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PAPER

High-resolution mid-infrared spectroscopy of buffer-gas-cooled methyltrioxorhenium molecules

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Abstract

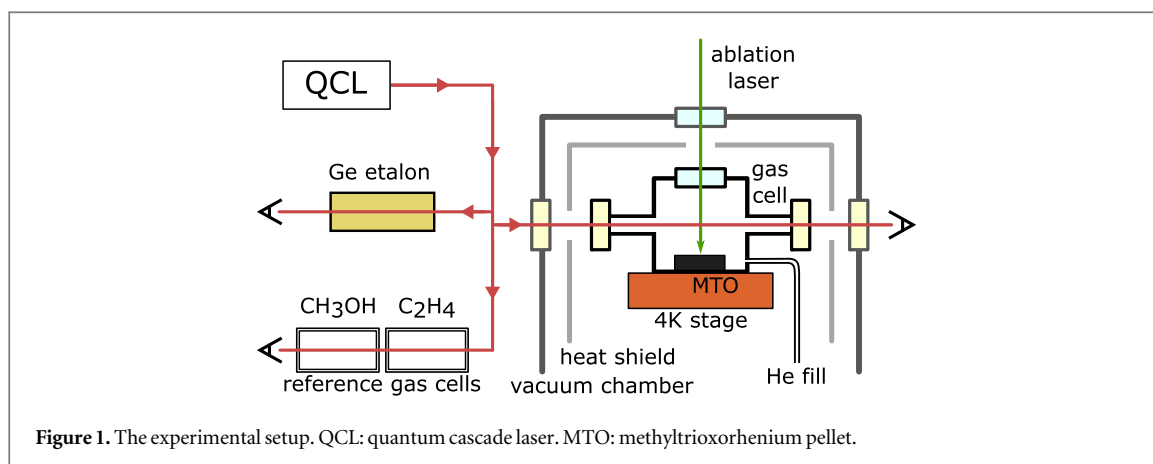
We demonstrate cryogenic buffer-gas cooling of gas-phase methyltrioxorhenium (MTO). This molecule is closely related to chiral organometallic molecules where the parity-violating energy differences between enantiomers is measurable. The molecules are produced with a rotational temperature of approximately 6 K by laser ablation of an MTO pellet inside a cryogenic helium buffer gas cell. Facilitated by the low temperature, we demonstrate absorption spectroscopy of the 10.2 μm antisymmetric Re=O stretching mode of MTO with a resolution of 8 MHz and a frequency accuracy of 30 MHz. We partially resolve the hyperfine structure and measure the nuclear quadrupole coupling of the excited vibrational state. Our ability to produce dense samples of complex molecules of this type at low temperatures represents a key step towards a precision measurement of parity violation in a chiral species.

1. Introduction

There is a demand for precise spectroscopy of increasingly complex molecules. Precise knowledge of molecular constants is required for modeling our atmosphere [1, 2], interpreting astrophysical and planetary spectra [3], studying collision physics [4, 5], and testing fundamental physics, including tests of fundamental symmetries [6–10], and measurements of fundamental constants [11, 12] and their possible variation [13–16].

One such test is the measurement of energy differences between chiral enantiomers induced by parity violation, an idea that dates back to the 1970s [17, 18]. A precise measurement could contribute to the determination of several parameters of the standard model of particle physics [19], calibrate relativistic quantum chemistry calculations [20, 21], and shed light on the question of biomolecular homochirality [22]. We are constructing a Ramsey interferometer to compare the vibrational frequencies of the two enantiomers of a chiral molecule [8, 20]. For this work, a cold, slow-moving, intense beam of these molecules is desirable to increase the resolution and statistical precision, and to reduce systematic uncertainties relating to the beam velocity. Buffer-gas-cooled beams can provide the low temperature, low speed, and high intensity needed [23, 24].

