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Exact Mass Measurement in the Absence of Calibrant by Fourier Transform Mass Spectrometry

Robert L. White, Emmanuel C. Onyiriuka, and Charles L. Wilkins*

Department of Chemistry, University of California—Riverside, Riverside, California 92521

Exact mass measurements with accuracy in the low parts-per-million range, suitable for elemental composition assignments, are obtained by Fourier transform mass spectrometry (FTMS) in the absence of calibration compound. It is determined that good results are obtained when measurements are made under the same conditions as was a calibrant and somewhat poorer results are obtained when other conditions are chosen and measurements are "corrected". The effects of both magnetic and electric field instabilities on mass measurement accuracy are considered and examples of accurate mass measurements yielding elemental composition assignments for unknown samples are presented.

In many cases, structure elucidation of unknown materials is facilitated by making accurate mass measurements of mass spectral fragment ions. If mass measurement accuracy of 5–10 ppm or better is obtained, elemental compositions of fragment ions can usually be determined or, at the very least, the number of compositions which need to be considered can be drastically reduced. Traditionally, such measurements are made relative to a calibration compound which is also present in the ion source and for which elemental compositions of mass spectral peaks have previously been determined. Obviously, this method introduces "chemical noise" and can interfere with mass assignments for low abundance ions or those coinciding in composition with calibrant ions. Thus, the ability to obtain highly accurate mass measurements at high resolving power in the *absence of calibrant* would be a significant improvement for both batch and gas chromatographic sample introduction modes. In this paper, it will be shown that Fourier transform mass spectrometry (FTMS) can yield mass measurements of sufficient accuracy to permit elemental composition assignments of fragment ions without simultaneously measuring calibrant peaks.

Early in the development of FTMS, Comisarow and Marshall pointed out that mass calibration of FTMS spectra could be relatively straightforward because the physical measurement of frequency can be extremely accurate by using available instrumentation (*1*). Subsequently (*2–5*), a mathematical relationship (eq 1) between ion cyclotron resonance frequency and mass was derived and used for exact mass measurements of fragment ions relative to calibrant peaks. The constants (*A*, *B*, *C*) in the calibration equation were determined by specifying three exact mass-frequency pairs derived from calibrant mass spectral peaks. By accurately measuring the ion cyclotron resonant frequency of an unknown ion, the exact mass of that ion was calculated by using the calibration expression and solving for m_i. This procedure has been used over a 156 amu mass range with an average measurement error of 5 ppm.

$$m_i^2 f_i^2 = A m_i^2 + B m_i + C \qquad (1)$$

To date, FTMS exact mass measurements have been limited to *relative* rather than *absolute* measurements. Presumably, this is due to the inability to correct for ion space charge effects. It has been shown that the magnitude of ion space charge is dependent on the total number of ions trapped in the analyzer cell and that changes in ion space charge produce cyclotron frequency shifts similar in magnitude to those resulting from small changes in trapping potential (*2*). We describe here a simple means of estimating the total number of positive ions produced by electron bombardment of gas-phase molecules in an FTMS cell. With this estimate, ion cyclotron resonance frequencies from various substances can be measured sequentially under identical ion space charge conditions. When this procedure is employed, it becomes possible to calibrate the FTMS under a "standard" set of conditions, pump away the calibration compound, and measure fragment ion exact masses in the absence of calibrant. Alternatively, "nonstandard" conditions may be employed and ion cyclotron resonance frequencies could be empirically "corrected" for the change in ion space charge field.

THEORY

Mass measurement accuracy in FTMS is dependent on controlling or accurately measuring three independent variables: magnetic field intensity, trapping potential, and ion space charge. Trapping potentials can easily be controlled to within a millivolt. Superconducting magnets provide a means of achieving constant and uniform magnetic field strengths. Ion space charge effects depend on the total number of charges trapped in the FTMS analyzer cell.

