Determination of Thermodynamic Functions from Absolute Intensity Measurements in Microwave Spectroscopy[1a]

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Abstract: A technique has been developed for measuring the absolute intensities of rotational spectral lines in the microwave region in which the spectrometer gain is calibrated by intensity measurement of a reference substance, in this case SO_2. The measurement of the peak height and the half-width of a rotational line of a sample of a pure substance determines the number of molecules per unit volume in the lower level involved in the transition. From this quantity and the pressure, the internal partition function and the free energy function of the substance are obtained. The method has been applied to the determination of the gas state free energy functions at room temperature of several representative molecules: difluoromethane, trimethylene oxide, tetrahydropyran, *m*-dioxane, and cyclohexanone. In general, the method appears capable of determining the free energy function within ±0.1 cal/(mol deg). The applications of the technique to the study of conformational isomerism and to the study of chemical reaction in equilibrium in the absorption cell are discussed.

Several years ago it was shown[2] that the number of molecules per unit volume in the lower state of a rotational transition may be determined from the measurement of the absolute intensity of the transition, and the additional knowledge of the pressure allows the determination of the internal partition function and the free energy function of the molecule from this quantity.

This work describes the technique of intensity measurement, the method of calibration of the spectrometer gain, and the results obtained for the free energy function at room temperature of five molecules: difluoromethane, trimethylene oxide, tetrahydropyran, *m*-dioxane, and cyclohexanone. The free energy functions have not been previously measured for the last four molecules.

This method has other useful applications. Two examples will be briefly described.

Intensity Measurement Theory

For most substances, only a Stark modulation spectrometer provides sufficient sensitivity for the observation of rotational transitions in combination with convenient operation. Since crystal detectors require moderately high microwave power levels in order to operate as efficient low noise mixers, careful consideration[3] has to be given to either avoid or know the extent of power saturation. The bridge arrangement[3] shown in Figure 1 allows the power level in the absorption cell to be changed without affecting the microwave power level at the crystal. Thus, the crystal operating characteristics may be kept constant. In this bridge arrangement, the phase angle between the sample arm and bridge arm microwave radiation is usually adjusted to be 180 or 0° in order to avoid the introduction of the dispersion component of the rotational transitions into the output.

Let us consider the process of relating the spectrometer phase sensitive detector output signal, S (in volts), to the Lambert's law extinction coefficient, γ (in reciprocal centimeters). The PSD output voltage, S, is related to i_m, the amplitude of the Fourier component of the crystal current at the Stark modulation frequency in phase for absorption, by

$$S = Ai_m \tag{1}$$

where A is an electronics gain in combination with impedance and has the dimensions of ohms.

If the operating conditions are such that power saturation is negligible and the line width is much greater than the modulation frequency (both conditions are satisfied in the experiments to be described), the microwave power modulation fairly faithfully reproduces the square wave Stark voltage. The Fourier component, i_m, at the fundamental frequency will be proportional to the difference between the power reaching the detector with the Stark field on and the Stark field off, ΔP.

$$i_m = \frac{2}{\pi}k\left(\frac{\Delta P}{P_0}\right)i_0 \tag{2}$$

where $(4/\pi)\Delta P$ is the amplitude of the Fourier component of the microwave power modulation at the modulation frequency

$$k = \left(\frac{\partial \ln i}{\partial \ln P}\right)_{i_0} \tag{3}$$

and i_0 and P_0 are the dc crystal current and average total microwave power at the crystal.

The frequency dependence of k for a fixed i_0 has been investigated by comparing power meter and crystal current readings. To the accuracy of such measurements, which is about 5%, k appears to be independent of frequency over the entire frequency band ot 26.5–40 GHz. Therefore, it has been assumed independent of frequency in the measurements reported here. As all results for the free energy function will be the average of measurements at several frequencies, it is hoped that any residual frequency dependence will be averaged out.

In the bridge, the amplitudes of the microwave electric fields are added (if the phase angle is 0°) or sub-

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[2] R. F. Curl, Jr., *J. Mol. Spectrosc.*, **29**, 375 (1969).

[3] (a) H. W. Harrington, *J. Chem. Phys.*, **44**, 3481 (1966); (b) *ibid.*, **46**, 3698 (1967); (c) *ibid.*, **49**, 3023 (1968).

tracted (if the phase angle is 180°) at the junction of the two arms. Thus, the amplitude of voltage modulation at the detector, $(\Delta V)_d$, is related to the amplitude of voltage modulation at the exit of the Stark cell, $(\Delta V)_e$, by a voltage attenuation factor, α_v.

$$(\Delta V)_d = \alpha_v(\Delta V)_e \qquad (4)$$

Since

$$\left(\frac{\Delta V}{V_0}\right)_d = \frac{1}{2}\left(\frac{\Delta P}{P_0}\right)_d \qquad (5)$$

the spectrometer signal may be written

$$S = A\left(\frac{2}{\pi}\right)ki_0 2\left(\frac{1}{V_0}\right)_d \alpha_v(\Delta V)_e \qquad (6)$$

By multiplying by (V_{0e}/V_{0d}) and using the fact that

$$\left(\frac{\Delta V}{V_0}\right)_e = \frac{1}{2}\left(\frac{\Delta P}{P_0}\right)_e \qquad (7)$$

the result obtained is

$$S = A\left(\frac{2}{\pi}\right)ki_0\alpha_v\left(\frac{V_{0e}}{V_{0d}}\right)\left(\frac{\Delta P}{P_0}\right)_e \qquad (8)$$

The quantity $\alpha_v(V_{0e}/V_{0d})$ can be related to the absorption cell attenuator setting at the time of intensity measurement, A_b (in decibels), and the absorption cell attenuator setting, A_i (in decibels), needed to give the crystal current, i_0, if no power comes through the bridge arm by the following arguments. (The subscript b on A_b indicates the bridge arrangement and the subscript i on A_i indicates the in-line arrangement.) If all power goes through the Stark cell arm and the crystal current is kept at i_0, the power at the detector and the voltage amplitude, V_{0d}, are still the same as in the bridge configuration at the time of measurement. However, the voltage amplitude at the Stark cell exit becomes V_{0d}/α_v. Thus, $\alpha_v(V_{0e}/V_{0d})$ is the ratio of the voltage amplitude at the Stark cell exit at the time of intensity measurement to that same voltage amplitude in the in-line configuration keeping i_0 constant. The input power into the Stark arm is constant so that the voltage amplitude at the Stark cell exit is proportional to $10^{-A/20}$. Therefore

$$\alpha_v\left(\frac{V_{0e}}{V_{0d}}\right) = 10^{+(A_i-A_b)/20} \qquad (9)$$

The quantity $(\Delta P/P_0)_e$ can be related to the Lambert's law extinction coefficient, γ, by

$$\left(\frac{\Delta P}{P_0}\right)_e = \gamma L \qquad (10)$$

where it is assumed that $\gamma L \ll 1$.

