Spectral Simplification by Enclosive Flow Cooling I - FT-IR Spectroscopy of Supercooled Gases at 100 K

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For the simplification of molecular spectra and increase of spectral line intensity the enclosive flow cooling technique was developed. The vertical cell arrangement only needs one warm window and proved to be robust and easy to manage. In this work, the room temperature absorption spectra of CO₂, CH₄ and CHF₃ are compared with the spectra at 100 K. The theoretically expected spectral simplification effects could be verified. As opposed to supersonic jet cooling, the optical absorption efficiency of the method is several orders of magnitude higher. Furthermore, the new cooling technique offers promising applications in generation and spectroscopy of molecular clusters, in trace gas analysis and in simulation of low-temperature processes in the atmosphere of the Earth and other planets.

1. SPECTRAL COOLING EFFECTS

The rotation-vibration spectra of gaseous molecules at standard conditions increase in complexity with increasing number of atoms and decreasing symmetry. A simplification of the spectrum can be achieved by cooling or supercooling the sample gas. The most important spectral simplifications observed when supercooling the sample gas can be traced to the reduction of the number of lines in rotational structures, of the total band extension, of the collision broadening γc ~ n' T" (μ = 0.5 under conditions of ideal gases), of the Doppler line width γ₁ ~ (T(1/2), of the hot bands and of the interference of perturbing gases.

Supercooling the sample gas also increases the height of some of the intense spectral lines in a rotation-vibration band. For constant particle number density n, the temperature dependence of the height of low-J rotation-vibration lines is approximately given by:

\[ \text{Maximum line height} \propto T^{-1.5} \]

The exponent -1.5 in equation (1) is composed of two summands: -0.5 results from reduction of the line width, and -1 roughly describes the increase of the population of low-lying energy levels with decreasing temperature (Table 1).

<table>
<thead>
<tr>
<th>Maximum line height</th>
<th>Temperature / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>293 (room temperature)</td>
</tr>
<tr>
<td>5</td>
<td>100 (this experiment)</td>
</tr>
<tr>
<td>7</td>
<td>77 (LN₂)</td>
</tr>
<tr>
<td>583</td>
<td>4.2 (LHe)</td>
</tr>
<tr>
<td>1548</td>
<td>2.2 (λ-point He)</td>
</tr>
</tbody>
</table>
2. COOLING PRINCIPLE

The enclosive flow cooling technique [1,2,3] works in the following manner. A cooling gas is sucked from the outside through radial holes in the wall of a metal hollow cylinder or through a porous sinter metal hollow cylinder towards its axis, Figure 1. A laminar, axially symmetrical flow of cooling gas develops to which the sample gas is added through a heatable tube at the cylinder front end. The cooling gas encloses the sample gas beam, confines it to form a narrow column, cools it down and advects it along the cylinder axis, preventing it from wall adsorption. The sample gas and the cooling gas are removed from the chamber through a suction torus located directly above a mirror at the bottom of the cell.

Optical absorption, e.g. of a laser beam, can be observed along the cylinder axis where the sample gas concentration is highest. Furthermore, the enclosive gas flow prevents the cold mirror from optically disturbing sample gas adsorption on its surface. The measuring light beam enters the cell from the top through a heated CaF₂ window and is reflected in itself by the heatable mirror. In this way the effective absorption length is twice the cell length, and only one warm window is required. The parameters that can be varied include: pressure, sample and cooling gas flow, average temperature, entrance temperature of the sample gas, flow profile of the cooling gas and nature of the cooling and the carrier gas.

3. EXPERIMENTAL SETUP

The prototype enclosive flow cooling cell has in practice proved to be robust and easy to handle. With liquid nitrogen as a coolant, a mean sample gas temperature of less than 100 K was obtained. The spectral simplifications which can be achieved by the new cooling method were investigated with tunable diode laser absorption spectroscopy (TDLAS, see accompanying paper II) and with a Magna 550 FTIR spectrometer from NICOLET. For this latter purpose a special device has been built to couple the strongly divergent beam of infrared light into and out of the cooling cell with an efficiency of > 30 %. In order to eliminate water vapor in the beam, the beam path is closed off from ambient air and flushed with nitrogen; remaining water vapor condenses at the cool lid of the cell.