To form a buffer-gas-cooled beam, hot molecules are introduced into a cell cooled to ~ 4 K, where they cool through collisions with helium gas and then flow out of an exit hole. Various methods have been demonstrated for loading molecules into the cell, including capillary injection [25], direct loading from an oven or beam [26], and laser ablation [23, 27, 28]. The methods were first developed for diatomic molecules, but more recently buffer-gas cooling of more complex molecules has been demonstrated. Organic molecules with high volatility have been introduced via direct gas flow [29] or from an oven or beam [30–34]. Various spectroscopic techniques have been applied to these cooled molecules, taking advantage of the narrow linewidths, larger signals and simplified spectra that result from the cooling. These include Fourier transform microwave



spectroscopy [26, 30–32], visible and ultra-violet light induced fluorescence [29, 33], cavity ring-down spectroscopy around $1.5\ \mu\text{m}$ [35], and cavity-enhanced frequency comb spectroscopy around $3\ \mu\text{m}$ [34]. These techniques have enabled the exploration of atom–molecule and molecule–molecule collisions [29, 30, 33, 34], measurements of rotational and vibrational relaxation cross-sections at low temperature [30], the elucidation of rovibrational structures and determination of molecular parameters [34], and the demonstration of a novel chiral analysis method for measuring enantiomeric excess [31, 32].

Here, we report the buffer-gas cooling of the first organo-metallic species, methyltrioxorhenium (MTO, CH_3ReO_3), a far less volatile polyatomic molecule and an achiral precursor of molecules of interest for parity violation measurements in chiral molecules [36]. We report a number of advances. (1) We extend buffer-gas cooling to a new class of molecules, and we introduce them into the cell by laser ablation, previously used only for diatomic molecules. We show that this species survives the ablation process and that the translational and rotational degrees of freedom cool efficiently through collisions with helium. MTO can also be brought into the gas phase by heating, but many other polyatomic molecules have little vapour pressure at easily accessible temperatures, so the ability to introduce them by laser ablation is important. (2) We demonstrate the first precise spectroscopic measurements of buffer-gas-cooled molecules in the mid-infrared region around $10\ \mu\text{m}$, obtaining rotational and hyperfine-resolved absorption spectra in the $\text{Re}=\text{O}$ stretching region of MTO. This demonstrates the potential for very high resolution spectroscopic measurements of these cooled molecules in the fingerprint region, at ro-vibrational temperatures that allow for unambiguous assignment of transitions. (3) We determine the nuclear quadrupole coupling of the excited vibrational state, which is unprecedented for such a complex molecule. Together, these advances demonstrate some of the methods needed for a measurement of parity violation in chiral molecules. We note that MTO has also recently been injected into a buffer-gas cell from a heated pulsed valve, and that broadband Fourier transform microwave spectroscopy of these cooled molecules was performed [37]. We also note the recent high-resolution microwave spectroscopy of a chiral oxorhenium compound [38] which is complementary to the vibrational spectroscopy technique used here.

2. Apparatus

The experimental setup is shown schematically in figure 1. The cryogenic apparatus [28] consists of a closed copper cell with a cubic internal void of 30 mm side length attached to the cold stage of a closed-cycle cryocooler. The cell has a measured temperature of 6 K. Windows are indium-sealed onto three sides of the cell to provide optical access, and a narrow tube fills the cell with helium gas. We find that the ablation process (see below) alters the pressure in the cell. During operation, the pressure measured at the room-temperature end of the tube is 1×10^{-2} mbar, which corresponds to a time-averaged helium density inside the cell of approximately $4 \times 10^{15}\ \text{cm}^{-3}$. The cell is surrounded by aluminium radiation shields at a temperature of about 40 K, and is housed in a vacuum chamber at a pressure of 4×10^{-7} mbar.