Substituting eq 9 and 10 into eq 8, the result is

$$S = \left[A\left(\frac{2}{\pi}\right)ki_0\right]10^{(A_i-A_b)/20}\gamma L \qquad (11)$$

Provided that all measurements are made at the same i_0, the quantities in the square brackets can be lumped together into an overall spectrometer gain, G, yielding

$$S = (GL)10^{(A_i-A_b)/20}\gamma \qquad (12)$$

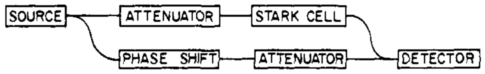

Figure 1. Stark modulation bridge spectrometer.

The Lambert's law extinction coefficient is given by a Lorentzian line shape formula convoluted over the Doppler center frequency distribution, resulting from the Boltzmann distribution of velocity components along the direction of radiation propagation. The Doppler width is much less than the Lorentz width for the transitions considered here and can be included in an effective Lorentzian with slightly greater line width. Then, γ is expressed as

$$\gamma = \frac{\gamma_0}{[(\nu - \nu_0)/\Delta]^2 + 1 + KI} \qquad (13)$$

where I is the radiation intensity, ν_0 is the peak absorption frequency, γ_0 is the unsaturated peak absorption coefficient, Δ is the half-width at half-height unsaturated, and K is the power saturation coefficient. All measurements reported here are made under conditions where $KI \ll 1$. The expression for $\gamma_0\Delta$ in terms of molecular parameters is

$$\gamma_0\Delta = \frac{8\pi^2}{3v_g kT}n_0|\mu_{01}|^2\nu_0^2 \qquad (14)$$

where the transition is considered to take place from state 0 to state 1, n_0 is the number of molecules per unit volume in state 0, μ_{01} is the electric dipole matrix element between state 0 and state 1, v_g is the group velocity of light, k is Boltzmann's constant, and T is the absolute temperature. In eq 14, it has been assumed that $h\nu_0 \ll kT$. When the spatial degeneracy is included, the expression becomes

$$\gamma_0\Delta = \left(\frac{8\pi^2}{3v_g kT}\right)n_{J,\tau}S^{\alpha}{}_{J,\tau;J',\tau'}|\mu_\alpha|^2\nu_0^2/(2J+1) \qquad (15)$$

where $n_{J,\tau}$ is the number of molecules per unit volume in level J,τ (level 0), $S^{\alpha}{}_{J,\tau;J',\tau'}$ is the line strength of the rotational transition from level J,τ (level 0) to level J',τ' (level 1), which is allowed by component α of the electric dipole moment.

The quantity $n_{J,\tau}$ may be related to the partition functions by

$$n_{J,\tau} = w_I(2J+1)N\exp(-E_{J,\tau}/kT)/Q_{int}Q_{ns} \qquad (16)$$

where w_I is the nuclear spin weight of level J,τ, N is the number of molecules per unit volume and may be calculated from the pressure and temperature, $E_{J,\tau}$ is the energy of level J,τ above the lowest level accessible to the molecule, Q_{int} is the rotation–vibration partition function, and Q_{ns} is the nuclear spin partition function. The quantity, Q_{int}, may be related to the standard free energy function (ideal gas reference state, practical scale for a single isotope)

$$-(G^\circ - H^\circ_0)/T = R\left(\ln Q_{int} + \frac{5}{2}\ln T + \frac{3}{2}\ln M\right) - 7.283 \qquad (17)$$

where $-(G^\circ - H^\circ_0)/T$ is in entropy units, T is in degrees Kelvin, and M is in atomic mass units.

If the rotational spectrum has been assigned and the Stark effect measured, the quantities $S^{\alpha}{}_{J,\tau;J',\tau'}$, $E_{J,\tau}$, and μ_a may be calculated. Thus, $\gamma_0\Delta$ may be related to the free energy function if the pressure is known.

In all the cases reported here, the most abundant isotopic species accounts for more than 90% of the molecules present. The free energy function of the other isotopic species present will not be very different from that of the most abundant species. Since the practical scale eliminates the entropy of isotopic mixing, the free energy functions of the different species should be averaged with a weighting factor proportional to their abundance. The result will be negligibly different from the free energy function of the most abundant species. Consequently, we have measured only the most abundant species, and the results reported are the free energy function of the most abundant species.

Let us return to the condition that $KI \ll 1$ and consider how it can be verified that this condition is met at the time of measurement. It has been established[3] that the spectrometer signal passes through a maximum as the power through the absorption cell is increased. If the power through the cell is 30 db below the power at the original maximum, the effects of the power saturation are negligible ($\sim 1\%$). At the pressures used in these experiments, insufficient power is available to reach the maximum spectrometer signal. However, this point can be reached at lower pressure and the maximum signal power at the high measurement pressure estimated, since the power saturation constant is inversely proportional to the square of the pressure. Experimental conditions can then be adjusted to make sure that power is 30 db below this point. This technique was checked by comparing the $\gamma_0\Delta$ reported with that obtained with 10 db more and less power.

Calibration

By measuring Δ, S (the peak unsaturated spectrometer signal), and the pressure for a calibration substance of known rotational constants, μ_α, and internal partition function, the spectrometer gain constant, GL, may be determined since $\gamma_0\Delta$ may be calculated for the substance. The instrumental constant GL of eq 10 was determined by measuring the signal strength S and Δ for three selected lines of SO_2. The transition dipole moment μ_{01} and the rotational energies were computed in rigid-rotor approximation using $\mu_b = 1.634$[4] and the rotational constants given by Kivelson.[5] The rigid-rotor approximation is also used in the calculations on the remaining molecules. The internal partition function was calculated based on the same data as used in the JANAF table.[6] For a given pressure and temperature, the product $\gamma_0\Delta$ could be calculated from eq 16 and 15. Thus, the measurement of pressure, temperature, S, Δ, A_b, and A_i on SO_2 determines GL by eq 12.

