Rotational Spectroscopy

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Direct Time-Domain Observation of Conformational Relaxation in Gas-Phase Cold Collisions

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Abstract: *Cooling molecules in the gas phase is important for precision spectroscopy, cold molecule physics, and physical chemistry. Measurements of conformational relaxation cross sections shed important light on potential energy surfaces and energy flow within a molecule. However, gas-phase conformational cooling has not been previously observed directly. In this work, we directly observe conformational dynamics of 1,2-propanediol in cold (6 K) collisions with atomic helium using microwave spectroscopy and buffer-gas cooling. Precise knowledge and control of the collisional environment in the buffer-gas allows us to measure the absolute collision cross-section for conformational relaxation. Several conformers of 1,2-propanediol are investigated and found to have relaxation cross-sections with He ranging from* $\sigma = 4.7(3.0) \times 10^{-18}$ *cm*^{2} *to* $\sigma > 5 \times 10^{-16}$ *cm*^{2}*. Our method is applicable to a broad class of molecules and could be used to provide information about the potential energy surfaces of previously uninvestigated molecules.*

The structure of organic molecules is critical to molecular function in biology and chemistry. In particular, understanding the properties of conformers, which are isomers differing by rotation about one or more chemical bonds, provides insight relevant to diverse phenomena such as chemical and catalytic activity,[1,2] the folding of proteins,[3–6] behavior of DNA,[1,7] metabolism of sugar,[8,9] and reactions of organic molecules with trapped ions.[10] Conformers may be observed in many environments, using a diverse set of spectroscopic methods. For example, molecular beam microwave spectroscopy can provide detailed information about structure and indirect measurement of conformer energies.[11–13] Cryogenic matrix isolation spectroscopy can measure dynamics in a solid state environment[14] and ultrafast spectroscopy can measure both structure and reaction dynamics.[15] Each method provides a window into certain conformational properties and provides data that can test quantum-chemistry theory calculations.

Much of our understanding of gas-phase conformers comes from jet cooled molecular beam spectroscopy and cryogenic matrix isolation spectroscopy experiments. The low ro-vibrational and moving-frame temperature of molecules in a supersonic jet allows for precise, conformer specific spectroscopy.[16] Although such experiments typically realize a rotational and translational temperature of a few Kelvin, in many cases excited conformers with energies of hundreds of Kelvin remain in the sample. The relaxation (cooling) of conformational degrees of freedom is the conversion of a high energy conformer into a lower energy conformer. It can be induced by gas-phase collisions or by couplings to a solid state environment, and typically happens substantially slower than rotational and translational cooling. Quantitative study of relaxation provides key information about conformational interconversion barriers. In jet cooled molecular beam spectroscopy, conclusions about the interconversion barriers separating conformers can be obtained by observing the relative population of conformers in the cold, collision free beam as the carrier gas is varied,[17,18] but direct, real-time observation of collision induced gas-phase conformational relaxation has not previously been achieved. The primary limitation preventing continuous relaxation measurements in jet cooled molecular beams is the short duration and rapidly changing conditions of the collisional environment in the supersonic expansion. Other methods to study conformational relaxation and potential energy surfaces include conformer-specific matrix isolation spectroscopy, stimulated emission pumping spectroscopy, and optical methods.[19–21]

Fourier transform microwave (FTMW) rotational spectroscopy is an efficient tool to study the dynamics of conformational relaxation. Spectral lines from distinct conformers are easily distinguished from one another. FTMW spectroscopy has been used to detect conformers, isotopomers, and clusters of molecules in the gas-phase. Due to the continuous nature of the buffer-gas source, microwave spectroscopy in a buffer-gas environment can be up to two orders of magnitude more sensitive than in comparable pulsed supersonic jet experiments[22] and has been used to perform mixture analysis, as well as measurements of the chirality of samples.[23] Buffer-gas cooling has been shown to cool a diverse set of organic molecules to the few Kelvin temperature range.[22,24,25] The density of buffer-gas in a buffer-gas cell is constant, low, and can be accurately

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measured. This allows for precise measurements of atom-molecule inelastic cross-sections.[26,27]

We report here direct observation of conformational relaxation using microwave spectroscopy paired with buffer-gas cooling. Owing to the controlled and well understood collisional environment in the buffer-gas, the conformation-changing scattering cross-section can be measured. This provides a probe of the conformational potential surface of the molecule. Collisional frequencies can be controlled via the buffer-gas density in the cell, which is low enough to allow for high precision, state-specific spectroscopy with resolution comparable to that achieved in jet cooled beams.