Inside the cell, mounted on one face, is a pellet made from 98% purity MTO (Strem Chemical Inc.) that has been ground in a mortar, mixed with a few percent of graphite to help make it opaque at 1064 nm, and then pressed for several minutes in a 2 ton pneumatic press. MTO molecules are injected into the cell by ablating this pellet with pulses of light from a Nd:YAG laser with wavelength 1064 nm, energy 30 mJ, duration 8 ns, and spot size $\sim 150\ \mu\text{m}$. These molecules thermalize with the helium buffer gas and are detected by laser absorption spectroscopy of the $\text{Re}=\text{O}$ antisymmetric stretching mode at about $976\ \text{cm}^{-1}$. The probe laser is a free-running continuous-wave single-mode distributed-feedback quantum cascade laser (QCL) with an estimated linewidth

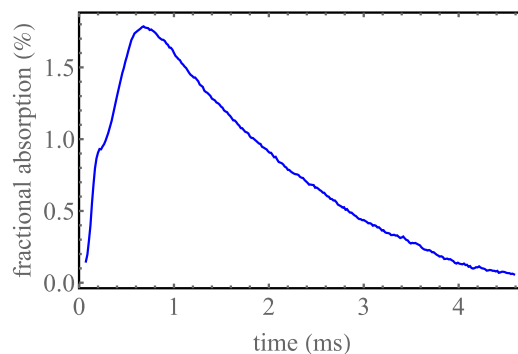


Figure 2. Laser absorption in the cell as a function of time after the ablation pulse, which defines $t = 0$. Average of 25 consecutive shots.

of about 1 MHz at 1 s (which is the typical timescale for a measurement at a single frequency; see later). When cooled to 263 K it delivers about 40 mW of light at $\sim 10.25 \mu\text{m}$. About $1 \mu\text{W}$ of this light, in a beam with a diameter of $\approx 3 \text{ mm}$, is sent through the cell via Zn:Se windows mounted on stand off tubes to minimize contamination by ablated material. The transmitted power is measured on a liquid nitrogen cooled HgCdTe detector. The laser frequency can be changed by stepping the supply current. The relative frequency is monitored by measuring the intensity transmitted through one of a pair of temperature-stabilized solid germanium etalons with free spectral ranges of 1450 and 490 MHz. Absolute laser frequencies are determined by measuring the transmission through a pair of reference cells containing methanol and ethene respectively at a pressure of approximately 3 mbar. The absorption line frequencies of these species are listed in the HITRAN database [39, 40].

3. Results

In each ‘shot’ of the experiment the probe laser has a fixed frequency and the intensities transmitted through the cryogenic cell, the etalon and the reference gas cells are recorded as a function of time t for 10 ms after an ablation pulse. Figure 2 shows MTO absorption as a function of time, averaged over 25 successive shots. With the laser on resonance with a strong transition, and under optimized conditions, we see a rapid rise in absorption to a peak of a few percent followed by a slower, roughly exponential, decay. This decay is due to diffusion to the cell walls, and the timescale of a few milliseconds is similar to that of diatomic molecules produced by laser ablation in similar-sized cells [23, 27, 41]. The peak absorption amplitude is relatively constant between successive shots but decreases slightly over a few minutes, which we attribute to a gradual reduction in ablation efficiency caused by modification of the pellet surface by the ablation process. The decay time of the absorption signal decreases much more significantly over this time, which we suggest is the result of changing helium density inside the cell—we observe that the MTO pellet adsorbs helium at low temperatures and speculate that a diminishing amount of this is liberated by successive ablation pulses.

At each laser frequency we average the data from 25 shots of the experiment. By using a repetition rate of 12.5 Hz, phase-locked to the 50 Hz mains frequency, we suppress electronic noise and ensure that the shots are equally sampled over the vibrations induced by the 1 Hz mechanical motion of the cryocooler. In the time-dependent absorption profiles such as the one in figure 2, we find that the peak absorption is more stable than the integrated absorption, and that the baseline varies greatly between shots primarily due to fringing effects caused by the windows which vibrate with the cooler. For these reasons, we determine the absorption at a given laser frequency by taking the standard deviation of the ordinate values in the averaged absorption signal.