The intensity measurements are made on the most abundant isotopic species of the molecules. Thus, the molecular weight M of the parent species is used rather than the average molecular weight, and also a correction is made for the purity factor of the parent species in converting the observed pressure to the total number density N. The purity factor is easily obtained from the chemical purity of the sample and the natural isotopic abundance data.

The Hewlett-Packard Model 8460A MRR spectrometer was used in the region 26.5–40 GHz. All the measurements were performed at room temperature. The sample of SO_2 was purchased from Matheson Company. Since the repeated degassing at liquid nitrogen temperature showed no sign of purification, the gas was subsequently used directly from the cylinder. The pressure was measured by a Baratron capacitance diaphragm gauge whose accuracy is estimated to be 2% in our pressure region of 15–60 μ. The absolute calibration of the pressure gauge is not necessary because the spectrometer is calibrated with SO_2 just prior to a set of measurements and all that is required is that the pressure reading be proportional to pressure. To the accuracy with which the intensity measurements can be made on SO_2, the SO_2 line intensities are proportional to the pressure readings.

To avoid the desorption of foreign gases from the inside wall, the cell was pumped with an ion pump prior to the measurement. Also to minimize the possible chemical reaction of the sample molecules inside the waveguide, a fresh sample was introduced for each measurement. The same procedures were usually taken in the experiments with other molecules. The pressure range of 25–30 μ was used for SO_2 experiments.

To check the consistency of the method and the approximate independence of GL of frequency, three transitions were used. Calculation showed for each of the three lines that all the Stark lobes are well separated from the zero field line at the Stark voltages used. There were no lines observed within 30 MHz of each of the three lines used. The spectrum is very sparse and accidental nearly exact overlap of some other lines with one of the three lines is unlikely. The quantity 20 log GL is measured in the experiment, and the results of the SO_2 calibration are shown in Table I. From the table it appears that the method is consistent and GL is fairly independent of frequency. However, the differences between the gain factor obtained from the different SO_2 lines are much larger than the uncertainty of the measurement of an individual line. This "residual frequency dependence" gives an expected standard deviation of 0.03 eu arising from the calibration.

Table I. SO_2 Calibration

Transition	ν_{obsd}, MHz	20 log GL, db
$16_{3,13} \rightarrow 17_{2,16}$	28858.03	82.064
$17_{3,15} \rightarrow 16_{4,12}$	31922.29	82.509
$16_{3,13} \rightarrow 15_{4,12}$	38518.23	82.151
Average		82.241 ± 0.409^a
$T = 298.55$°K		

[a] Three times the estimated standard deviation of the average $= 3[\Sigma(X_i - \bar{X})^2/N(N-1)]^{1/2}$.

Using the gain factor GL determined from the SO_2 experiment, Q_{int} could now be measured for other molecules. In order to avoid error due to time variation of the gain, the calibration was performed immediately before or after each set of measurements on a chosen molecule. The SO_2 line at 28858.03 MHz was chosen for this purpose and the average GL of several repeated measurements was taken as the calibration factor for that set of experiments. Since the gain obtained for the 28858.03-MHz line was 0.18 db less

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(4) R. D. Brown, F. R. Burden, and G. M. Mohay, *Aust. J. Chem.*, 22, 251 (1969).

(5) D. Kivelson, *J. Chem. Phys.*, 22, 904 (1954).

(6) D. R. Stull and H. Prophet, "JANAF Thermochemical Tables," 2nd ed, *Nat. Stand. Ref. Dat. Ser., Nat. Bur. Stand.*, 37 (1971).

than the average of the three lines, 0.18 db was added to the gain found for this line. The time variation of the measured GL was small, however.

Measurement of the Free Energy Function for Selected Molecules

Difluoromethane, for which the free energy function is known, was first chosen to further check the validity of the method, and then the application was extended to trimethylene oxide, tetrahydropyran, *m*-dioxane, and cyclohexanone. Before the results on the individual molecules are reported, let us consider the general features of the measurements.

The absorption lines on which the intensity measurements are performed must be very carefully selected if the measurements are to be meaningful. Primarily, the spectral lines whose intensities are measured must be free from "overlapping." The term "overlapping" includes negative overlap due to the Stark lobes of its own or of some other lines, as well as the positive overlap due to the accidental near coincidence in frequency with some other transitions. Critical tests on overlapping were done before selecting lines for the measurement. To do this, the spectrum was first recorded at very low pressure ($\sim 3\ \mu$) to better detect possible close overlaps and then at higher pressures (20–30 μ) to check the approaching of the tail ends of nearby lines. Due care was taken to remove the Stark lobes from the main line and to avoid accidental crossing of Stark lobes coming from other lines. This introduces stringent restrictions on the Stark voltage which was carefully chosen to satisfy these requirements.

The search for good lines was generally limited to the strong lines. Since the experiment is performed under low power conditions, it becomes very important for molecules having weak absorption lines to maintain the signal to noise ratio above a certain level.

The selection of lines was easy for SO_2, CH_2F_2, and trimethylene oxide. But for larger molecules, the task, in general, becomes increasingly more difficult due to the smaller rotational constants and the presence of low-lying vibrational states which make the spectrum dense.

Usually each measurement for a batch sample takes less than 5 min. The pressure change during the scan over the absorption line was generally small, but whenever a pressure change was noted, the mean value was taken for the pressure. The pressure was stable in difluoromethane, tetrahydropyran, and *m*-dioxane, but less so for other molecules.

In considering the scatter of the experimental results, the general conclusion was that the reproducibility of measurements on a single line was better than the consistency of results between different lines. It is not clear whether this results from a residual frequency dependence of the apparatus, possibly due to reflections, or to overlap of weak lines. Since it is found for difluoromethane (*vide infra*) which has a very sparse spectrum, we are inclined to the former view.