For meaningful exact mass measurements without calibrant, the number of ions trapped in the cell during each pulse sequence should be known. An estimate of the total positive charge produced by electron impact can be made without analyzer cell modification if an ionization gauge is used for vacuum chamber pressure measurement.

At a fixed ionizing potential, the instantaneous positive ion current (I_+) produced by an electron beam passing through gaseous molecules can be represented by (*6*)

$$I_+ = Q_i I_e d N \qquad (2)$$

where Q_i is the ionization cross section of the gaseous molecules at the specified ionizing potential, I_e is the instantaneous electron emission current, d is the distance that ionizing electrons travel, and N is the concentration of gas-phase neutrals in the vicinity of the electron beam. For a pulsed electron beam such as employed in FTMS, the quantity of positive charge produced during a single beam pulse or duration t_B can be given by the integral

$$\int_0^{t_B} I_+ \, dt = Q_i d N \int_0^{t_B} I_e \, dt \qquad (3)$$

The number of ions produced (n_+) thus becomes

$$n_+ = \frac{Q_i d N I_e t_B}{z} \qquad (4)$$

where z is the charge on a single ion. Employing the ideal gas law, the substitution, $N = P/kT$ can be used to obtain

$$n_+ = \frac{Q_i d P I_e t_B}{zkT} \qquad (5)$$

in which P is the total pressure, T is the temperature of the

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Table I. Mass Calibration Results with 1,1,2,2-Tetrachloroethane and H_2O

ion	freq, kHz	exact mass, amu	calcd mass, amu	error,[a] ppm
H_2O^+	1618.60	18.010 56	18.010 57	0.3
$CH^{35}Cl_2^+$	351.191 24	82.945 50	82.945 46	−0.3
$CH^{35}Cl^{37}Cl^+$	342.926 79	84.942 57	84.942 46	−1.3
$C_2H_2{}^{35}Cl_2{}^{37}Cl^+$	219.026 91	132.919 25	132.919 57	2.4
$C_2H_2{}^{35}Cl_4^+$	175.429 29	165.891 05	165.890 86	−1.1

[a] Calibration error was calculated as the difference in calibration points from the best fit calibration equation.

gas-phase neutrals, and k is the Boltzmann constant. The total pressure of the vacuum system can be measured with an ionization gauge if the ionization cross section of the gas-phase molecules is known (ionization gauges are usually calibrated for nitrogen)

$$P = P_{\text{gauge}} \frac{Q_i(N_2)}{Q_i} \tag{6}$$

where P_{gauge} is the observed pressure gauge reading and $Q_i\ (N_2)$ is the ionization cross section for nitrogen gas. Substitution of eq 6 into eq 5 yields

$$n_+ = \frac{dP_{\text{gauge}} I_e t_B Q_i(N_2)}{zkT} \tag{7}$$

By specifying the analyzer cell geometry (0.0254 m^3 in this case) and assuming that only singly charged particles are formed, eq 7 can be simplified

$$n_+ = KP_{\text{gauge}} I_e t_B \tag{8}$$

where $K = dQ_i(N_2)/zkT$ and temperature was chosen to be constant. Experimentally, eq 8 implies that an uncalibrated ionization gauge reading can be related to the total number of positive ions formed by electron bombardment regardless of the identity of the substance introduced into the vacuum system. Theoretically, eq 8 could be used to "adjust" exact mass measurements made under various operating conditions to standard (calibrant) conditions. However, eq 8 will be valid only under conditions when the number of trapped ions is a constant proportion of the total number of ions formed. The results presented in this paper indicate that this condition is satisfied for normal FTMS measurements.

EXPERIMENTAL SECTION

The FTMS used for the experiments described here was a Nicolet FT/MS-1000 equipped with a 1.9-T superconducting magnet, 0.0254 m^3 analyzer cell, and a dual gas/liquid heated inlet system. All chemicals were reagent grade quality and were not further purified. Samples were subjected to two freeze–thaw cycles prior to admission to the FTMS vacuum system. Pressure measurements were made with a Granville-Phillips Series 280 ion gauge controller. Instantaneous electron beam emission current was monitored by measuring the voltage drop across the 1 MΩ input of a Tektronix Model 475 oscilloscope, generated by the current from the analyzer cell collector plate. The electron beam pulse duration was controlled by the FTMS Nicolet 1280 minicomputer.

