Direct Determination of the Boltzmann Constant by an Optical Method

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We have recorded the Doppler profile of a well-isolated rovibrational line in the ν2 band of 14NH3. Ammonia gas was placed in an absorption cell thermalized by a water-ice bath. By extrapolating to zero pressure, we have deduced the Doppler width which gives a first measurement of the Boltzmann constant kB by laser spectroscopy. A relative uncertainty of 2 × 10−4 has been obtained. The present determination should be significantly improved in the near future and contribute to a new definition of the kelvin.

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The tremendous progress in high precision measurements during recent decades will lead unavoidably to a complete renewal of fundamental metrology. There is a strong tendency to relate the base units to fundamental constants [1]. As an example, this was done in 1983 by fixing the velocity of light c and thus defining the length unit from the time unit, because the second is the fundamental unit which is realized, by far, with the best accuracy. The unit of temperature could follow the same line. Up to now, the kelvin was defined by the temperature (273.16 K) of the triple point of water (TPW) which implies a particular property of macroscopic matter. Instead, the temperature of a sample has a microscopic interpretation and can be related through the Boltzmann constant to the mean energy E per particle and per degree of freedom according to the well-known expression

\[ E = \frac{1}{2} k_B T. \]

This energy may itself be related to a frequency via the Planck constant. This Letter presents a first accurate experiment which gives a direct measurement of such a frequency in a gas at a well-defined temperature. Fixing the value of kB would connect temperature and time units. But, before fixing the value of the Boltzmann constant, it is necessary to verify precisely the consistency of the value of kB in the present context. The accepted value in the CODATA [2] \[ k_B = 1.3806505(24) \times 10^{-23} \text{ J K}^{-1} \] is derived from the value of the ideal gas constant R and the Avogadro constant NA by the relation \[ k_B = R/NA. \]

The relative uncertainty of kB is 1.8 × 10−6 and should come mostly from that for R because the uncertainty of NA is 1.7 × 10−7 [2]. But there is presently an inconsistency at the level of 10−6 between the values of NA derived from the Si sphere and from the watt balance experiment [3]. Very few experiments lead to an accurate determination of kB or R [4]. Up to now, the accepted value of R has come from a single experiment by Moldover et al. [5] performed before 1988 by acoustic gas thermometry.

An alternative and indirect measurement of the Boltzmann constant was proposed along an approach based on the vibrational expansion of the Clausius-Mossotti equation [6]. This relates the permittivity of helium e to its molar polarizability \( A_e \), which implies a QED calculation. Here we propose a direct determination of the Boltzmann constant by laser spectroscopy [1]. The principle consists in recording the linear absorption in a vapor phase and measuring the Doppler width of an atomic or molecular line in a cell in thermodynamic equilibrium. In the Doppler limit, the line shape is a Gaussian (for an optically thin medium) and \( k_B T \) is given by

\[ k_B T = \frac{m c^2}{2} \left( \frac{\Delta \nu}{\nu} \right)^2. \]

\( \Delta \nu \) is the e-fold half-width, \( \nu \) is the frequency of the molecular line, and \( m \) is the molecular mass. \( \Delta \nu \) and \( \nu \) are determined experimentally. The probed atoms or molecules belong to a single quantum level of a well-defined isotopic species, which avoids uncertainties coming from macroscopic quantities as is the case in the schemes mentioned above. Strictly speaking, we are sensitive to the temperature of one translational degree of freedom of a subset of molecules. Since the temperature is measured on the walls of the cell containing the gas, the determination of \( k_B \) using different rovibrational lines can lead to a verification of the equipartition of energy principle. This experimental situation benefits from an analysis considerably more straightforward than other methods, as we will see.

Ion mass ratios can now be measured in Penning traps with 10−9−10−10 accuracies [7], and binding energies for a molecule can be easily calculated to keep the accuracy of the molecular mass expressed in atomic units at the same level. However, because of the definition of the kilogram, its absolute value implies the Avogadro constant NA as in the previous experiments, but, since atom interferometry yields a direct determination of the quantity \( h/m c^2 \) [8], the present experiment gives directly the ratio \( k_B/h \).