In the tables, uncertainties are given both for the reproducibilities of the individual lines and for the scatter between lines. Because of the conclusion stated above, in calculating the average result of measurements on several lines, an unweighted average of the lines was taken, even though more measurements were made on some lines. The uncertainties quoted in the overall average were also based on the scatter between different rotational lines with each line given the same weight. The uncertainties quoted are three estimated standard deviations of the average (*i.e.*, $(\sigma_{\bar{X}})_{\text{est}} = [\Sigma(X_i - \bar{X})^2/N(N-1)]^{1/2}$ where N is the number of lines or, for an individual line, the number of measurements). For the final result at 298.15°K for each molecule, the contribution to the uncertainty arising from the uncertainty in the calibration was included by squaring this calibration uncertainty (3×0.03 eu) and adding it to the square of the uncertainty found for each molecule and then taking the square root. No contribution to the uncertainty arising from uncertainties in the dipole moment has been included. In principle, the dipole moment could be measured more accurately for all molecules. These numbers can be corrected as more accurate dipole moments become available.

Difluoromethane. The sample was purchased from Matheson Company and was used without further purification. Eight transitions were chosen to investigate the experimental accuracy of the results. The assignment of the lines and the dipole moment is based on microwave work by Lide[7] and by Hirota, *et al.*[8] Calculation showed that at the Stark voltages chosen, partial overlap of the Stark lobe on the main line occurs for the $M = 7$ lobe of the transition $9_{2,7} \rightarrow 10_{1,10}$ and also for the $M = 10$ lobe of $11_{3,8} \rightarrow 12_{2,11}$.

The first set of experiments was performed on the eight lines at $p = 58.8\ \mu$ using the same batch sample, and then on a different day the measurement was repeated on four lines using a different pressure 31.8 μ. The temperature was 25.3 ± 0.3°. The pressure reading was very stable in the case of CH_2F_2. The reproducibility of the results on the same line was good.

Proper correction is made for the nuclear spin statistical weight on each transition. The nuclear spin contribution to the free energy function is subtracted and the practical scale values are listed in Table II.

Table II. Free Energy Function of CH_2F_2

Transition	ν_{obsd}, MHz	$-(G° - H°_0)/T$, cal/(mol deg)
$1_{01} \rightarrow 1_{10}$	39892.53	50.30 ± 0.02[a]
$4_{13} \rightarrow 3_{22}$	31543.82	50.37 ± 0.02
$5_{15} \rightarrow 4_{22}$	29268.57	50.35 ± 0.05
$9_{27} \rightarrow 10_{1,10}$	30679.10	50.49
$8_{26} \rightarrow 7_{35}$	31763.69	50.39
$11_{38} \rightarrow 12_{2,11}$	32507.71	50.50
$12_{3,10} \rightarrow 11_{47}$	34755.89	50.36
$6_{25} \rightarrow 7_{16}$	39501.07	50.46
Average		50.40 ± 0.08[a] at 298.5 ± 0.3°K
Obsd		50.39 ± 0.12[b] at 298.15°K
JANAF value (interpolated)		50.37 at 298.15°K

[a] Three times the estimated standard deviation of the average for the measurements on this molecule alone. [b] Three times the estimated standard deviation of the average combining as the sum of squares the estimated standard deviation of the measurements on this molecule with the estimated standard deviation of the SO_2 calibration measurements.

Table II also lists the value of the free energy function at 298.15°K taken from a JANAF table.[6] A good

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(7) D. R. Lide, *J. Amer. Chem. Soc.*, **74**, 3548 (1952).

(8) E. Hirota, T. Tanaka, A. Sakakibara, Y. Ohashi, and Y. Morino, *J. Mol. Spectrosc.*, **34**, 222 (1970).

agreement is observed between the present result and the literature value. Moreover, only a small variation is observed between the values of the free energy function obtained from different lines.

Trimethylene Oxide. The sample was purchased from Aldrich Chemical Co. Analysis by gas chromatography showed about 2% impurity content. As in later experiments with liquid samples, the liquid trimethylene oxide is stored in a small bottle with a vacuum stopcock. Prior to the experiment, the sample is cooled below its melting point and pumped for some time to remove foreign low-boiling materials, such as air. After the pump-out, the sample is brought back to room temperature and the vapor is introduced to the waveguide. We assume, for liquid samples in general, that the impurity content in the vaporized sample is the same as that of the original liquid.

The spectrum is sparse in most of the spectral region, and there was no difficulty in selecting prominent well-isolated lines for the measurement. The satellite lines, although strong, are generally well separated from the ground state lines. Some centrifugal distortion effects are observable for high-J Q-branch lines. The frequency deviation of the line $15_{11,4} \rightarrow 15_{13,3}$, for instance, is about 15 MHz between the observation and the rigid-rotor calculation. The centrifugal distortion is neglected, however, in the calculation of transition dipole moment, as in the case of other molecules. The pertinent molecular parameters were taken from the microwave data of Chan, *et al.*[9]

Only two measurements were made for each of the seven selected lines, but the results were very reproducible. The pressure range of 18–22 μ was used. As for difluoromethane, proper correction is made for the nuclear spin statistical weights, and the practical values of the free energy function determined by the experiment are listed in Table III.

Table III. Free Energy Function of Trimethylene Oxide

Transition	ν_{obsd}, MHz	$-(G^\circ - H^\circ_0)/T$, cal/(mol deg)
$1_{11} \rightarrow 2_{12}$	31925.945	54.65 ± 0.01[a]
$9_{63} \rightarrow 9_{82}$	27303.133	54.73 ± 0.00
$10_{73} \rightarrow 10_{92}$	28125.195	54.70 ± 0.02
$11_{83} \rightarrow 11_{92}$	29252.591	54.67 ± 0.12
$13_{94} \rightarrow 13_{11,3}$	36410.728	54.67 ± 0.09
$14_{10,4} \rightarrow 14_{12,3}$	36782.101	54.61 ± 0.05
$15_{11,4} \rightarrow 15_{13,3}$	37349.635	54.66 ± 0.02
Average (not corrected for 0.2°K purity)		54.67 ± 0.04[a] at 299.9 ±
Purity of sample = 98%		
$-(G^\circ - H^\circ_0)/T$ corrected for impurity		54.63 ± 0.04[a] at 299.9 ± 0.2°K
Obsd		54.58 ± 0.10[b] at 298.15°K
Calcd from spectroscopic data		54.48

[a] See footnote *a* of Table II. [b] See the footnote *b* of Table II.