Mass calibration was accomplished at high resolving power (ca. 10 000 fwhh) by monitoring a 6-kHz frequency window centered on the cyclotron frequency of the selected calibrant ion. Using the heterodyne mode and zero filling, it was possible to produce well-defined (20–30 data points per peak) frequency peaks. The centroid of each peak was taken as the cyclotron resonant frequency. Unknown ion cyclotron frequencies were measured in the same manner. Typical mass calibration conditions were 1.0×10^{-7} torr calibrant pressure (uncalibrated ion gauge reading), 10 ms electron beam duration, 100 nA instantaneous emission current, and 1.0 V trapping potential.

RESULTS AND DISCUSSION

For reproducible exact mass assignments, it is crucial that instabilities in magnetic field intensity and trapping potential do not severely limit exact mass measurement accuracy. Therefore, before examining the effects of ion space charge on cyclotron resonance frequency, it is worthwhile to determine the measurement error introduced by the inherent instability of trapping potential and magnetic field strength.

Trapping Potential Stability. A study of the variation of trapping potential with time revealed that the voltage applied to the trap plates could be regulated to within 1 mV over a period of days. These measurements were made with a digital voltmeter at a precision of about ±0.2 mV. The effect of small trapping potential changes on ion cyclotron frequency was investigated by varying this potential and observing the change in resonant frequency for the I^+ fragment ion from CH_3I. The slope of the least-squares straight line through a plot of cyclotron frequency vs. trapping potential was calculated to be −0.1072 Hz/mV. This corresponds to a maximum frequency shift of 1 ppm at m/z 270. Because of the inverse relationship between resonant frequency and mass, the relative error resulting from trapping potential instability increases with increasing mass and, at m/z 1354, could be as much as 5 ppm. Clearly, it is necessary to accurately and precisely measure trapping potential when determining exact masses of high mass ions. However, for masses below m/z 200, the measurement error introduced by trapping potential instability is insignificant (<1 ppm) and can be neglected.

Magnetic Field Stability. Superconducting magnets can be employed to minimize magnetic field fluctuations. The Oxford superconducting magnet supplied with the FT/MS-1000 is specified to lose no more than 0.1% of its magnetic field intensity annually. Assuming a constant rate of decay, a maximum rate of decrease in cyclotron frequency can be calculated to be 0.79 Hz per day. At this rate of field decay, a 1 ppm error at m/z 37 would be observed after a single day. The magnetic field decay for the FT/MS-1000 in our laboratory must be much lower than 0.1/year as evidenced by the fact that the m/z 166 ion from 1,1,2,2-tetrachloroethane was reproducibly measured over a 6-day interval with a variability of only 1 ppm. If this deviation were due to magnetic field decay alone, the rate of field decay would be 0.006% annually.

The studies of magnetic field and trapping potential instabilities indicate that routine exact mass measurements of masses below m/z 200 should be possible and that mass calibrations should be valid for at least 1 week. However, at high masses, the effects of magnetic and electric field instabilities will be important and should be considered.

Exact Mass Measurement Accuracy. The accuracy of exact mass measurement was evaluated for a variety of compounds based on a mass calibration derived from four 1,1,2,2-tetrachloroethane fragments (m/z 83, 85, 133, 166) and background water (m/z 18) at a total pressure of 1.0×10^{-7} torr (uncalibrated ion gauge reading). The results of the mass calibration are given in Table I. The calibration error represents the difference in actual exact mass and back-calculated exact mass for each ion based on the best curve through the calibration data. The average calibration error was 1.1 ppm with the largest deviation being 2.4 ppm. The results of 31 exact mass measurements for various fragment ions from several compounds based on the calibration in Table I are compiled in Table II. Each compound was measured under the same FTMS operating conditions as was the calibrant,

