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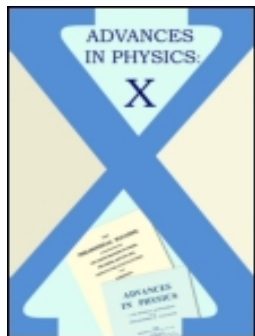
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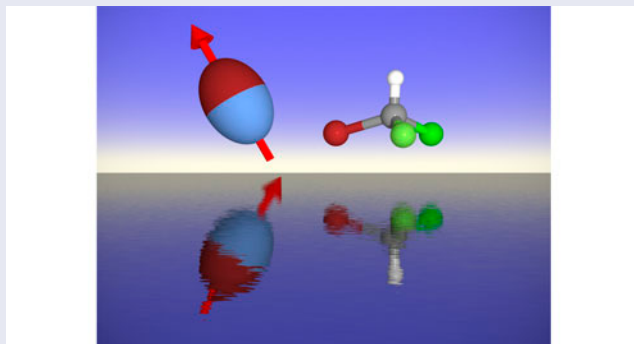
Laser spectroscopy of cold molecules

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ABSTRACT

This paper reviews the recent results in high-resolution spectroscopy on cold molecules. Laser spectroscopy of cold molecules addresses issues of symmetry violation, like in the search for the electric dipole moment of the electron and the studies on energy differences in enantiomers of chiral species; tries to improve the precision to which fundamental physical constants are known and tests for their possible variation in time and space; tests quantum electrodynamics, and searches for a fifth force. Further, we briefly review the recent technological progresses in the fields of cold molecules and mid-infrared lasers, which are the tools that mainly set the limits for the resolution that is currently attainable in the measurements.



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1. Introduction

With the exception of a few dimers formed by the photo-association or magneto-association of pre-cooled alkali-metal atoms [1,2], the ultracold world (microkelvin and below) is presently confined to atomic and ionic systems. Recent spectroscopic measurements in atoms and atomic ions have reached fractional accuracies of parts in 10^{18} [3]. Precision measurements on ultracold atoms and atomic ions are at the heart of the very best clocks in the world [4],

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magnetometers [5], gyroscopes [6], and gravimeters [7], and these devices are even being developed into commercial products.

The precision of spectroscopic studies on the molecular counterparts, though, is worse by more than three orders of magnitude. This is a consequence of the richer internal structure of molecules that makes cooling and detection more complicated than in atoms. However, the internal structure and symmetry of molecules, and the strong intramolecular fields open the door to new kind of measurements [8]. Spectroscopic studies on cold molecules yield insight into new physics, in some cases to a deeper level than using atoms despite the lower precision of the bare measurements [9–16]. In some cases, laboratory measurements on cold molecules can even compete in the search for new particles with the largest particle accelerator facilities available [10]. The central part of this paper will review the recent results in precision spectroscopy of cold molecules.

The limits to the precision that is attainable in spectroscopic studies on molecules are currently given by the cooling techniques and by laser technology. Therefore, we will also briefly review here the recent progresses in these two fields, from the perspective of high-resolution molecular spectroscopy.

2. Techniques for the production of cold molecules

The shot-noise limit in a frequency measurement is given by $\delta\nu = 1/\tau\sqrt{N}$, where τ is the coherence time for the measurement and N is the number of detected molecules. The advantage offered by using a cold sample of molecule is twofold. First, by cooling the internal degrees of freedom of a molecular sample, the distribution of populated quantum states is narrowed according to the Boltzmann statistics. Thus, N is greatly enhanced if the state under investigation is the ground state, or a state that is energetically close to the ground state, compared with $k_{\text{B}}T$. As an aside, we note that a current limit in molecular spectroscopy is posed by the lack of generally applicable methods to prepare a large population of molecules in highly excited states. Second, cooling the external degrees of freedom yields slower molecules that allow for measurements with longer coherence time τ . Moreover, lower velocities yield reduced Doppler broadenings [17].

The coldest molecular species attainable to date are the ultracold alkali dimers created by associating ultracold atoms [2]. They have been employed, for instance, in the studies of ultracold bimolecular reactions [18,19] and have been trapped in optical lattices to analyze their quantum dynamics, which represents the first step toward using these systems to explore many-body dynamics in regimes that are inaccessible to current theoretical techniques [20]. However, as interesting as these species are in the quest for new physical phenomena, they have not been at the focus of the spectroscopists' attention. Instead, their attention has been directed at less exotic molecular species, cooled by direct

methods. Here, we will briefly review the main achievements in direct molecular cooling.