We also calculated the free energy function from the available spectroscopic data. The rotational partition function was calculated using the high-temperature approximation. For the vibrational partition function, the harmonic approximation was made for the first 23 normal modes with the frequencies taken from Zürcher and Günthard's data.[10] For the ring-puckering mode, the contribution was calculated by term-by-term summation based on the recent far-infrared data of Wieser, *et al.*,[11] where the inclusion of levels up to $v = 11$ was found sufficient.

The calculated free energy function of trimethylene oxide is also included in Table III. Comparison shows the intensity measurement method gives an accurate value for this molecule. The sparseness of the spectrum and the fairly strong intensities are thought to be the main reasons.

In choosing normal-mode frequencies of trimethylene oxide and also tetrahydropyran, *m*-dioxane, and cyclohexanone for the calculations, we found some ambiguities in the literature as to which values to use, although the normal-mode assignments on these molecules have been fairly well worked out.

For the purpose of later reference, we list in the Appendix the normal-mode frequencies used here, as well as the rotational constants and the dipole moments for all the molecules. Small uncertainties in the higher frequency modes (> 1000 cm^{-1}) have a negligible effect on the results.

Except for the ring-puckering vibration of trimethylene oxide discussed above, the effect of anharmonicity was ignored. Cyclohexanone is the only one of the molecules considered for which this approximation is expected to lead to an error of more than 0.05 eu because it is the only molecule which has a mode of low enough frequency (105 cm^{-1}) to give a major contribution from the second excited state.

Tetrahydropyran. The sample was purchased from Aldrich Chemical Company. The analysis by gas chromatography and nmr showed no appreciable impurities. The spectrum is much denser than that of trimethylene oxide. The most prominent feature is three series of Q-branch lines with the series heads occurring every ~4 GHz, as is mentioned by Rao and Kewley.[12a] We chose six a-type lines for the experiment, five of them being high-J Q branches (see Table IV). The Q-branch lines with $J = 14$ and 15, and also the R branch with $J'' = 5$, are actually unresolved K

Table IV. Free Energy Function of Tetrahydropyran

Transition	ν_{obsd}, MHz	$-(G^\circ - H^\circ_0)/T$, cal/(mol deg)
$5_{05} \rightarrow 6_{06}$ $5_{15} \rightarrow 6_{16}$	33196.235	60.53 ± 0.04[a]
$14_{5,10} \rightarrow 14_{5,9}$ $14_{4,10} \rightarrow 14_{6,9}$	37591.66	60.65 ± 0.03
$15_{79} \rightarrow 15_{78}$ $15_{69} \rightarrow 15_{88}$	33583.10	60.46 ± 0.08
$29_{20,9} \rightarrow 29_{22,8}$	32344.55	60.64 ± 0.14
$30_{21,9} \rightarrow 30_{23,8}$	32169.18	60.57 ± 0.14
$32_{28,10} \rightarrow 32_{23,9}$	36144.23	60.72 ± 0.08
Average		60.59 ± 0.12[a] at $T = 299.4$°K
Obsd		60.54 ± 0.15[b] at $T = 298.15$°K
Calcd from spectroscopic data		60.27

[a] See footnote *a* of Table II. [b] See footnote *b* of Table II.

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(9) S. I. Chan, J. Zinn, J. Fernandez, and W. D. Gwinn, *J. Chem. Phys.*, **33**, 1643 (1960).

(10) R. F. Zürcher and H. H. Günthard, *Helv. Chim. Acta*, **40**, 89 (1957).

(11) H. Wieser, M. Danyluk, and R. A. Kydd, *J. Mol. Spectrosc.*, **43**, 382 (1972).

(12) (a) V. M. Rao and R. Kewley, *Can. J. Chem.*, **47**, 1289 (1969); (b) *ibid.*, **50**, 955 (1972).

doublets. The computed asymmetry splittings for these lines are ~1, <1, and ~3 kHz, respectively, based on rigid-rotor calculation with the data of ref 12a. The dipole moment matrix elements are practically the same within a pair. Since the experimental values of Δ for these lines were in the range 330–420 kHz, these lines were regarded as single lines with doubled intensities. The centrifugal distortion is observed to produce ~30-MHz deviation for the lines $32_{23,10} \rightarrow 32_{23,9}$. For the five Q branches, calculation showed that $M = 0$ Stark lobes are not displaced from the main lines, but all the lobes with $|M| \geq 1$ are sufficiently displaced. Since the $M = 0$ lobe has zero intensity for Q-branch transitions, the five lines are thus free from intensity depletion. For the remaining R-branch line, all the Stark components are also removed. The intensity pattern of Q branch lines ($\propto M^2$) makes it advantageous to select them for the measurement because the Stark lobes that are sometimes difficult to remove have weak or zero intensities.

The results of our measurements are listed in Table IV. The temperature was 26.2° and the pressure range of 16–18 μ was used. Three measurements were made for each line. The dipole moment value was taken from ref 12b. The scatter of the experimental results is somewhat larger for this molecule than the previous ones. The main reason is thought to be the richness of the spectrum and the weaker intensities of the lines.

The calculation of the free energy function was also carried out. We chose a set of normal-mode frequencies on the basis of liquid ir and Raman data by Baggett, *et al.*,[13] who assigned most of the normal modes, and a more recent work by Pickett and Strauss.[14] One of the low-frequency ring modes is left unassigned in ref 14, but their normal coordinate analysis indicates that the unassigned frequency ω_2 in their notation is close to ω_1, to which they assign 251 cm^{-1}. Therefore, 251 cm^{-1} was used for ω_2 also. The calculated free energy function differs by ~0.3 eu from our measurements. Because of normal-mode ambiguities and the possible existence of a twisted conformer, it is difficult to decide which result is more nearly correct.

***m*-Dioxane.** The sample was purchased from K & K Chemical Company. Analysis by gas chromatography showed no appreciable impurities. The richness of the spectrum is similar to that of tetrahydropyran. The most prominent feature of the spectrum is three series of b-type Q-branch lines with the series heads occurring at ~4.3 GHz interval, as is mentioned by Kewley.[15] We chose five b-type lines for the experiment, four of them being high-J Q branches (see Table V). The first four lines of Table V are unresolved asymmetry doublets. The calculated splittings of these doublets are about 2 kHz or less, and these doublets are again regarded as single lines with doubled intensities. The rotational constants and the dipole moment were taken from ref 15. For the four Q-branch lines, calculation showed that all the Stark lobes other than $M = 0$ are removed, and therefore, no intensity depletions occur for these lines. For the R-branch line too, all the Stark lobes are removed. A typical frequency deviation caused by centrifugal distortion is ~12 MHz for the transition $22_{15,8} \rightarrow 22_{16,7}$.