Table II. Exact Mass Measurement for a Variety of Compounds Based on the Calibration in Table I[a]

compound	calcd mass	error, ppm		possible composition								
				C	H	O	N	^{35}Cl	^{37}Cl	^{79}Br	^{81}Br	I
p-chlorotoluene	91.053 94	9.2	*[b]	7	7	-	-	-	-	-	-	-
	126.023 33	2.4	*	7	7	-	-	1	-	-	-	-
			*	-	5	-	6	-	1	-	-	-
acetone	58.041 27	10.3	*	3	6	1	-	-	-	-	-	-
				-	9	-	1	1	-	-	-	-
	15.023 53	3.3	*	1	3	-	-	-	-	-	-	-
	43.018 51	2.8	*	2	3	1	-	-	-	-	-	-
methyl iodide	141.928 61	4.7		2	-	2	1	1	1	-	-	-
				-	3	-	2	-	3	-	-	-
			*	3	3	-	-	-	-	-	-	1
	126.904 44	0.2	*	-	-	-	-	-	-	-	-	1
	15.023 57	6.0	*	1	3	-	-	-	-	-	-	-
xylenes	106.078 05	1.9	*	8	10	-	-	-	-	-	-	-
	91.054 53	2.7	*	7	7	-	-	-	-	-	-	-
	77.039 11	0.2	*	6	5	-	-	-	-	-	-	-
octane	114.141 07	1.8	*	8	18	-	-	-	-	-	-	-
	85.102 24	6.0	*	6	13	-	-	-	-	-	-	-
	57.070 96	8.8	*	4	9	-	-	-	-	-	-	-
	43.055 10	7.0	*	3	7	-	-	-	-	-	-	-
N,*N*-diisopropylethylamine	129.150 91	6.5	*	8	19	-	1	-	-	-	-	-
	114.127 85	3.5	*	7	16	-	1	-	-	-	-	-
	72.081 52	2.8	*	4	10	-	1	-	-	-	-	-
bromobenzene	155.957 26	1.7		1	1	5	2	1	-	-	-	-
			*	6	5	-	-	-	-	1	-	-
	157.955 69	1.0	*	6	5	-	-	-	-	-	1	-
	77.039 22	1.3	*	6	5	-	-	-	-	-	-	-
2-pentanol	45.034 40	8.0	*	2	5	1	-	-	-	-	-	-
	43.018 80	9.5	*	2	3	1	-	-	-	-	-	-
	43.055 25	11.0	*	3	7	-	-	-	-	-	-	-
heptanal	43.018 75	8.4	*	2	3	1	-	-	-	-	-	-
	43.055 20	10.0	*	3	7	-	-	-	-	-	-	-
	70.078 94	9.9	*	5	10	-	-	-	-	-	-	-
	44.026 82	13.6	*	2	4	1	-	-	-	-	-	-
	81.071 47	13.0	*	6	9	-	-	-	-	-	-	-
	55.055 23	8.4	*	4	7	-	-	-	-	-	-	-
	57.034 69	11.4	*	3	5	1	-	-	-	-	-	-
				-	8	-	1	1	-	-	-	-

[a] All measurements were performed in the absence of calibrant. [b] * actual composition.

but in the absence of calibrant. A maximum error of 13.6 ppm was obtained for the m/z 44 peak of heptanal and the average measurement error for all 31 fragment ions was 6.0 ppm. For masses above 100 amu, the average error was 2.6 ppm. If all fragment ions are considered to be combinations of C, H, O, N, ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br, and I, the accuracy of these measurements is sufficient to unambiguously assign elemental compositions for 26 of the 31 ions. For the other five measurements, the possible elemental compositions for the given error range consisted of the true assignment and a few unreasonable compositions. For example, measurement of the m/z 58 ion from acetone with an accuracy of 10.3 ppm reduces the possible elemental compositions to $C_3H_6O^+$ (actual composition) or $H_9N^{35}Cl$.

