cdot\exp(-k_\nu\cdot x) = I^\circ(\nu)\cdot\exp(-\sigma_{1,2}\cdot N_1\cdot x) \tag{2}$$

where k_ν is the absorption coefficient. The fraction N_1/N, where N is the total number of molecules per cm^3, is given by the Boltzmann-distribution expression. The ex-

perimentally determined quantity is the integral of the absorption coefficient ($S_{1,2}$), which is given by:

$$S_{1,2} = \int_0^\infty k_\nu \cdot d\nu = N_1 \int_0^\infty \sigma_{1,2} \cdot d\nu \tag{3}$$

for the single rotational line of the fundamental band of $H^{35}Cl$ corresponding to this transition. $S_{1,2}$ is proportional to N, so that $S_{1,2} = S°_{1,2} \cdot N$. For $H^{35}Cl$ the experimental values are $S°_{1,2} = 24 \cdot 10^{-20}$ and $S°_{1,0} = 32 \cdot 10^{-20}$ cm/molecule. Introducing the mean absorption cross-section over the width $\Delta\nu$ by the relation:

$$\bar{\sigma}_{1,2}(\Delta\nu) \cdot \Delta\nu = \int_0^\infty \sigma_{1,2} \cdot d\nu \tag{4}$$

one obtains:

$$\bar{\sigma}_{1,2}(\Delta\nu) = \frac{S°_{1,2} \cdot N}{\Delta\nu \cdot N_1} \tag{5}$$

For $J'' = 1$ and $T = 300°K$, $N/N_1 = 10$. Substituting expression (5) in equation (1), it follows that:

$$\Delta n/n = Z(\nu; \Delta\nu) \cdot \frac{N}{N_1} \cdot \frac{(S°_{1,2} + S°_{1,0})}{\Delta\nu} \tag{6}$$

Selecting the value of $Z(\nu; \Delta\nu)$ for $T = 3000°K$ and $\nu = 3333$ cm^{-1} in Table I, the attenuation of the molecular beam becomes:

$$\Delta n/n = 235 \times 10^{10} \times \frac{10}{1} \cdot \frac{(24 + 32) \times 10^{-20}}{0.1} = 1.3 \times 10^{-4}$$

to which the detector still responds.

INTEGRAL INFRARED MICROSPECTROMETER

Infrared spectra could be obtained with infrared radiation of only moderate intensity by a molecular-beam electric-resonance apparatus using a specialized design of the rotational state selector which is analogous to the Toepler arrangement for schlieren optics[12]. This selector, which is partly shown in Fig. 1, renders an additional rotational state analyzer (as in the differential microspectrometer) unnecessary.

This more sensitive version of the microspectrometer will now be described in some detail. Its major components are the source, the velocity selector, the rotational state selector, and the detector.

The construction of the source of the molecular beam depends on whether stable molecules or free radicals are to be analyzed. For capillary gas chromatography, a bundle of parallel, closely-spaced source canals is employed to conserve material by producing a narrow shower of weak molecular beams. The vapor bands must be eluted at low pressure, so that the mean free path of the molecules exceeds

the length of the canals. For free radicals continuously produced in gases, a source aperture of nearly negligible width, followed by a collimating aperture, is adequate. The resulting beam of molecules and free radicals is passed through an inhomogeneous magnetic field which separates them by deflecting only the latter.

The mechanical velocity selector serves to prevent slow molecules with a high rotational quantum number from overlapping with fast molecules with a low rotational quantum number, which would experience the same deflection in the rotational state selector. In the case of gas chromatography, it also retains the macromolecular vapors from the stationary phase and facilitates selective evacuation of the molecular-beam apparatus by scattering the atoms of the helium used as carrier gas. In the microspectrometer, the mechanical velocity selector must be rapidly adjustable over a velocity range, and hence low inertia and little precision are required. A simpler device than the conventional Fizeau velocity selector, which chops the molecular beam by nine parallel slotted wheels rotating perpendicularly to it, should be used. A satisfactory design could be based on a paddle-wheel, installed between two collimating apertures, whose blades move tangentially in the direction of the molecular beam.

In the electrostatic rotational state selector an intense inhomogeneous electric field with a gradient perpendicular to the molecular beam deflects polar molecules. An asymmetric pair of electrodes suffices to produce a field with which molecules in one particular rotational state can be selected[3,4]. It was found advantageous to add to this field a focusing effect, similar to that of an electrostatic lens, by using electrodes consisting of four parallel metal rods arranged in a square and charged alternately positive and negative[5-8]. The resulting electric quadrupole field is weak near the axis and becomes stronger towards the electrodes outside.
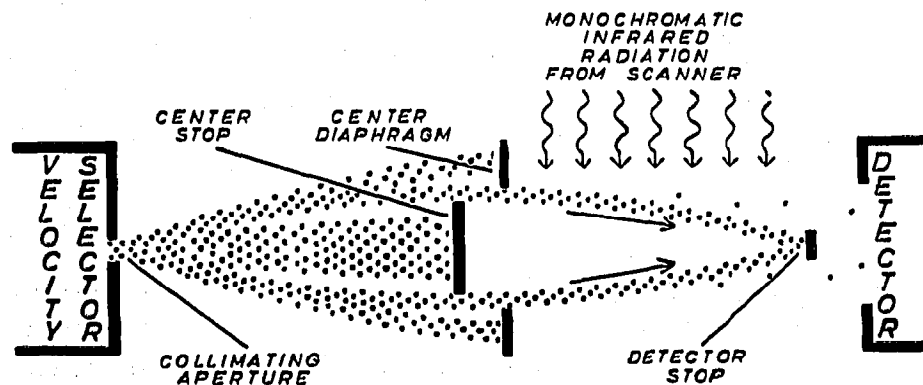