Table V. Free Energy Function of *m*-Dioxane[a]

Transition	ν_{obsd}, MHz	$-(G° - H°_0)/T$, cal/(mol deg)	
$14_{59} \rightarrow 14_{68}$ $14_{69} \rightarrow 14_{78}$	36381.162	59.89 ± 0.15[b]	
$12_{39} \rightarrow 12_{48}$ $12_{49} \rightarrow 12_{58}$	36418.848	60.18 ± 0.10	
$5_{05} \rightarrow 6_{16}$ $5_{15} \rightarrow 6_{06}$	35229.785	60.39 ± 0.07	
$11_{38} \rightarrow 11_{47}$ $11_{48} \rightarrow 11_{57}$	32127.015	60.12 ± 0.10	
$22_{15,8} \rightarrow 22_{16,7}$	31465.789	60.08 ± 0.09	
Average		60.13 ± 0.24[b]	at 298.9 °K
Obsd		60.10 ± 0.26[c]	at 298.15 °K
Calcd from spectroscopic data		59.76	

[a] Values were corrected to $T = 25.7°$. The experimental temperatures were in the range 24.7–27.4°. [b] See footnote *a* of Table II. [c] See footnote *b* of Table II.

The results of our measurements are listed in Table V. Six measurements were made for each line. There were some temperature variations between the measurements, the range being 24.7–27.4°. The calculated temperature dependence of the free energy function at 300°K is 0.040 eu/deg. To take a meaningful average of the measurements, all the experimental values were corrected to the average temperature of 25.7° (298.9°K) by assuming the above linear dependence. Then the average was taken for each line and finally among the five lines. The temperature corrections are small. The values listed in Table V are the corrected values.

The rotational constant data of ref 15 and the normal coordinate data of Pickett and Strauss[14] were used to compute the free energy function. The microwave relative intensity measurements of ref 15 on five low-lying vibrational states are in good agreement with the ir and Raman data of ref 14. The computed free energy function at 298.15°K is included in Table V. Again, there is a small discrepancy between the measured and the calculated free energy functions, the magnitude being similar to the case of tetrahydropyran. Once again, it is difficult to decide which result is more nearly correct. The experimental scatter also appears to be similar between *m*-dioxane and tetrahydropyran.

Cyclohexanone. The sample was purchased from Aldrich Chemical Company. The stated purity is 99.8% and the analysis by gas chromatography showed no appreciable impurities. The microwave spectrum of the ground vibrational state has been analyzed by Ohnishi and Kozima.[16] More than 40 a-type R-branch lines arising from $J'' = 5$–9 are observed. These are the strongest lines in the spectral region, but none of them have outstanding intensities. The vibrational frequencies of the ring-deformation modes are generally lower than those of teyrahydropyran and *m*-dioxane,[17,18] and each rotational line is surrounded by many satellite lines which have appreciable intensities. This makes it very difficult to find good isolated lines. The pressure must be kept lower to avoid overlap, and it is difficult to perform the experiment without

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(13) N. Baggett, S. A. Barker, A. B. Foster, R. H. Moore, and D. H. Whiffen, *J. Chem. Soc.*, 4565 (1960).

(14) H. M. Pickett and H. L. Strauss, *J. Chem. Phys.*, **53**, 376 (1970).

(15) R. Kewley, Fourth Austin Symposium on Gas Phase Molecular Structure, Paper W16, Austin, Texas, Feb 1972.

(16) Y. Ohnishi and K. Kozima, *Bull. Chem. Soc. Jap.*, **41**, 1323 (1968).

(17) L. A. Carreira and R. C. Lord, *J. Chem. Phys.*, **51**, 3225 (1969).

(18) H. Fuhrer, V. B. Kartha, P. J. Krueger, H. H. Mantsch, and R. N. Jones, *Chem. Rev.*, 72, 439 (1972).

partial power saturation. Since the strong lines are all R branches, the $M = 0$ Stark lobes must be removed. The upper limit of the usable Stark voltage puts some restriction on the selection of lines. Furthermore, since the satellite lines have stronger relative intensities compared with tetrahydropyran and *m*-dioxane, there is generally a larger chance of intensity enhancement or depletion due to the near coincidence of frequency and the crossing of the Stark lobes.

After an extensive search, four lines were chosen for the experiment. Six measurements were made for each line. The temperature was 25.0–26.0° and the pressure range of 14.5–18.0 μ was used. The calculated temperature dependence of the free energy function is 0.048 eu/deg at 300°K. All the experimental results were corrected to 25.5°, using this value.

The results (after the correction) are summarized in Table VI. The rotational constants and the dipole moment were taken from ref 16. The centrifugal distortion effects were small for the four lines, the largest frequency deviation being 2.0 MHz for the transition $9_{18} \rightarrow 10_{19}$.

Table VI. Free Energy Function of Cyclohexanone[a]

Transition	ν_{obsd}, MHz	$-(G° - H°_0)/T$, cal/(mol deg)
$6_{24} \rightarrow 7_{25}$	31800.28	64.16 ± 0.10[b]
$8_{36} \rightarrow 9_{37}$	37955.83	63.50 ± 0.07
$9_{18} \rightarrow 10_{19}$	39193.82	63.61 ± 0.03
$7_{34} \rightarrow 8_{35}$	37076.48	63.75 ± 0.04
Average		63.76 ± 0.44[b] at 298.7°K
Obsd		63.73 ± 0.45[c] at 298.15°K
Calcd from spectroscopic data		63.75 at 298.15°K

[a] Values are corrected to $T = 25.5°$. The experimental temperatures were in the range 25.0–26.0°. [b] See footnote *a* of Table II. [c] See footnote *b* of Table II.

The normal coordinate data by Fuhrer, *et al.*,[18] as well as the structure data of ref 16, were used to compute the free energy function, and the result is included in Table VI. A large experimental scatter is observed between the results on different lines. One of the conceivable reasons is that there is some hidden overlapping (positive and negative) on the lines that we used.