To evaluate the effect of changing the number of trapped ions on cyclotron resonance frequency, we monitored five different fragment ions (m/z 18, 43, 117, 210, 355) as a function of electron beam duration. The observed changes in cyclotron resonance frequency for each of these fragments attributed to variations in space charge field was found to be constant to within 2%. It seems that all cyclotron resonance frequencies are perturbed by the same amount when the total number of trapped ions is varied. Therefore, if space charge effects on cyclotron reasonance frequency are well-known, fragment ion exact masses could be corrected for these effects when data are obtained under conditions other than calibrant conditions.

The results presented in Table II were obtained by measuring fragment ion cyclotron resonance frequencies under exactly the same operating conditions as the calibrant. However, as mentioned above, it should be possible to vary pressure, electron emission current, or electron beam pulse duration and then correct the measured frequencies for these changes (eq 8). As a test of this hypothesis, the resonant frequency of the I^+ fragment ion in the electron impact mass spectrum of CH_3I was measured under several different combinations of the three parameters and the frequency change from standard (calibrant) conditions was calculated. A least-squares straight line fit of frequency change as a function of number of ions formed resulted in a calculated slope of -9.75×10^{-4} Hz/ion formed. The pressure gauge reading for this series of measurements was varied from 5.0×10^{-8} torr to 2.5×10^{-7} torr; emission current was adjusted between 100 and 500 nA; and the electron beam duration was varied from 2.5 ms to 10 ms. Combinations of these parameters resulted in calculated total number of formed ions of between 3000 and 70 000. The difference in the measured frequency change and the least-squares calculated frequency change due to a calculated change in the number of ions was used to predict the accuracy with which deviations from standard (calibrant) measurement conditions could be corrected. On the basis of 24 measurements at different conditions, an average back-calculation error of 11.5 ppm was obtained. Although this is roughly twice the error obtained

Table III. Mass Calibration Results with Tris(perfluoroheptyl)-*s*-triazine

ion	freq, kHz	exact mass, amu	calcd mass, amu	error,[a] ppm
CF_3^+	422.463 85	68.995 21	68.995 13	−1.0
$C_{12}F_{15}N_3^+$	61.769 51	470.985 27	470.986 85	3.3
$C_{18}F_{32}N_3^+$	33.533 13	865.958 12	865.954 72	−3.9
$C_{24}F_{44}N_3^+$	24.869 83	1165.938 95	1165.940 85	1.6

[a] Calibration error was calculated as the difference in calibration points from the best fit calibration equation.

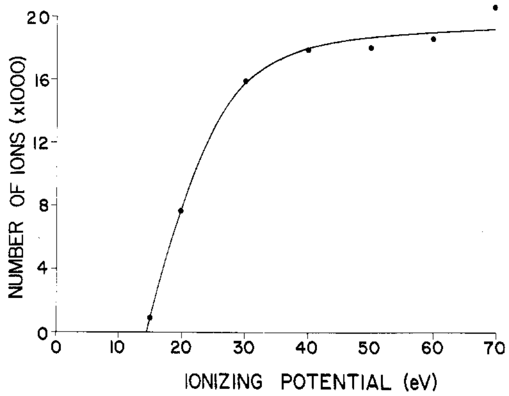


Figure 1. Effect of ionizing electron beam voltage on the calculated number of ions.

when measurements were made under "calibrant conditions", measurements of such accuracy could significantly reduce the number of possible elemental compositions for fragment ions below *m/z* 200.

Further investigations of the effect of FTMS operating conditions on cyclotron resonance frequency indicated that the total number of ions formed by electron beam ionizing voltages between 40 and 60 eV was essentially constant, even though the relative number of fragment ions may change slightly. Below 40 eV, however, the total number of ions formed was found to drop rapidly with decreasing beam voltage (Figure 1). As a result, mass calibrations performed by using ionizing voltages less than 40 eV were expected to be highly variable and were not used in this work.