Fig. 1. Illustration of the paths followed by the molecular beam within the rotational state selector of the integral microspectrometer.

Fig. 1 illustrates the effect of the rotational state selector on the molecular beam, which in this case is defined by the collimating aperture together with the stop and the diaphragm that are placed at the center. The four electrodes (not shown in Fig. 1) are kept at such a low electric potential that only molecules in the lowest rotational state are focused; they follow a sigmoid path around the center-stop and fall on the stop placed before the detector. The inhomogeneous electric field acts only on molecules which traverse its gradient by entering it at an aperture angle large enough to prevent their collision with the center-stop. Molecules in higher rotational

states are not deflected sufficiently to avoid colliding with the center-diaphragm. The entire chamber containing this selector and a detector is cooled by liquid nitrogen which prevents the flow of less volatile molecules scattered from the beam and provides additional evacuation by cryogenic pumping.

The molecules in the segment of the molecular beam behind the center-stop and diaphragm do not reach the detector because they impinge on the detector-stop which retains them. This segment of the beam is irradiated by spectrally resolved radiation from a fast-scan infrared source. Molecules which capture photons, experiencing transitions in rotational state and moment of inertia, are not converged on the detector-stop and thus can reach the detector. The plot of wavelength of the infrared radiation *versus* detected molecular-beam intensity gives the spectrum of the beam material.

The combination of velocity selector and rotational state selector will resolve, without preliminary separation, only simple mixtures of free radicals.

The molecular-beam detector must be extremely sensitive to the small fraction of the beam which is analyzed, without responding to residual gases. Usually an electron bombardement detector is employed. It consists of an electron ionizer (adjustable so as not to ionize helium), a simple mass spectrometer such as a quadrupole mass filter[14,13], and finally an electron multiplier which counts positive ions. Its sensitivity is limited by the difficulty of removing positive ions from the electron space charge.

In a photoionization detector as used in gas chromatography[15], molecular beams could be ionized by ultraviolet radiation of very short wavelength without a space charge being created.

A fluorescence detector for beams of molecules absorbing in the near ultraviolet region could be made selective enough to dispense with a mass spectrometer. The molecular beam is irradiated by a collimated beam of ultraviolet radiation and the photons re-emitted in different directions are measured. In a collision-free beam, electronically excited molecules can dissipate their energy only by radiative processes. The residual gas is not excited when the radiation from a discharge lamp is filtered through a cell containing a gas mixture of the same composition.

A proportional detector for beams of not too small organic molecules could be constructed by combining pyrolysis and field ionization as follows. Organic vapors are cracked on tungsten filaments electrically heated to $1500°K$, giving free radicals which are ionized (with extremely low efficiency) by the tungsten surface[16]. By field ionization, organic vapors are quantitatively ionized on the surface of tungsten wires with a diameter of 2.5 microns charged with a positive potential of 15000 V (ref. 17). The detector should hence consist of a network of parallel tungsten filaments, with diameter, temperature and potential as described, together with an electron multiplier. When the molecular beam falls on the incandescent charged tungsten filaments, each organic molecule will give rise to a burst of singly charged fragments. The resulting large pulses of the electron multiplier could easily be distinguished from those due to the residual gas.

The sensitivity of the integral infrared microspectrometer, unlike that of the differential version, depends not only on the intensity of the radiation but also on the intensity of the irradiated segment of the molecular beam. The latter can be evaluated by supposing that at a length of 50 cm from the source, for both selectors, a

molecular beam of $7 \cdot 10^{10}$ molecules/mm²/sec contains $5 \cdot 10^{-4}$ molecules in the lowest quantum state which are converged 300-fold by the quadrupole field. If 1 % of the sample consists of the molecules or free radicals to be analyzed, some 10^8 of them per sec will be focused on a detector-stop with a surface area of 1 mm². Under the conditions of the above mathematical treatment of a beam of HCl molecules, 10^{-4} of them would capture photons, leaving a beam of 10^4 molecules or free radicals per sec to reach the detector. An electron bombardment detector can measure a molecular beam with a sensitivity of 2.5 % of the molecules[18]. In the chamber cooled by liquid nitrogen, which is evacuated by a mercury diffusion pump, there will be no interfering background of organic molecules.