**Experiment.**—The experiment consists simply in recording an absorption line. The selected line for these first experiments is the ν2 as \( Q(6, 3) \) rovibrational line of the ammonia molecule 14NH3 at the frequency \( \nu = 28953694 \text{ MHz} \). The choice of the molecule is governed by two main reasons: a strong absorption band in the spectral region of 8–12 μm of the ultrastable spectrometer that we have developed over several years and a well-
isolated Doppler line to avoid any deformation of the line shape due to neighboring lines. Clearly, the conditions for such an experiment can be obtained with a wide set of molecules or even atoms in various spectral regions and also over a large range of temperatures. In our experiment, the gas pressure varies from 0.1 to 10 Pa. The 37 cm-long absorption cell is placed in a large thermostat filled with an ice-water mixture, fixing the temperature at 273.15 K. Several temperature probes based on 100Ω platinum resistors with a 0.39Ω K⁻¹ dependency are firmly attached to the cell to follow the temperature changes or gradients. These probes were calibrated against a TPW. A conservative uncertainty of 20 mK ($7 \times 10^{-5}$) was guaranteed in this experiment. This can be easily improved in the future.

The laser source is based on a CO₂ laser stabilized on an absorption line of OsO₄. The laser frequency control is a key point of the experiment: The laser spectral width is less than 10 Hz as measured by the beat note between two independent lasers, and the Allan deviation at 100 s can reach 0.1 Hz ($3 \times 10^{-15}$) [9]. Recently, we have measured the absolute frequency of our laser source against the Cs fountain of SYRTE (Paris Observatory) through an optical fiber link connecting our two laboratories. The uncertainty of 1 Hz ($3 \times 10^{-14}$) [10] shows that the relative accuracy of the frequency axis of the recorded Doppler profile (width of about 100 MHz) can reach $10^{-8}$. This is 2 orders of magnitude better than the present accuracy of the Boltzmann constant and will not be a limitation. The tunability of the laser source is obtained with an 8–18 GHz electro-optic modulator (EOM) [11] which generates two weak sidebands (SB) ($10^{-4}$–$10^{-3}$ efficiency). The sideband, red-detuned by 13 GHz from the R(6) CO₂ laser carrier, is brought into resonance with the desired molecular transition. The full Doppler profile is scanned by detecting the light transmitted by the cell on a HgCdTe photodetector. The main difficulty in this experiment is our capability to record a signal which reflects perfectly the absorption signal of the molecular gas recorded with a constant incident laser power. Starting from a laser carrier of 1.5 W, the available power in the cell can be chosen between 0.1 and 3 μW for a beam diameter of 11 mm. The Doppler profile of about 100 MHz width is recorded over 250 MHz by steps of 500 kHz with a time constant of 20 ms. However, the important frequency step which is also applied to the filtering cavity by the way of a servo loop imposes a time delay of about 200 ms between two points to prevent extra noise. The time for recording a spectrum is thus about 110 s, with the relative transmission normalized by the incident laser power.

**Methodology of the line shape analysis.**—The theoretical description of this experiment corresponds to the well-

![FIG. 1. Experimental setup. $f = 8$ kHz, $f_1 = 17$ kHz, $f_2 = 1.7$ kHz, $f_3 = 2.2$ kHz. Only the sideband $\SB$ from the EOM is kept after filtering for recording the NH₃ absorption profile.](image-url)
established situation of the linear absorption of a sample in a cell at thermal and pressure equilibrium. However, an accurate determination of the linewidth requires a very accurate description of the line shape. In the case of an optically thick medium, the line shape is given by the Beer-Lambert law \( \exp(-aL) \), where \( L \) is the length of the absorption cell and where the absorption coefficient \( a \) has a Gaussian shape in the Doppler limit, as mentioned above. Experimentally, we have tried to work as close as possible to this regime. In practice, several causes of broadening must be taken into account. In the first place, the pressure broadening and the natural width are responsible for the homogeneous width \( \gamma_{\text{hom}} \). In this case the line shape is a Voigt profile, that is, the convolution of a Gaussian and a Lorentzian. In linear absorption spectroscopy and for an isotropic velocity distribution, a detailed calculation of the line shape, taking into account all transit effects, shows that these effects are already included in the usual Doppler broadening [12]. Two other effects must be considered: the unresolved hyperfine structure of the transition and the modulations applied for experimental reasons which broaden the laser spectrum. In a first approach, these two effects act in the same way: In the first case, the line shape is exactly the sum of the individual hyperfine components, and, in the second case, the frequency comb of the laser spectrum due to the frequency modulation \( f_i \) (which is the main effect here) generates absorption signals which reflect the laser spectrum (positions and relative intensities). We have checked that our experiments were performed in the low field limit, far from saturation. In order to derive the theoretical line shape, one can take into account exactly all of these effects. However, since experimentally we are very close to the Doppler limit, the actual line shape cannot be easily distinguished from the exponential of a broadened Gaussian. We have fitted the theoretical line shape with the exponential of a Gaussian and calculated numerically the relative broadening caused by the various effects mentioned above: For the homogeneous broadening, we found \( 0.484 \gamma_{\text{hom}}/\Delta_D \); the hyperfine structure and the laser frequency modulation depth create respective broadenings equal to \( 0.254(\Delta_{\text{hyp}}/\Delta_D)^2 \) and \( (\text{depth}/\Delta_D)^2 \), where \( \Delta_{\text{hyp}} \) is the total width of the structure. The coefficient 0.254 corresponds to the less favorable case of a doublet of equal amplitude. The line under study has a 12 components hyperfine structure of the order of 150 kHz which can be calculated or measured by saturation spectroscopy [13]. Its contribution to the linewidth could be also precisely taken into account, reducing the associated uncertainty to a negligible level. Finally, at a relative uncertainty of \( 10^{-6} \), only the homogeneous broadening, which ranges between \( 10^{-2} \) and \( 10^{-4} \) \( \Delta_D \) under our experimental conditions, contributes to the linewidth. The natural linewidth of the order of 1 Hz is negligible. The only parameter of importance is the relative pressure in the cell which is carefully measured, as explained below.