We choose the chiral molecule 1,2-propanediol as the subject for this conformational relaxation study. 1,2-propanediol is spectroscopically well understood and has been previously used in both pulsed-jet and buffer-gas cooling microwave spectroscopy experiments.[22,28] Conformers of 1,2-propanediol and similar molecules have been spectroscopically identified in pulsed-jet experiments and ab-initio calculations on the conformational potential surface have guided the spectroscopic analysis of these molecules.[29–31] In our current study, we observe seven conformers of 1,2-propanediol, conformers #1–#7, which are described in detail in Ref. [28].[*]

The experimental apparatus used for these measurements is a chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer that uses a cryogenic buffer-gas cooling cell (see Figure 1). Previous generations of the apparatus, similar to the one used here, are described in detail elsewhere.[22,23] Briefly, a 20 cm sided cubic buffer-gas cell is held at 6 Kelvin by a pulse tube cryocooler. On one side of the buffer-gas cell is a 1.5 cm diameter inlet hole through which molecules are introduced. Located 1.5 cm from this cell is a fast valve at temperature $T = 320$ Kelvin. This valve is backed by pure gaseous 1,2-propanediol at a few torr. The low backing pressure and lack of carrier gas imply that little or no cooling will occur as molecules effuse through the valve. Warm molecules effusing from this pulsed valve enter the cell and cool translationally and rotationally in 1–2 ms. The cold molecules remain in the cell until they are lost via diffusion to the cell wall after undergoing approximately one thousand collisions in 10 ms. The input flow of molecules can be operated in either a pulsed mode, or a continuous mode where the valve is held open. Further details of the apparatus are described in the supplementary material.

The experimental timing sequence is shown in Figure 2. Microwave spectra of 1,2-propanediol are recorded during 8 ms long time windows after the opening of the pulsed valve, delayed by an interval Δt ranging from $\Delta t = 10$ ms to $\Delta t = 34$ ms. After this time Δt, 200 microwave drive chirps of 100 MHz in width polarize the molecules. After each chirp, a 20 μs long FID trace is collected via the receiver horn. These FID signals are summed and then Fourier transformed to produce a spectrum.

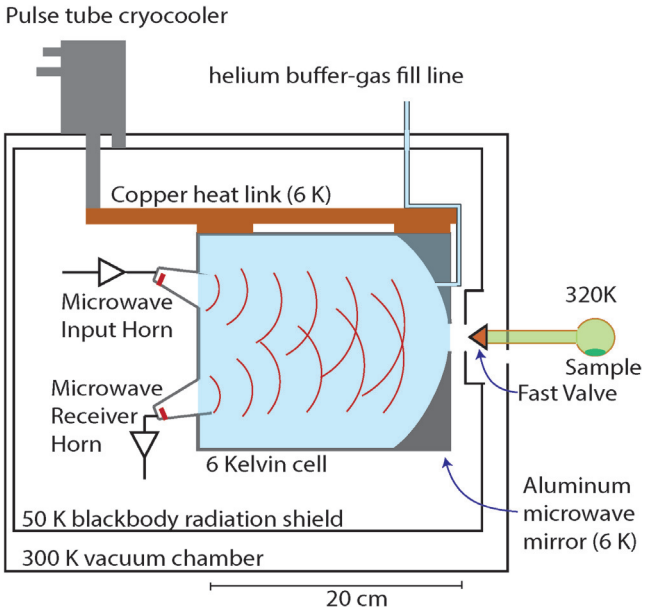

Figure 1. Experimental apparatus (not to scale). Molecules are loaded into the cold cell via injection from a warm ($T = 320$ Kelvin) pulsed valve and through a hole in a microwave mirror, where they thermalize and eventually diffuse to the cold cell walls and freeze. The translationally and rotationally cold gas is polarized by a brief, strong microwave pulse emitted from the microwave input horn. The resulting free induction decay is collected by a microwave receiver horn coupled to the same microwave mode. The signal from the receiver horn is amplified, mixed down to RF frequencies, and digitized.