Up to here it was assumed that the rotational state of a molecule which captures an infrared quantum is changed, permanently. However, a transition such as from $v'' = 0$; $J'' = 1$ to $v' = 1$; $J' = 1$ involves a change, not in rotational state but in moment of inertia of the molecule, which will thus also be discriminated by the molecular-beam electric-resonance apparatus. The lifetimes of most of the excited molecules suffice for their discrimination, and only a part of those molecules which re-emit their vibrational energy too early will return to their original rotational state.

The theory of electrostatic focusing of polar molecules has only been worked out in detail for diatomic molecules. Polyatomic molecules are also deflected by an inhomogeneous electric field, but their rotational states lie much closer together. The selector will hence converge on the detector-stop polyatomic molecules in the lowest group of rotational states which will overlap due to the comparatively low resolution attainable at present.

APPENDIX: DEFINITION AND UNITS OF SYMBOLS

$I°(\nu)$, $I(\nu)$	= radiation intensities at wave number ν before and after traversing a layer x of absorbing gas, respectively, arbitrary units
k_ν	= absorption coefficient at wave number ν, cm^{-1}
l	= length of molecular beam which is irradiated, cm
N	= number of molecules per unit volume, cm^{-3}
N_1	= number of molecules per unit volume, which are in a specified quantum state, cm^{-3}
n	= number of molecules irradiated by the $Z(\nu; \Delta\nu)$ photons, no units
Δn	= number of molecules which experience rotational transitions, no units
$S_{1,2}$	= integral over absorption coefficient for rotational line corresponding to the transition $J'' = 1 \rightarrow J' = 2$ as defined by equation 3, cm^{-2}
$S°_{1,2}$	= $S_{1,2}$ per number of molecules per unit volume N, cm
T	= absolute temperature, °K
v''; J''	= vibrational and rotational quantum number in the lower energy level, no units
v'; J'	= the same quantum numbers in the upper energy level, no units
w	= velocity of molecules in the beam, cm·sec^{-1}
x	= thickness of the layer of irradiated absorbing gas, cm
$Z(\nu; \Delta\nu)$	= number of photons emitted per cm² of black body within a width $\Delta\nu$ around ν in time τ, no units
μ	= wavelength, microns

ν = wave number, with subscripts referring to rotational quantum numbers, cm^{-1}

$\Delta\nu$ = arbitrary narrow width around the wave number ν, cm^{-1}

σ = absorption cross-section, with subscripts referring to rotational quantum numbers, cm^2

τ = time necessary for molecules to travel through the length l of the beam, sec

SUMMARY

Infrared spectra of samples, too small for conventional spectrometry which measures the effect of the sample on radiation, could instead be obtained by measuring the effect of radiation on the sample. The sample is passed through a proposed infrared microspectrometer in which it is converted into a molecular beam and irradiated. The sensitivity of the microspectrometer depends on the intensity of the available infrared radiation and on the intensity of the detected molecular-beam. The effect of the radiation intensity is calculated for one example, and new detectors for beams of organic molecules are suggested.

REFERENCES

1 P. A. WILKS AND R. A. BROWN, Anal. Chem., 36 (1964) 1896.
2 K. C. HERR AND G. C. PIMENTEL, Appl. Opt., 4 (1) (1965) 25.
3 R. O. CARLSON, C. A. LEE AND B. P. FABRICAND, Phys. Rev., 85 (1952) 784.
4 C. A. LEE, R. O. CARLSON, B. P. FABRICAND AND I. I. RABI, Bull. Am. Phys. Soc., 27 (1) (1952) 32; Phys. Rev., 86 (1952) 607.
5 J. P. GORDON, H. J. ZEIGER AND C. H. TOWNES, Phys. Rev., 95 (1954) 282.
6 H. G. BENNEWITZ, W. PAUL AND CH. SCHLIER, Z. Physik, 141 (1955) 6.
7 CH. SCHLIER, Z. Physik, 147 (1957) 600.
8 J. P. TOENNIES, H. G. BENNEWITZ AND K. H. KRAMER, Discussions Faraday Soc., 33 (1962) 96.
9 S. BEHRENDT, Nature, 201 (1964) 70.
10 W. ABERTH, Rev. Sci. Instr., 34 (1963) 928.
11 W. S. BENEDICT, R. HERMAN, G. E. MOORE AND S. SILVERMAN, Can. J. Phys., 34 (1956) 850.
12 S. BEHRENDT, Dr.-Thesis, Göttingen University, 1964.
13 J. MARTELLY, Compt. Rend. Acad. Sci. (Paris), 215 (1942) 106.
14 W. PAUL AND H. STEINWEDEL, Z. Naturforsch., 8a (1953) 448.
15 D. C. LOCKE AND C. E. MELOAN, Anal. Chem., 37 (1965) 389.
16 W. SCHÜRLE, Diplom-Thesis. Bonn University, 1964.
17 H. D. BECKEY, Z. Anal. Chem., 197 (1963) 80.
18 R. WEISS, Rev. Sci. Instr., 32 (1961) 397.