Finally, the experimental spectra have been fitted with the exponential of the Gaussian profile:

\[
\alpha(\nu) = An_0 \exp\left(-\frac{(\nu - \nu_0)^2}{\Delta(n_0)^2}\right),
\]

where \( n_0 \) is the population density in the considered lower level, a quantity proportional to the pressure, \( A \) is a constant specific to our transition, \( \nu \) is the laser frequency, \( \nu_0 \) is the resonance frequency, and \( \Delta(n_0) \) is the 1/e-fold half-width of the Gaussian. The fit gives the two key parameters: the width of the Gaussian and the amplitude. As the pressure is decreased to zero, the width converges linearly to the Doppler width, and we have checked that the residuals become negligible. The amplitude \( An_0 \) determined by the fit is, in fact, a relative measurement of the pressure. This way to calibrate the pressure is much more precise than by a pressure gauge and is particularly appropriate for an extrapolation to zero pressure. However, this parameter is related to the pressure of the active gas, while the width of the Gaussian depends on the total pressure including the impurities in the cell which must be eliminated as much as possible for a correct extrapolation to zero pressure.

**Results and discussion.**—Figure 2 displays a series of absorption spectra at pressures between 0.2 and 10 Pa. To obtain a good signal-to-noise ratio, we operate with an absorption between 10% and 80%, and at the highest pressures the line shape clearly differs from a Gaussian. The absolute pressure is measured with a Baratron gauge, but this value is not used for the analysis of the results, as explained above. A typical signal-to-noise ratio \( (S/N) \) under the best conditions is \( 10^3 \) for a time constant of 20 ms. A set of 2000 spectra was recorded over more than one month. Figure 3 displays the linear regression which leads to the determination of the Doppler width by extrapolation to zero pressure. Experimental linewidths depart from the Doppler limit by less than 2%, which confirms that the profile is very close to the exponential of a Gaussian. The relative calibration of the pressure axis is systematically performed by the amplitude of the signal, as explained in the previous section. This uncertainty which is directly related to the \( S/N \) is negligible for the extrapolation. The resulting Doppler e-fold half-width is

<table>
<thead>
<tr>
<th>Pressure (Pa)</th>
<th>Absorbed Amplitude (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>10%</td>
</tr>
<tr>
<td>1</td>
<td>80%</td>
</tr>
<tr>
<td>10</td>
<td>70%</td>
</tr>
</tbody>
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**FIG. 2.** Series of absorption spectra at different pressures.
Boltzmann constant which reaches an uncertainty of 10^-6 level, a potential accuracy comparable to that of the acoustic method should be possible. This method is very general and is a direct application of the first principles: the direct measurement of the thermal energy related to 1 degree of freedom of the system. In fact, the line profile reflects the velocity distribution along the laser beam axis for molecules in a given rovibrational level, while the measured temperature is that of the whole sample. Thus, the observation of a common value by using various transitions and temperatures leads to a partial check of the equipartition principle. Moreover, our method can be easily applied to different physical systems, different molecules, and isotopes in a very large range of temperatures. One should also explore, especially at higher pressure, the influence of the adsorption energy on the walls, the nonideal character of the gas for a possible departure from a Maxwell-Boltzmann distribution. In addition, our experiment will open access to a detailed study of the Lamb-Dicke effect. Finally, the measurement of the Doppler width in gases will give an universal way to measure the absolute thermodynamical temperature.

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