A conceptually simple method for preparing cold molecules is the buffer-gas cooling pioneered by J. Doyle [21]. The cooling is achieved via collisions with cryogenically cooled helium atoms and the temperature of the cold molecules is typically around 1 K. A large variety of atoms and molecules has been cooled using this technique, ranging from atoms and dimers to benzonitrile, fluorobenzene, anisole, for instance [22]. Further, buffer-gas cooling has been used for the production of molecular beams both of gaseous precursors and of laser-ablated species [23]. If curved guides are coupled to this kind of sources, the subset of molecules that are moving sufficiently slowly are extracted from the output of the source [24]. Spectroscopy on buffer-gas cooled species has been performed both inside the cooling cell [22,25,26] and on the molecular beam [10].

Supersonic molecular beams are a classical method to produce cold molecular samples. The first molecular beam was reported in 1911 [27] but it was only after Stern and Gerlach's famous experiment in 1922 [28] that this technique emerged as a planned scientific effort [29]. A molecular beam is generated by letting a gas expand from a high-pressure source into a low-pressure ambient background via some sort of nozzle. In the expansion region of the beam, the initial enthalpy of the gas is converted into forward velocity of the beam and the temperature is consequently reduced. By seeding the molecules in an inert gas, different final velocities can be obtained depending on the average molecular weight of the gas mixture. A supersonic molecular beam, thus, is a fast moving beam of internally cold molecules and it facilitates spectroscopic studies by providing a lack of collisional perturbations and the strong reduction of inhomogeneous broadening. However, typical molecular beams have speeds of the order of 300–1000 m/s and several techniques have been developed to manipulate and control their motional degrees of freedom.

Stark and Zeeman effects are used to manipulate polar and paramagnetic molecules with electric and magnetic fields, respectively [30,31]. Stark deceleration was first demonstrated by Gerard Meijer using metastable CO [32]. Molecules with a permanent electric dipole moment (EDM) convert part of their kinetic energy into Stark energy upon entering an electric field if they are in an appropriate quantum state. If the electric field is switched off before the molecule has left the electric field, the lost kinetic energy will not be returned. This process can be repeated over multiple stages until the molecules reach the desired final velocity. Once the average velocity is low enough, molecules can be loaded in a trap [33], for instance. Zeeman deceleration is entirely analogous, except that the force is exerted by a magnetic field on a magnetic dipole moment [34]. Alternative to the method of abruptly switching between different static field configurations, molecule can be captured in traveling potential wells [35,36] directly from the supersonic molecular beam and then decelerated. These methods are used to prepare a molecular beam in a single quantum state and at a mean

speed adjustable between 400 and 500 m/s to rest, with translational temperature tunable from 1 K to 5 mK. High-resolution spectroscopy of decelerated species has been performed for NH_3 [37] and hydroxyl radicals (OH) [38,39]. In these experiments, an interaction time as long as one millisecond was obtained.

In 2008, Stuhl et al. [40] identified a class of diatomic molecules that presented almost-cycling transitions, which can be used for laser cooling. A couple of years later the DeMille group demonstrated the action of a radiative force acting on SrF [41], and then transverse laser cooling [42] and deceleration [43] of a SrF beam. Finally, in 2014, they were able to trap SrF in a three-dimensional magneto-optical trap [44]. In the meanwhile, laser cooling of YO [45] and CaF [46] has also been reported.

Typical temperatures reached with all these techniques are in the range of a half [47] to about a 100 mK, whereas the densities are in the range of 10^7 molecules per cubic centimeter.

3. Spectroscopic studies with cold molecules

3.1. The EDM of fundamental particles

If a particle has an intrinsic EDM, the EDM must necessarily lie along its spin axis because all other perpendicular components would average out to zero. Time inversion (T) would only reverse the direction of the spin, whereas parity inversion (P) would only reverse the sign of the EDM. Therefore an EDM different from zero leads to violations of T invariance (and P) [48]. The CPT theorem states that the combined operations of P, T, and charge conjugation (C) must be conserved in any Lorentz-invariant theory [49]. Moreover, in nearly all current theories, violation of T implies a violation of CP symmetry. Indeed, CP violation was first observed about 50 years ago in the decay of the neutral kaon [50] and such violation can be explained through the standard model (SM). However, the SM does not contain enough CP violation to explain the current matter–antimatter asymmetry in the universe [51], while also leading to EDMs too small to be seen in any current or contemplated experiments. Some theories that go beyond the SM generally provide for more CP violation, and therefore, larger EDMs [52–54]. This makes the search for EDMs a powerful way to search for new physics and constrains the possible extensions.