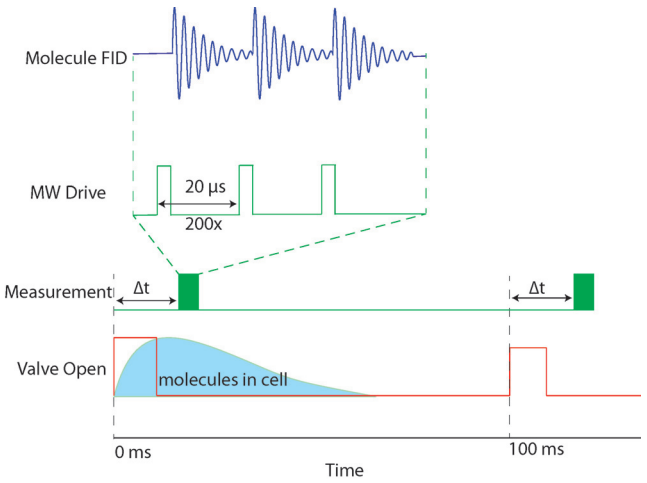

Figure 2. The experimental timing protocol. The pulsed valve is opened for 10 ms, which introduces the packet of molecules into the cell. Molecules diffuse through the cell for 10–20 ms, as shown by the blue shaded region. At a time Δt after the valve is triggered, the measurement sequence begins. The measurement is composed of 200 polarizing chirped microwave pulses with a repetition rate of 50 kHz, which is limited by the mean helium collision time of 10 μs. The free induction decay (FID) signal is recorded in the time following the polarizing pulse. All FID signals for a given Δt are averaged together. Varying Δt allows construction of a "movie" of the conformer populations.

This timing sequence allows us to measure the conformer populations as a function of time after warm molecules are

[*] Throughout this paper, we use the conformer labels from Lovas et al.[28] Conformer #3 is the ground state.

introduced into the cell. Population dynamics reflect both diffusion to the cell walls and conformational relaxation. Our initial model includes non-zero couplings between conformers as suggested in Lovas et al. A schematic of this model is shown in Figure 3. Diffusion dynamics in the absence of conformational relaxation were first characterized by studying methyl acetylene, a symmetric top molecule with only a single conformer. Details of both the diffusion model and the conformational relaxation model are presented in the supplementary material. A typical set of spectra is shown in Figure 4, measured populations are shown in Figure 5, and measured relaxation cross rates and cross sections are presented in Table 1.

We see clear evidence for conformational relaxation along all of the pathways suggested to be strong by Lovas et al. We also observe a similar relaxation rate out of conformer #4, which is not predicted by Lovas et al. Our method cannot unambiguously determine which state conformer #4 is decaying into.

The measured relaxation rates differ significantly from conformer to conformer, suggesting that this measurement is

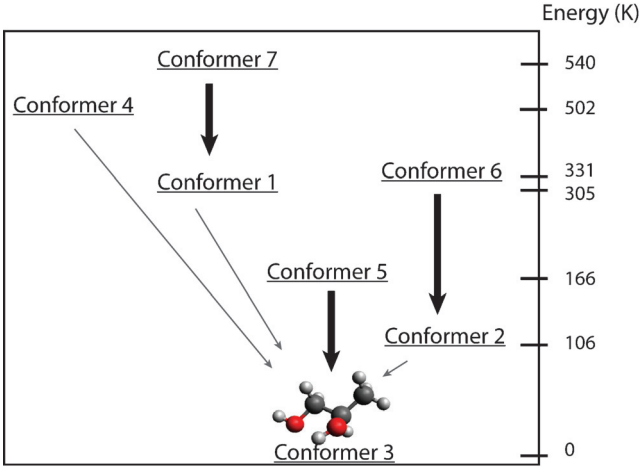

Figure 3. The observed 1,2-propanediol system with hypothesized conformational cooling pathways for 1,2-propanediol. Pathways denoted with thick black arrows involve a 110–120 degree rotation of an almost free OH group and are expected to have relatively large relaxation rates. Pathways denoted with thin gray arrows are weaker channels and represent relaxations involving a greater degree of structural change to the molecule, as discussed in Ref. [28].