Comparison of Absolute Intensity Data from Different Spectrometers

All data discussed above were obtained on the Rice University spectrometer. In order to test whether systematic errors peculiar to a particular spectrometer might affect the reliability of absolute intensity data, an independent measurement of the free energy function of tetrahydropyran was made at Hewlett-Packard, again using an 8460A spectrometer.

Measurement procedures were basically the same as those used at Rice. However, the OCS $J = 2 \rightarrow 3$ line was used for calibration. Calibrant gas showed less than 1% impurity by gas chromatography. The sample of tetrahydropyran also showed less than 1% impurity. Pressures in the range 10–13 mTorr were used for calibration and 9–13 mTorr for tetrahydropyran. Temperatures in the range 293 to 297°K were recorded during the experiments. Data were corrected to 295°K, the average temperature for all measurements.

The free energy functions determined from data on five transitions common to both studies are compared in Table VII. The calculated temperature dependence of 0.04 eu/°K was used to correct data from 295 to 299.4°K. The root mean square deviation between values from the two spectrometers for these five transitions is 0.08 eu, equivalent to a 4% rms deviation between experimental values of $\gamma_0\Delta/p$. The average values differ by 0.08 eu, two standard deviations of the measurement mean. It is encouraging also that the error limits in the two studies are essentially identical.

Table VII. Comparison of Free Energy Function Data for Tetrahydropyran Measured on Different Spectrometers

Transition	$-(G° - H°_0)/T$, cal/(mol deg) A[a]	B[b]	Diff
$5_{05} \rightarrow 6_{06}$ $5_{15} \rightarrow 6_{16}$	60.53 ± 0.04	60.52 ± 0.09[c]	+0.01
$15_{79} \rightarrow 15_{78}$ $15_{69} \rightarrow 15_{88}$	60.46 ± 0.08	60.38 ± 0.10	+0.08
$29_{20,9} \rightarrow 29_{22,8}$	60.64 ± 0.14	60.62 ± 0.16	+0.02
$30_{21,9} \rightarrow 30_{23,8}$	60.57 ± 0.14	60.53 ± 0.15	+0.04
$32_{23,10} \rightarrow 32_{23,9}$	60.72 ± 0.08	60.51 ± 0.14	+0.21
Average	60.59 ± 0.12[d]	60.51 ± 0.12	+0.08

[a] Values derived from Rice University data ($T = 299.4°K$). [b] Values derived from Hewlett-Packard data ($T = 299.4°K$). [c] Error estimates for individual transitions are three times the standard deviations of the mean values. [d] Error estimate is three times the standard deviation of the mean value for five transitions.

Discussion

It is worthwhile to summarize the main sources of error in the present method. They may be categorized as follows: (a) spectrometer characteristics ($\gamma_0\Delta$), (1) under modulation, (2) overlapping with other lines or Stark lobes, (3) partial saturation, (4) electronic nonlinearity or drift in gain, (5) base line affected by pickup; (b) sample (N), (1) impurities in the sample, (2) impurities in the calibration sample, (3) outgassing of impurities from the cell, (4) nonlinearity or drift in the pressure gauge; (c) dipole matrix element (μ_{01}), (1) error in the dipole moment measurement, (2) centrifugal effects on dipole moment. We tried to reduce the errors due to items a and b.

In comparing the measured free energy function with the calculated ones, we have to remember that the calculation is also subject to certain sources of error. They include: (1) uncertainties in the normal-mode frequencies, (2) anharmonicities of vibrational levels (for trimethylene oxide, this was partially included), (3) possible existence of conformational isomers, (4) centrifugal distortion effect on the rotational energy levels, (5) variation of the rotational constants with vibrational states. The effect of (5) is appreciable only for low-lying vibrational states. Our test calculation on trimethylene oxide, using the rotational constants reported for $v = 0$–4 of the ring-puckering mode,[9] shows that this effect produces only ~0.006 eu difference in the free energy function at 300°K. When a molecule has conformational isomers with appreciable Boltzmann factors, ignorance of the existence of such isomers can lead to a sizable deviation of the calculated free energy function from the true value. For all the molecules studied here, we assumed a single conformation. The effect of anharmonicity depends very much on the frequencies of the lowest modes. If these are all above 250 cm^{-1}, the effect of an anharmonicity which shifts the overtone level by 5 cm^{-1} from twice the fundamental is less than 0.05 eu. Such effects may become quite large if low-frequency modes are present. In cyclohexanone the free energy function would become 0.19 eu larger at 298.15°K because of such shift in every vibration primarily because of the 105-cm^{-1} mode. We did not make any quantitative estimates concerning item 4, but the effect of centrifugal distortion is presumably small.

Since the accuracy of measuring the signal height and the half-width depends on the individual molecule, the accuracy of the measured free energy function varies from one case to another. In favorable cases, however, the present method appears capable of determining the free energy function within ±0.1 eu.

The usual methods of determining the free energy function at room temperature are calculation from spectroscopic data and integration of functions of heat capacity from absolute zero to room temperature. The latter method requires calorimetric determination of the heat capacity from liquid hydrogen temperature to room temperature.

For small rigid molecules, calculation from spectroscopic data is by far the most accurate method, giving uncertainties as low as 0.001 eu in the free energy function. There is usually little ambiguity in the assignment of vibrational normal modes, and the molecule exists in only one conformation. However, for larger nonrigid molecules, especially those which have more than one stable conformation, the spectroscopic method is usually unsatisfactory. Frequent ambiguities occur in the assignment of normal modes of vibration. The energy difference between the conformers is required and is usually not accurately known.

In such cases, calorimetric determination of the heat capacity and the microwave intensity method may be used. The accuracy for these two methods is about the same, ±0.1 eu. The microwave intensity measurement method requires that the molecule have a permanent electric dipole moment and that the rotational spectrum of at least one conformer has been analyzed and the Stark effect measured. Great difficulty in finding a line suitable for measurement may be encountered if the rotational spectrum is very dense. Further, the calorimetric measurements yield the heat capacity, entropy, enthalpy function, and free energy function at all temperatures from absolute zero to room temperature, as well as the room temperature free energy function. While in principle, the temperature range of the microwave method can be extended and the entropy and enthalpy function (and even in principle, the heat capacity) can be obtained by taking temperature derivatives, such studies will require development of a temperature controlled absorption cell and careful investigation of the error in taking the temperature derivatives.