Spectra are obtained by linearly stepping the laser current, I_{QCL} , recording the 25 shots at each frequency. At regular intervals we carry out wide scans covering up to 10 GHz to reconstruct a frequency scale. We divide up the etalon transmission signal into sections, typically 1–2 fringes wide, and fit Airy functions $A[f(I_{\text{QCL}})]$ to each section, where $f(I_{\text{QCL}})$ is a polynomial function. These fits establish the relationship between I_{QCL} and the relative frequency, giving a linear frequency scale with a relative uncertainty of a few MHz. These wide scans include a number of absorption lines from the reference cells which we use to establish the absolute frequency with an accuracy of about 30 MHz. The accuracy and the relative uncertainty of the frequency scale are mainly limited by residual long-term thermal drifts of the etalon length which can be reduced with an improved temperature stabilization. We use this periodically recalibrated frequency scale to carry out high-resolution scans over smaller regions that contain specific MTO absorption features of interest.

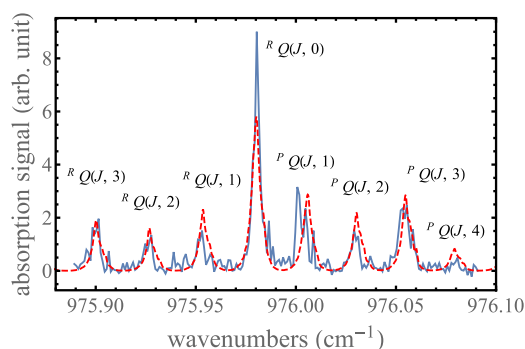


Figure 3. Linear absorption spectrum of the Q branch of the antisymmetric Re=O stretching mode of the ^{187}Re isotopologue of MTO. The height of the central peak corresponds to a few percent of absorption. The dashed (red) curve is a fit to the data (see text) from which a rotational temperature of 6 ± 3 K is inferred. Transitions are labeled using the notation $^{\Delta K}Q(J, K)$, and lines corresponding to different values of J are unresolved.

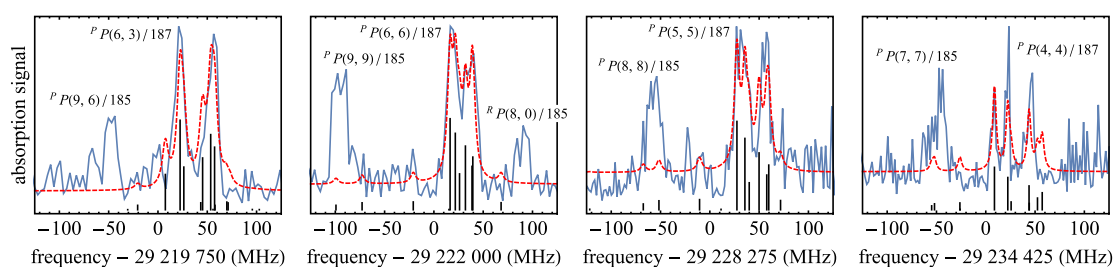


Figure 4. Linear absorption spectra in the P branch of the antisymmetric Re=O stretching mode of both MTO isotopologues. The highest peaks correspond to a few percent absorption. The observed lines are labeled with transition assignment/rhenium atomic mass number. The dashed (red) curve is a fit to the data that takes into account the hyperfine structure in the lower and upper vibrational levels of the ^{187}Re isotopologue. The bar spectrum indicates the positions and relative intensities of the fitted hyperfine components. The model spectrum does not include the ^{185}Re isotopologue, for which the hyperfine structure is not sufficiently resolved.