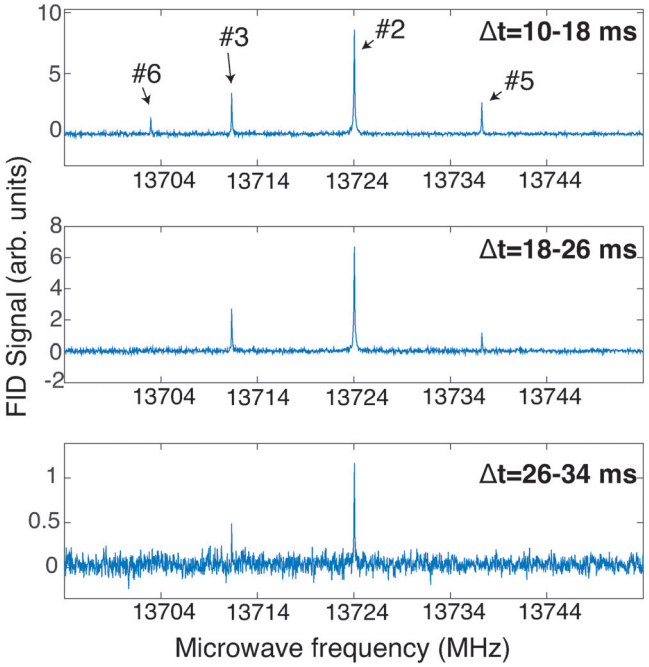

Figure 4. Spectra of 1,2-propanediol in the region from 13 694 MHz to 13 754 MHz taken at different time intervals Δt after the pulsed valve opens. The molecular signal decays over time due to diffusion to the cell walls, but is plotted on axes scaled to the magnitude of the signal. This decay results in decreased signal, and thus decreased signal to noise, at later times. Conformational relaxation is visible as the changing ratio of peak heights over time. Here, conformer #6 is the fastest to relax, followed by conformer #5. Conformer #2 appears to decay very slowly, if at all, to the ground state (conformer #3).

Table 1: Rates α, collision cross-sections σ, and values of the ratio $\gamma_R = \bar{\sigma}_R/\sigma_{a\to b}$ for the five measured conformational relaxation rates and the 1,2-propanediol diffusion rate as measured at the buffer-gas density of $n_{He} = 1.35\times10^{14}$ cm^{-3}.

Pathway	ΔEnergy [K]	α ($\times10^3$ s^{-1})	σ ($\times10^{-14}$ cm^2)	γ_R
#2–#3	106	0.01(1)	$4.7(3.0)\times10^{-4}$	$>10^4$
#5–#3	166	0.15(6)	$7.0(4.5)\times10^{-3}$	$8.2(3.3)\times10^2$
#6–#2	225	0.3(1)	$1.4(0.9)\times10^{-2}$	$4.1(1.6)\times10^2$
#7–#1	235	>0.5	$>5\times10^{-2}$	$<10^2$
#4–#3	502	0.12(5)	$5.6(3.6)\times10^{-3}$	$1.0(0.4)\times10^3$
Diffusion	–	0.14(6)	$6.6(3.3)\times10^{-3}$	–