The calorimetric method may give erroneous results because of frozen disorder in the solid at low temperatures. The microwave intensity method requires a few days work to determine the free energy function at room temperature, while a calorimetric investigation usually requires months of extremely painstaking labor.

The general uses of the free energy functions, such as relating the enthalpy change in a chemical reaction to the extent of reaction, are well known. Perhaps it is of some value to discuss two further applications in the particular experimental situation.

Table AI

Trimethylene oxide		Tetrahydropyran		*m*-Dioxane	Cyclohexanone
Mode[a]	Freq[a]	Mode	Freq[c]	Freq[d]	Freq[e]
(A_1)				(A')	(A')
1	2959	CH_2 asym str	2957	2974	105
2	2930		2929	2968	313
3	1473		2910	2929	411
4	1461		2849	2862	490
5	1342		2815	2861	655
6	1134	CH_2 sym str	2735	2856	752
7	1018		2700	1488	841
8	908		2672	1480	861
			2644	1446	993
(A_2)			2603	1378	1019
9	3000	CH_2 scissor	1470	1297	1117
10	1283		1455	1200	1220
11	1185		1445	1167	1248
12	986		1433	1097	1311
			1386	995	1346
(B_1)		CH_2 wag	1363	906	1421
13	2966		1352	837	1449
14	1508		1310	652	1462
15	1458		1303	453	1718
16	1363		1275	435	2859
17	1228	CH_2 twist	1270	262	2865
18	936		1260		2899
			1246	(A'')	2920
(B_2)			1197	2968	2950
19	3007		1171	2861	2961
20	2940	CH_2 rock	1160	1465	
21	1225		970	1435	(A'')
22	1142		856	1408	189
23	836		759	1380	460
24[b]			737	1339	490
		Ring	1093	1291	752
			1047	1233	894
			1030	1121	907
			1013	1058	1049
			873	1018	1075
			817	899	1185
		Ring deform	563	488	1248
			455	262	1263
			432		1311
			402		1338
			251		1346
			251		1429
					1449
					2865
					2894
					2940
					2961

[a] For the approximate description of the mode and the original ir and Raman peaks, see ref 10. [b] Far-infrared data of ref 11 were used. [c] Based on ref 13 and 14. [d] Based on ref 14. For the description of each mode, see the same reference. [e] Based on ref 18. For the description of each mode, see the same reference.

In microwave investigations of molecules which might exist in more than one conformation, it is often possible to assign readily the spectrum of one conformer. However, it is often very difficult to assign additional conformers. In deciding how diligently to pursue the assignment or such additional conformers, it is very helpful to know the total concentration of these additional conformers. For example, the prospects for assigning an additional conformer in 30% concentration are much brighter than if the concentration is less than 5%.

In most cases, a free energy function of the assigned conformer may be calculated spectroscopically. The rotational constants are known. Vibrational satellite lines of excited states of the low frequency normal modes can be observed and the normal-mode frequencies determined from relative intensity measurement. The vibrational dependence of rotational constants allows the separation of normal mode from combination lines in the satellite spectrum. When these are compared with an infrared spectrum, most normal modes can be assigned. Ambiguities in normal-mode assignment in the mid ir (above 600 cm^{-1}) have little effect on the free energy function.

By making absolute intensity measurements on the assigned conformer and using the spectroscopically calculated free energy function, the partial pressure of the assigned conformer can be calculated. When this is subtracted from the total pressure, the residual may be interpreted as the total pressure of unassigned conformers.

The other application to be discussed concerns situations in which a reaction is at equilibrium in the absorption cell. A now familiar case of this is that of conformational isomerism. By measuring the relative intensity of rotational transitions of two conformers, the energy difference between the conformers may be determined.[19] It is interesting to note that the reaction need not be an isomerization in order to determine the ground state energy change. Consider, for example, the dimerization

$$A + B \rightleftharpoons AB$$

If the intensity of a transition of all three species may be measured, the bond dissociation energy, D_0, of AB may be determined regardless of whether the free energy function of any of the species is known. Referring to eq 15, it can be seen that n_0, the number of molecules in the lower energy level per unit volume, can be determined by measuring $\gamma_0\Delta$. The rotational energy can be calculated, and the number of molecules in the ground state of the molecule can be obtained by using the Boltzmann factor

$$n_{AB}^{(0)} = n_{0AB}\exp[(\epsilon_0 - \epsilon^{(0)})/kT] \qquad (18)$$

Defining the quantity, K^*, by

$$K^* = \frac{n_{AB}^{(0)}}{n_A^{(0)} n_B^{(0)}} \qquad (19)$$

the bond dissociation energy of AB is given by

$$D_0 = RT \ln K^* + \frac{3}{2}RT \ln \mu T + 92.78T \qquad (20)$$

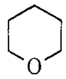
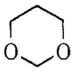
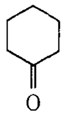
where $\mu = M_A M_B/(M_A + M_B)$ in atomic mass units, T is in degrees Kelvin, K^* is cubic centimeters per molecule, and D_0 is in calories. This result does not depend upon sample purity, pressure measurement, or the absence of other dimerization reactions, such as $2A \rightleftharpoons A_2$, as long as intensities of all three species can be measured.

Acknowledgment. Professor Frederick Rossini provided much useful information concerning the thermodynamic data available on possible molecules to be studied.

Appendix

(1) Normal-mode frequencies (in reciprocal centimeters) used in the calculation appear in Table AI. (2) Rotational constants (in megahertz) and dipole moments (in Debye) appear in Table AII.

Table AII

	SO_2	CH_2F_2				
A	60778.79	49138.4	12045.2	4673.48	4999.94	4195.30
B	10318.10	10603.89	11734.0	4495.02	4807.61	2502.57
C	8799.96	9249.20	6730.7	2602.31	2757.12	1754.49
Ref	5	7	9	12a	15	16
μ_a	0.00	0.00	1.93	1.39	0.00	2.74
μ_b	1.634	1.96	0.00	0.00	1.61	0.00
μ_c	0.00	0.00	0.00	0.74	1.29	0.86
Ref	4	7	9	12b	15	16

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[19] E. Saegebarth and E. B. Wilson, Jr., *J. Chem. Phys.*, **46**, 3088 (1967).