Figure 3 shows an example spectrum. The observed structure corresponds to the rovibrational contour of the Q branch of the ν_{as} antisymmetric Re=O stretching mode [42] of the ^{187}Re isotopologue of MTO centered around 976 cm^{-1} . Near its centre, this ν_{as} perpendicular band consists of a series of $^PQ(J, K)$ and $^RQ(J, K)$ branches for which K is fixed. In this notation, K is the quantum number for the projection of the total orbital angular momentum onto the molecular symmetry axis, and the superscripts P and R refer to transitions with $\Delta K = -1$ and $\Delta K = +1$ respectively. Each branch is composed of a number of lines which are unresolved in the spectrum shown, each corresponding to a different value of J (the total orbital angular momentum quantum number), with $J \geq K$. The figure also shows a fit of the data to a model calculated using a bar spectrum convolved with Lorentzian profiles. In this model, the line centers and intensities are found from an analysis of this vibrational mode of MTO that combines microwave, millimeter-wave and infrared data, as well as the data presented in this paper [43]. We use PGOPHER [44] to simulate spectra and fit the overall shape of the experimental data. Once the line centers and relative intensities are fixed, the remaining free parameters are a vertical scaling, the rotational temperature, T_{rot} , and the width of the individual Lorentzian profiles. We find $T_{\text{rot}} = 6 \pm 3$ K. Here, the uncertainty is dominated by a correlation between the vertical scaling factor and T_{rot} , and it is determined from the deviation in T_{rot} values found after various modifications in the fitting procedure (choice of initial parameter guesses, convolution with a Lorentzian or a Gaussian). Spectra acquired in various time windows following ablation indicate that T_{rot} has reached its final value within $440\text{ }\mu\text{s}$.

Further to the red of the Q branch, several P lines of both the ^{185}Re and ^{187}Re isotopologues of MTO were also probed. Figure 4 shows four of these spectra exhibiting both $^PP(J, K)$ and $^RP(J, K)$ lines. Here, the splitting in J is far bigger, and isolated rovibrational lines can thus be observed. Using these data, we measure the absolute frequencies of a number of transitions, as listed in table 1. The quantum number assignments are determined with the help of data from Asselin *et al* [43]. In the data shown in figure 4, we resolve neighbouring rovibrational lines of the ^{185}Re and ^{187}Re isotopologues of MTO. The observed relative line intensities are consistent with the natural isotopic abundances, allowing unambiguous assignments. This improves on two previous spectroscopic studies of supersonic jet-cooled MTO where the resolutions were 150 MHz (Fourier transform infrared spectroscopy [42]) and 120 MHz (laser absorption spectroscopy [43]). Thus, our data improves the accuracy of

Table 1. Centre frequencies of assigned rovibrational lines. The isotopologue is identified by the rhenium atomic mass number. Unresolved lines are assigned the same frequency. The 30 MHz uncertainty on transition frequencies is dominated by the long term drift of the reference etalon (see text).

Transition	Isotopologue	Frequency (THz)
$^P P(9, 6)$	185	29.219696(30)
$^P P(6, 3)$	187	29.219788(30)
$^P P(9, 9)$	185	29.221909(30)
$^P P(6, 6)$	187	29.222026(30)
$^R P(8, 0)$	185	29.222090(30)
$^R P(5, 0)$	187	29.224478(30)
$^P P(8, 3)$	185	
$^P P(8, 8)$	185	29.228220(30)
$^P P(5, 5)$	187	29.228315(30)
$^R P(4, 0)$	187	29.231475(30)
$^P P(7, 3)$	185	
$^P P(7, 7)$	185	29.234375(30)
$^P P(4, 4)$	187	29.234450(30)

some of the spectroscopic constants when used in a combined analysis with other datasets at various resolutions [43]. Here, we focus on an analysis of the hyperfine structure, which is partially resolved in our spectra.

The hyperfine structure is dominated by the interaction between the rhenium nuclear quadrupole moment and the gradient of the electric field at the nucleus. The spin-rotation interaction between the magnetic field induced by the molecular rotation and the magnetic moment of the rhenium nucleus is much smaller, but large enough that we include it in our analysis [42, 43]. Smaller magnetic hyperfine structure resulting from the spins of hydrogen nuclei can be neglected. We also neglect matrix elements of the electric quadrupole Hamiltonian that are off-diagonal in J , since their inclusion shifts the transition hyperfine components by less than 170 kHz.