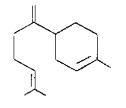
As a test of the ability to measure exact masses for ions of greater mass than those in Table II, tris(perfluoroheptyl)-*s*-triazine was used as a mass calibrant over a 1100 amu mass range. The results of mass calibration by using this compound are given in Table III. Extending the calibration to higher masses resulted in slightly increased calibration error as is evident from a comparison of Tables I and III. With this calibration, 10 arbitrarily chosen peaks in the mass spectrum of PFK were measured in the absence of calibrant. The results of these measurements are presented in Table IV. The measured masses extended from *m/z* 69 to *m/z* 331 and an average measurement error of 9.2 ppm was calculated, with the maximum deviation being 15 ppm at *m/z* 181.

Application of Exact Mass Measurement. During the course of the studies described in this paper, two exact mass measurement applications to unknown sample analyses were performed. One application was the determination of the elemental compositions of two substances extracted from termite soldiers. Each of these substances produced what was believed to be a molecular ion at *m/z* 204. With a previously derived PFK calibration spanning the range *m/z* 69 to *m/z* 331, the exact masses of the two substances were each calculated to be 204.1863. Assuming a mass measurement error of 25 ppm (twice that of the maximum error in Table II), nine elemental compositions are possible if only the elements C, H, O, and N are considered. All but one of these combinations contain both oxygen and nitrogen atoms. However, it was known that neither of the samples contained nitrogen, so that the only possible elemental composition was $C_{15}H_{24}$. This composition was consistent with mass spectral fragmentation patterns and NMR results. On the basis of these measurements and other studies, the two substances were determined to be β-bisabolene (structure A) and (*Z*)-α_2-bisabolene (structure B) (7). Because $C_{15}H_{24}$ was indeed the correct elemental composition assignment, the actual mass measurement error was only 7 ppm. Therefore, the 25 ppm error assumption represented a gross underestimate of the exact mass measurement capability of the FTMS intrument for this analysis.

Table IV. Exact Mass Measurement of Some PFK Fragments Based on the Calibration in Table III[a]

ion	exact mass, amu	measd mass, amu	error, ppm
CF_3^+	68.995 21	68.995 63	6.0
$C_2F_4^+$	99.993 61	99.994 10	4.9
$C_2F_5^+$	118.992 01	118.993 44	12.0
$C_3F_5^+$	130.992 01	130.993 28	9.7
$C_3F_7^+$	168.988 82	168.991 25	14.0
$C_4F_7^+$	180.988 82	180.991 56	15.0
$C_5F_9^+$	230.985 63	230.988 21	11.0
$C_6F_9^+$	242.985 63	242.988 35	11.0
$C_5F_{11}^+$	268.982 43	268.984 53	7.8
$C_7F_{13}^+$	330.979 24	330.979 30	0.2
		av	9.2

[a] All measurements were performed in the absence of calibrant.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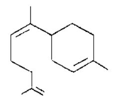
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As a second application of FTMS high-resolution accurate mass measurement, the identities of the *m/z* 45 and *m/z* 47 ions in the mass spectra of $(CH_3O)_2CH_2$ and $HO(CH_2)_2OCH_3$ were determined. Low-resolution mass analysis of these isomers showed that the base peak in both instances was *m/z* 45 and *m/z* 47 was a low intensity fragment (ca. 5% of the base peak). The exact mass measurements of these ions were based on the same PFK calibration used for the termite-derived substances but 2 days after calibration. For both isomers, the *m/z* 45 fragment ion was determined to have the composition of C_2H_5O (probably $CH_3O^+{=}CH_2$) and the *m/z* 47 ion that of C_2H_7O (probably $(CH_3)_2OH^+$). In each instance a rearrangement is necessary to form *m/z* 47 while the base peak (*m/z* 45) could be formed by simple cleavage. In all four of these exact mass measurements, the observed exact mass was within 0.002 amu of the calculated exact mass.