The lowest average gas temperature reached during the measurements was about 85 K. Within the flow path, the temperature gradient is below 10 K / 0.4 m. The vertical cell arrangement with only one window has proved a viable construction concept. Stable temperature layers appear. The window is heated to room temperature to avoid sample gas adsorption, the mirror at the cell bottom can be heated when necessary. The cooling cell works for two weeks without warm-up and cleaning.
4. RESULTS AND DISCUSSION

The effects of spectral simplification can be seen in Figures 2 to 9. In Figures 2 and 3, room-temperature and low-temperature spectra of the $\nu_3$ normal vibration mode of carbon dioxide are presented. The band width in the low-temperature spectrum is reduced by a factor of about 2/3. The hot band, strongly present at room temperature, disappears completely at 135 K. The reduction of contributions from interfering gases is demonstrated in the example of the $^{13}$CO$_2$ isotope band between 2250 and 2310 cm$^{-1}$. In the low-temperature spectrum the region around 2305 cm$^{-1}$ in which isotope and hot band are superimposed on the $^{12}$CO$_2$ band becomes nearly free from any spectral lines. The intensity of cluster formation that manifests itself by a superimposed peak near 2360 cm$^{-1}$ can be adjusted in a wide range by variation of the experimental parameters. This is in agreement with results of ref. [4].

In Figures 4 and 6, room-temperature and low-temperature spectra of the degenerated $\nu_3$ deformation mode of methane at 293 K are presented. By cooling to 100 K, the band width decreases to about half its value. At 100 K, the Q branch is simplified considerably and thinned out with respect to its rotational structure, see Figures 5 and 7. The $T^{0.5}$ dependence of pressure and Doppler broadening was examined with TDLAS [5]. Figures 8 and 9 show room-temperature and low-temperature spectra of the interacting $\nu_2$, $\nu_3$ and $\nu_3 + \nu_6$ bands of trifluoromethane, previously investigated in ref. [6]. One can clearly see the $\nu_2$ band at 1142 cm$^{-1}$ come out at 105 K. The width of the central region is reduced to about 2/3 of its room-temperature value.

The advantages of enclosive flow cooling over supersonic jet cooling [7] are the following ones. The sample gas is in thermal equilibrium, thus rotation, vibration and translation temperatures are the same. The optical absorption efficiency is two orders of magnitude higher because of the longer absorption path (about 1 m compared to a few mm). If absorption efficiency is...
Figures 4 and 5. FTIR spectrum of CH$_4$ at 293 K, 100 mbar, 3995 ppmv CH$_4$ in N$_2$, 0.1 cm$^{-1}$ resolution, cuvette.

Figures 6 and 7. FTIR spectrum of CH$_4$ at 100 K, 100 mbar, 3995 ppmv CH$_4$ in N$_2$, 0.1 cm$^{-1}$ resolution, cooling cell.
defined relatively to the sample gas quantity, the improvement amounts to 5 to 6 orders of magnitude because the flow velocity is much lower (about 0.03 compared to 1000 m/s), adsorption losses considered.

5. OUTLOOK

Owing to the great potential for line intensity increase at very low temperatures (see Table 1) liquid-helium (LHe) flow cooling is planned for the near future. The following applications will benefit from the new cooling technique: • investigation of spectral features of molecular gases, • study of diffusion processes of supercooled gases, • generation, spectroscopy and investigation of the diffusion behaviour of molecule clusters, • trace gas analysis by FTIR and TDL spectroscopy, and • simulation of low-temperature processes in the atmosphere of the Earth and other planets.

Figures 8 and 9. FTIR spectrum of CHF₃ at 100 mbar, 1040 ppmv in N₂, 0.1 cm⁻¹ resolution, enclosive flow cooling cell. Top: 293 K. Bottom: 105 K.

REFERENCES