Both rhenium isotopes have nuclear spin $I = 5/2$, so each of the rovibrational levels corresponding to the transitions in figure 4 is split into six F components, where F is the quantum number of the operator $\mathbf{F} = \mathbf{J} + \mathbf{I}$. The electric quadrupole interaction of vibrational state v is characterized by the quadrupole coupling constant eQq^v . For a symmetric top like MTO, the first-order energy shift is [45]

$$\Delta E_Q^v = eQq^v \left(3 \frac{K^2}{J(J+1)} - 1 \right) f(J, I, F),$$

where

$$f(J, I, F) = \frac{0.75C(C+1) - I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)},$$

and

$$C = F(F+1) - I(I+1) - J(J+1).$$

The centrifugal distortion induced modification of the electric field gradient leads to a dependence of the quadrupole coupling constant on J and K [46]

$$eQq^v = eQq_0^v + eQqJ^v(J(J+1) - K^2).$$

The energy shift due to the nuclear spin-rotation magnetic interaction in the vibrational state v is characterized by the spin-rotation parameters C_{aa}^v and C_{bb}^v (because of the C_{3v} symmetry of MTO, $C_{bb}^v = C_{cc}^v$) and is given by [45]

$$\Delta E_{\text{SR}}^{\nu} = \left(C_{\text{bb}}^{\nu} + (C_{\text{aa}}^{\nu} - C_{\text{bb}}^{\nu}) \frac{K^2}{J(J+1)} \right) C.$$

The experimental spectra of the $^P P(6, 3)$, $^P P(6, 6)$, $^P P(5, 5)$ and $^P P(4, 4)$ lines of the ^{187}Re MTO isotopologue displayed in figure 4 have been fitted by a bar spectrum convolved with Lorentzian profiles. Each of these transitions has six strong $\Delta F = \Delta J = -1$ hyperfine components and nine weaker $\Delta F = 0, +1$ components. Their relative intensities, proportional to the square of the dipole moment matrix elements, are [47]

$$(2F^1 + 1)(2F^0 + 1) \begin{Bmatrix} J^1 & F^1 & I \\ F^0 & J^0 & 1 \end{Bmatrix}^2,$$

where F^{ν} and J^{ν} are the quantum numbers in the lower ($\nu = 0$) and upper ($\nu = 1$) states. There are two sets of constants eQq_0^{ν} , $eQqJ^{\nu}$, C_{aa}^{ν} and C_{bb}^{ν} for the lower ($\nu = 0$) and the upper ($\nu = 1$) rovibrational levels. Those in $\nu = 0$ are fixed to the values extracted primarily from microwave and millimeter-wave spectroscopy [43]. The spin-rotation parameters in the excited state are too small for us to determine and so we fix them to their values in $\nu = 0$ ($C_{\text{aa}}^1 = C_{\text{aa}}^0$ and $C_{\text{bb}}^1 = C_{\text{bb}}^0$). The centrifugal distortion parameter in the excited state, $eQqJ^1$, is also too small to determine, and we set it to zero. This leaves only the excited state quadrupole coupling constant $eQq^1 = eQq_0^1$ which we float in the fitting procedure. Other adjustable parameters were, for each rovibrational line, the baseline offset, and the central frequency and width (identical for all the hyperfine components of a given line) of the Lorentzian. The four lines are fitted together as a single data set to obtain the best estimate of eQq^1 . In these fits, we assign identical error bars to each point of a spectrum, deduced from the standard deviation of values measured in spectral regions where no signal is present.