CONCLUSIONS

All of the mass measurements reported in this work were accomplished in the absence of calibrant but based on a previous mass calibration. In general, mass measurements were found to be most accurate at higher cyclotron resonance frequencies (lower mass). With an increase in the FTMS magnetic field strength, it would be expected that highly accurate mass measurement capabilities could be extended to higher masses. In future work, we intend to test this premise by carrying out similar studies for molecules with masses above 1000 amu under higher magnetic field conditions.

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Photoacoustic Cell for Fourier Transform Infrared Spectrometry of Surface Species

John B. Kinney[1] **and Ralph H. Staley***[1]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

A photoacoustic cell designed for chemical studies is described which incorporates temperature and atmosphere control. The design utilizes a Helmholtz resonance to enhance sensitivity over a broad acoustic frequency range for use with Fourier transform infrared (FTIR) instrumentation. The effective efficiency at resonance is 90 Pa/W. Fourier transform infrared spectrometry with photoacoustic detection is demonstrated as a useful technique for obtaining mid-infrared spectra of surface species. Examples are given of molecules on silica powder and supported metal catalysts. The quantitative dependence of signal intensity on various factors is discussed.

Photoacoustic spectroscopy (PAS) has, in recent years, been developed into a useful technique for the study of the optical and thermal properties of solids (*1, 2*). Most of the work done with PAS has been in the ultraviolet–visible region of the spectrum. This is primarily because PAS requires a moderately intense light source. Extension of PAS into the mid-infrared region has been difficult due to the absence of widely tunable infrared light sources with sufficient power to make PAS a practical technique for obtaining mid-infrared spectra. Fourier transform infrared (FTIR) spectrometry with photoacoustic detection has recently been demonstrated as a useful technique for obtaining mid-infrared spectra (4000–500 cm^{-1}) of solids (*3–6*). The advantages inherent in Fourier transform techniques more than compensate for the low light intensity of the glow-bar source used in these instruments. The combination of FTIR with PAS makes it possible to obtain infrared spectra of solids with the convenience of PAS. In particular, essentially no sample preparation is necessary.

The properties of PAS make it a potentially valuable tool for the study of surface species. This capability has been demonstrated in both the ultraviolet–visible–near-infrared (*7–9*) and mid-infrared (*10, 11*) regions by using conventional PAS. In this paper, we demonstrate the utility of FTPAS for obtaining mid-infrared absorption spectra of surface species.

Even with the signal-to-noise enhancement of Fourier transform techniques, study of flat surfaces is not practicable. It is essential to have a sample with a moderate surface area, $>1\ \mathrm{m}^2/\mathrm{g}$, with higher surface areas desirable. Powder samples generally provide adequate surface areas. The powders used in these experiments generally have high surface areas, 10–100 m^2/g. Examples are given of spectra of surface species on two types of surfaces, oxide powders and supported-metal powders. The oxide powder used here is a high-surface-area silica powder. The supported-metal powders are commercially available catalysts with a loading of about 5% metal on the alumina.

It is useful to understand the relationship between the photoacoustic signal strength for surface absorptions and the amount of light absorbed. In conventional transmission spectrometry, Beer's law states that $A = abc$, where A is absorbance, a is absorptivity, b is the path length through the sample, and c is concentration. For a solid sample this may be rewritten as $A = \beta b$ where β is the optical absorption coefficient. Theoretical analysis of the photoacoustic signal generated by a one-dimensional system shows that the signal intensity depends on a number of parameters in a complicated expression (*12–14*). Fortunately, it is often possible to make approximations that greatly simplify the final expression. Three parameters that are important in making approximations in the theoretical expression are β, b, and μ_s, the thermal diffusion length of the sample. For a monolayer of molecules on a surface, only a small fraction of the light is absorbed in a single pass through the surface layer, indicating that the

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[1] Current address: Central Research and Development, E. I. du Pont de Nemours and Co., Experimental Station, E356, Wilmington, DE 19898.

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