Edward Purcell and Norman Ramsey initiated a search for an EDM of the neutron over 60 years ago and obtained a result that is consistent with zero [55,56]. Thereafter, a long series of ever more sensitive EDM experiments began, on neutrons, atoms, and molecules. The neutron was initially chosen because of the difficulties related with measurements on charged particle. Moreover, in the non-relativistic limit, an atom does not have an EDM even if the electron does [48]. But it was shown that if relativity is taken into account, neutral atoms and molecules can have an EDM [57] and this effect increases rapidly with the nuclear charge. Thus, experiments have been performed on atoms and molecules

with heavy nuclei, like Tl [58] and PbO [59]. To date, the most accurate EDM experiments measure the electron EDM in YbF and ThO molecules [9,10]. This larger accuracy is due to the polarizability of a typical polar diatomic molecule, which is about three orders of magnitude larger than in an atom. This is reflected in the interaction energy of the electron EDM with the electric fields inside these molecules, which is hundreds of times larger than in Tl [60]. Moreover, the strong tensor polarizability of polar molecules greatly reduces the systematic errors with respect to the measurements in atoms [61]. Efforts are currently being made to cool further the molecular samples used in these experiments in order to improve the sensitivity of the measurements [62]. Furthermore, there has been notable progress by the Cornell group on the measurements using trapped HfF^+ or ThF^+ molecular ions. By applying a rotating bias electric field, they demonstrated effective polarization of trapped molecular ions [63].

Extensions of the SM that provide enough CP violation to explain the matter–antimatter asymmetry do so by introducing new particles that couple to the electron. The present experimental limit of sensitivity is obtained with a cold sample of ThO molecules from a cryogenic buffer gas beam source [10] and sets an upper limit of the electron EDM of $8.7 \times 10^{-29} \text{ e} \cdot \text{cm}$, which constrains the new supersymmetric particles to masses larger than TeV/c^2 [52,53]. It is thus remarkable how laser spectroscopy on cold molecules can compete in this field with the largest particle accelerator facilities in the world.

3.2. Parity violation

Another unresolved puzzle is about the overwhelming dissymmetry or chirality of Earth biochemistry, which is based on L-amino acids and D-sugars [64]. While the efficiency of homochiral chemistry and its stability toward natural selection is clear, little is known about the origin of this particular choice. It might well be a pure matter of chance that the initial enantiomeric distribution did not show an excess of D-amino acids and L-sugars, which might in fact be the chirality of the carbon-based life on another planet.

The origin of the observed chirality in biochemistry may be an effect of the weak nuclear interaction. The weak interaction is unique in its non-conservation of P [65,66] and this fact allows the effects of the weak interaction to be distinguished from the much stronger, but P-conserving, electromagnetic interaction. In chiral molecules, the energy shift caused by the weak interaction changes sign from one molecule to its mirror image [67]. Therefore, P does not generate a true enantiomer because of the slight energy difference, whereas the combined CP operation generates a mirrored molecule composed of antiparticles and exactly the same energy. This follows from the CPT theorem and the assumption that T is not violated [68,69]. It was suggested over 40 years ago that energy differences between enantiomers should be measurable as differences in the electronic [70] and vibrational [71] energies of the two enantiomers of a chiral molecule. Further, cumulative amplification mechanisms have been proposed that allow

the tiny energy differences between enantiomeric molecules to yield observable consequences for the chirality of our biochemistry [72]. With such mechanisms, a minute but systematic chiral interaction can determine which enantiomer will dominate in the long term.

The first experiments probing P violation in chiral molecules were performed on CHFCIBr [73,74], using saturated-absorption laser spectroscopy in two Fabry–Perot cavities containing samples with different enantiomeric excesses, around a wavelength of 10 μm . In these experiments, the centers of the absorption lines were determined to the Hz level, yielding an upper bound of $\Delta\nu/\nu \sim 5 \times 10^{-14}$ for the P violation effect. However, theoretical studies [75,76] predict the line shift to be in the mHz range, corresponding to a precision of the order of parts in 10^{16} . Therefore, new experiments are planned [8] to improve the precision of the measurements. The new generation of experiments is based on the measurement of Doppler-free two-photon Ramsey fringes around 10 μm on a molecular beam [11].