Figure 4 shows the satisfactory agreement between the data and the fit. Note that the additional lines in figure 4 are signals from the ^{185}Re isotopologue and are irrelevant to this discussion. We obtain $eQq^1 = 716(3)$ MHz, to be compared to $eQq^0 = 716.573(3)$ MHz in the ground vibrational state [43], and conclude that there is little variation of the quadrupole coupling constant with vibrational quantum number. We compare these results to those of ammonia, one of the few species whose hyperfine structure is known in both the ground and excited vibrational states. The eQq parameter depends on the product of the nuclear electric quadrupole moment and the electric field gradient at the nucleus. The value of eQq in ammonia is a factor of 160 smaller than in MTO [48, 49]. The quadrupole moment of the ^{14}N nucleus is about 100 times smaller than that of the ^{185}Re or ^{187}Re nuclei. Thus, the difference in the eQq parameters can be attributed mainly to the difference in quadrupole moments, implying that the electric field gradient at the N nucleus of ammonia is very similar to the field gradient at the Re nucleus of MTO. In ammonia, there is a 1%–10% variation of eQq depending on the vibrational state considered [48, 49]. In MTO, eQq is the same to within 0.4% in the two vibrational states we studied, showing that the electric field gradient at the Re nucleus is the same for the two vibrational states at this level of accuracy. Its variation is in fact calculated to be about 0.5% [50], at the level of our experimental uncertainty. Note that the parameter uncertainty on eQq^1 reported by the fitting procedure is 1 MHz. We estimate a more conservative uncertainty from the range of values obtained after various modifications in the fitting procedure, including convolution with a Lorentzian or a Gaussian, fits with single or multiple spectra of the same line, and fits of only three among the four groups of lines.

From our fit, the full width at half maximum of individual hyperfine components is found to be 8 ± 2 MHz. This linewidth is a combination of the Doppler width, residual laser frequency fluctuations, and collisional broadening. The helium pressure and the He-MTO collision cross-section are not well known in this regime and so the contribution from collisional broadening is difficult to estimate. We have observed that laser ablation of pressed powder targets can liberate enough helium from the target to significantly alter the pressure in the cell, and so the transient helium density following an ablation shot can be considerably larger than the time-averaged density. For this reason, the helium pressure is particularly difficult to control. The laser linewidth is 1 MHz at 1 s, but the spectra take much longer to record than this. The uncertainty in the relative frequency scale, determined using the data from the reference cells and the etalon, is typically a few MHz, and so probably makes a significant contribution to the observed linewidth. Based on previous measurements on buffer gas cooled diatomic molecules, it is unlikely that the translational temperature could be higher than the rotational temperature. Since the rotational temperature is consistent with the measured cell temperature, it is likely that the translation temperature is also around 6 K. In this case, the Doppler broadening contributes around 3 MHz to the measured linewidth.

4. Conclusion

We have demonstrated the vibrational spectroscopy of an organometallic molecule cooled to low temperature in a helium buffer gas cell. The signal-to-noise ratio of our spectroscopy is similar to that of other techniques (jet-cooled Fourier transform infrared [42] or laser absorption fast-scan [43] spectroscopy), but has a resolution 20

times higher. This allows studies of hyperfine structure in the excited vibrational state, which is only known for a few polyatomic species and is certainly unprecedented for such a complex molecule. Higher resolution could be reached using saturated absorption spectroscopy in the buffer-gas cell once the QCL is stabilized to an ultra-stable mid-infrared or near-infrared frequency reference as we recently demonstrated [51, 52]. Higher sensitivity could also be reached by increasing the effective interaction length of the light and the molecular absorbers with an enhancement cavity. Similar ~ 10 MHz resolution and accuracy have for instance recently been obtained with an $8.44\ \mu\text{m}$ QCL-based cavity ring-down spectrometer coupled to a heated supersonic expansion [53]. The present study used molecules inside the buffer-gas cell where the molecular density is highest, and we are now working to extract a beam from the cell. Our work is a first step towards producing an intense, slow-moving beam of cold chiral molecules for measurements of parity violation.

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