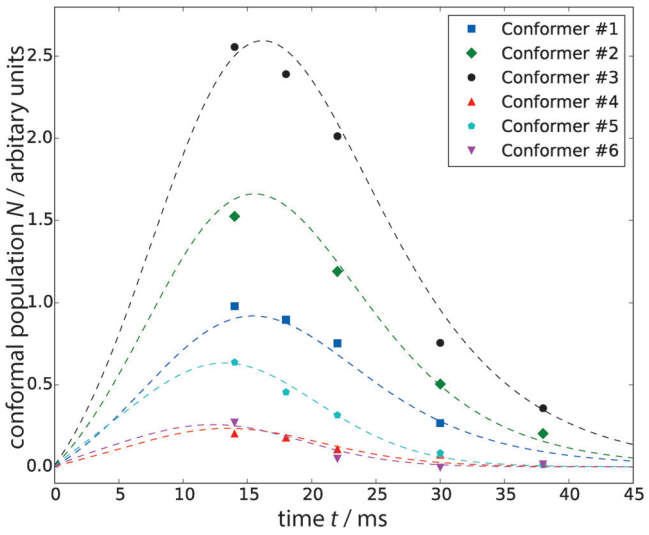

Figure 5. Measured time-dependent populations of conformers #1–#6 of 1,2-propanediol in the buffer-gas cell at a helium density $n_{He} = 1.4(7)\times10^{14}$ cm^{-3}. Each population is calculated from the observed line strength by dividing by the predicted line strength, as calculated from the PGOPHER program. The time evolution of the conformer populations is fit to a simple diffusion model with one free parameter, $\alpha_{a\to b}$, for each conformer. The time for each point is set to the center of the integration window.

sensitive to the potential barrier. Conformers #4, #5, and #6 are measured to have inelastic relaxation rates of $\alpha_{4\to3} = 0.12(5)\times10^3\ s^{-1}$, $\alpha_{5\to3} = 0.15(6)\times10^3\ s^{-1}$, and $\alpha_{6\to2} = 0.3(1)\times10^3\ s^{-1}$ respectively, compared to the diffusion rate of $\alpha = 0.14(6)\times10^3\ s^{-1}$. We also see trace levels of conformer #7 when opening the valve continuously, but this conformer is not detectable when operating the valve in the pulsed mode. This trace signal, and the high initial populations of conformer #1, lead us to hypothesize a high rate of relaxation from conformer #7 into conformer #1 of $\alpha_{7\to1} > 0.5\times10^3\ s^{-1}$. Table 1 summarizes the inelastic relaxation rates of the conformers and their ratios with the elastic cross sections at a buffer-gas density of $n_{He} = 1.4(7)\times10^{14}\ cm^{-3}$. Although the relaxation from #2→#3 listed in Table 1 does not appear to be statistically significant, we see additional evidence for slow relaxation along this path in high-sensitivity steady state data taken with the valve held open continuously.

The experiment was repeated at a helium density higher by a ratio of $r = 1.33(6)$. The relaxation rates are observed to scale linearly with the buffer-gas density, while the diffusion rate α scales as n_{He}^{-1}, as expected in a simple diffusion model. This is additional evidence that the conformational relaxation we see here is the result of collisions with the helium buffer-gas. We assign a conformational relaxation collision cross-section to each pathway using the standard definition of cross-section,

$$\sigma_{a\to b} = \alpha_{a\to b}/n_{He}\bar{\nu}, \quad (1)$$

where $\bar{\nu}$ is dominated by $\bar{\nu}_{He}$ to the 95% level. These values are summarized in Table 1. Also shown is the ratio of rotational relaxation to conformational relaxation collision cross-sections, $\gamma_R = \bar{\sigma}_R/\sigma_{a\to b}$. The rotational relaxation rate $n\bar{\nu}\sigma_R$ can be measured directly from the lifetime of the microwave free induction decay. The rotational relaxation cross section σ_R is measured to be $\bar{\sigma}_R = 5.8(2.9)\times10^{-14}\ cm^2$ and is found to vary by less than 25% across all conformers and rotational states. The quoted error in Table 1 is combined statistical and systematic, and is dominated by uncertainties in the absolute frequency dependent gain of the detection system and the absolute buffer-gas density in the cell.

In conclusion, we have directly observed conformational relaxation of 1,2-propanediol in a cryogenic environment. Relative conformer populations have been observed during cooling and relaxation cross-sections of five of the excited conformers have been derived from these measurements. Our measurements show agreement with the strong relaxation pathways previously predicted and discover an additional strong pathway, previously thought to be weak.

A detailed understanding of the mechanisms behind the conformational relaxation remains unknown. Further measurement using different isotopologues, rotational states, or at different collision energies (e.g. via adjusting the buffer-gas temperature) would provide more data for theoretical comparison and model building. This method can be applied to any polar, vaporizable molecule. In this way, information about cooling pathways and conformational structure can be gained for a wide range of important molecules.

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