In diatomic free radicals, it is possible to bring two states of opposite parity to near degeneracy by inducing a Zeeman shift as large as the rotational splitting. Near such a level crossing, the mixing of these long-lived states due to nuclear spin-dependent P-violating interactions is greatly enhanced [77]. It has been suggested that these systems could be used to measure classes of P-violating electroweak interactions that are difficult to access otherwise [77,78], such as those due to nuclear anapole moments and axial hadronic-vector electronic electroweak couplings [79]. Results in this direction are expected by ongoing experiments in the DeMille and in the Hoekstra groups [80,81].

3.3. Variations of fundamental constants

The search for EDMs of fundamental particles and the measurement of P violation in chiral molecules question the extent to which the symmetry-conservation rules postulated in the SM hold. Another aspect of the SM that is presently under scrutiny is whether its fundamental constants are fixed parameters, or are rather changing over time, in space, or in dependence of matter density. This issue is not of secondary importance, as the comparison and reproduction of experiments is at the foundation of the scientific method, but it is only meaningful if the natural laws do not depend on time and space (Einstein's equivalence principle).

The question of a possible variation of the fundamental constants was probably first posed by Dirac in the 30s [82], and since then many other theories have been developed [83,84]. Moreover, the observations of the last 20 years that indicate that the universe is expanding at an accelerating rate [85–87] leads to the postulation of an unknown form of energy, known as dark energy. Two proposed hypotheses for dark energy are the cosmological constant and the dynamical action of a scalar field [88]. For the latter case, it has been shown that the scalar field must interact with matter, giving rise to a variation of the

fundamental coupling constants [89,90] and reinvigorating the interest for this field of research.

While models of the big bang nuclear synthesis set limits on the variation of fundamental constants at extremely high redshifts [91], the measurement of atomic and molecular transition frequencies is the most natural way to look for variation of the fine structure constant, α , and the electron-to-proton mass ratio, μ , from intermediate redshifts ($z \sim 5$) to the current epoch. Observation of intergalactic species found in the line-of-sight of quasars yields sufficient spectral quality up to about $z = 4$ [12], whereas measurements of samples from within the Milky Way can test the hypothesis that fundamental constants may differ between the high- and low-density environments of the Earth and the interstellar medium [92], or between the gravitational potential of white dwarfs and the Earth [93].

Of course, it is essential that the different transitions being compared have different dependency on α and μ . Amy-Klein and co-workers, for example, compared a vibrational transition in SF₆, which depends directly on μ , to a hyperfine transition in a Cs clock, which depends on α instead [11]. The comparison of different clock transitions in ultracold atoms or atomic ions provides a high signal-to-noise ratio and can be carried out under very well-controlled conditions [94]. Alternatively, one can choose systems that are not necessarily ideal for precision measurements, but present an enhanced sensitivity (up to three orders of magnitude) to a variation of physical constants. Several molecular systems have been proposed in which a near degeneracy between electronic levels of different symmetry [95], between hyperfine and rotational levels [96], or between fine structure and vibrational levels [97,98], leads to particularly large sensitivities.

Currently, all relevant experimental results on the variation of μ are obtained by measuring molecular transitions. The present-day limit is set in the laboratory with SF₆ at $\dot{\mu}/\mu = (-3.8 \pm 5.6) \times 10^{-14} \text{ yr}^{-1}$ [11]; the comparison of modern measurements of the Lyman and Werner band of H₂ and the astrophysical observations from 12.4 billion years ago yields $\Delta\mu/\mu = (-9.5 \pm 5.4_{\text{stat}} \pm 5.3_{\text{syst}}) \times 10^{-6}$ [12]; a similar study for methanol using a radio-telescope to look back 7 billion years yields $\Delta\mu/\mu = (-0.0 \pm 1.0) \times 10^{-7}$ [13]. Measurements within our galaxy, testing whether constants depend on the local density, are available for methanol maser lines and set an upper limit of $|\Delta\mu/\mu| = 2. \times 10^{-8}$ (1σ) [14]. However, comparisons of terrestrial and astrophysical microwave transitions in ammonia and other molecules, find an eight-standard-deviation systematic difference. This suggests a fractional change in μ of 2.6×10^{-8} when going from the Earth to the interstellar medium, tentatively supporting the chameleon hypothesis [15,16]. Also the strongest limit on the dependency of α on matter density has been obtained with a molecular measurement, CH [92]. This was done by measuring microwave transitions in CH and by comparing these frequencies with those measured from sources of CH in the Milky Way.

High-precision measurements of the most sensitive molecular transition frequencies are thus required, together with higher quality astronomical observations.

3.4. Test of QED and fifth force

A further approach to probe experimentally new physics is the search for a new attractive or repulsive force (a *fifth force*) with precision metrology measurements on calculable molecular systems. In recent years, thorough level structure calculations, including QED and high-order relativistic contributions, have been carried out for the neutral hydrogen molecules and the deuterated isotopologues [99–102]. In these systems, the energy level shifts due to weak interaction and gravity are orders of magnitude away from the experimental sensitivity. The effect of the strong interaction is confined to the fm scale and its influence on atomic and molecular energy levels enters into the calculations via the nuclear g_N factor and the nuclear spin. Thus, a search for deviation from the QED predictions in atomic and molecular energy levels would either hint at a new kind of interaction or at some unaccounted effects within QED. Furthermore, whereas lepton–nucleon and lepton–lepton interactions may be probed in atomic hydrogen and helium, the search for long-range interactions between hadrons requires a molecular system [103]. The measurements with the highest precision to date are in perfect agreement with the calculation [104]. However, the accuracy level of QED calculations is claimed to be one order of magnitude better than the present experiments [102], thus improved experimental tests are currently required.

3.5. Determination of the Boltzmann constant

The Boltzmann constant, k_B , conventionally considered as fundamental, plays an important role for a possible redefinition of the kelvin, one of the seven SI base units [105]. Currently, the most precise determination of k_B comes from measurements of the speed of sound in a noble gas inside an acoustic resonator [106]. The measured value is $k_B = 1.380\,651\,56\,(98) \times 10^{-23} \text{ J K}^{-1}$, with a relative uncertainty of 0.71×10^{-6} . Thanks to recent developments of frequency-stabilized ultra-narrow coherent sources, precise determination of the Boltzmann constant beyond the 10^{-6} -level via spectroscopic measurements becomes a concrete target. This method, called Doppler broadening thermometry (DBT), consists in retrieving the Doppler width of a given atomic or molecular line in a gas sample at thermodynamic equilibrium by highly accurate spectroscopic detection of the line profile. The first DBT experiment was performed at LPL with an ultra-narrow CO_2 laser [107]. The thermometric gas employed was ammonia, kept in thermal water-ice bath at 273.15 K. The Doppler width of an ammonia absorption line around $10.36 \mu\text{m}$, extrapolated at zero gas pressure, allowed for k_B determination with a relative uncertainty of 2×10^{-4} . Critical factors affecting the measurement come from both the spectroscopic apparatus (stability and

homogeneity of the gas temperature in the spectroscopic cell, frequency and amplitude stability of the laser source, linearity and noise level of the detection chain) and data analysis (line-shape modeling and fitting procedure). Similar results have been obtained with DBT measurements on a CO₂ transition around 2 μm using an extended-cavity diode laser [108], while a precision of 2.4×10^{-5} has been achieved on H₂ ¹⁸O transitions at 1.39 μm [109] mainly thanks to a more refined line-shape model. Significant improvements can be expected both by a better laser stabilization and by adopting a more sophisticated line-shape model for highly accurate retrieval of the Doppler width [110].

4. Laser sources in the mid IR

The most straightforward spectral region for high-resolution spectroscopy are the microwaves, where radiation sources are very reliable, stable, easy to use, and powerful; Doppler-broadenings are tiny; and spatial coherence is easily achieved over the typical sizes of an experimental apparatus. However, for a given molecular velocity (i.e. translational temperature), the interaction time of a molecule with the radiation is limited, thus increasing the frequency of the measured transition allows for an improvement in the relative precision of the measurement. The mid IR (MIR) corresponds to the frequencies of nuclear vibrations and is, thus, a natural spectral region for molecular studies, in which one finds intense rovibrational transitions, accompanied by Hz-level natural linewidths. The larger Doppler effect (which is proportional to the radiation frequency) must be dealt with an intrinsic sub-Doppler spectroscopic technique, like two-photon spectroscopy or saturated-absorption spectroscopy. Therefore, moving from the GHz to the THz frequency range can produce a dramatic increase in the precision but it requires the development of intense and narrow-linewidth laser sources to be referenced to the primary microwave standard. In other words, the precision of a molecular spectroscopic measurement is the result of the efforts toward the cooling of the molecules, which are reviewed in Section 2, and toward the improvement of the light sources, mainly in terms of frequency stability, which are reviewed below. These two technological fields are somehow complementary. Doppler broadening can be reduced either by slowing down the molecular motion or by adopting a sub-Doppler spectroscopic technique, if the available laser intensity is sufficient. Similarly, the coherence time is improved with slower molecules, and a more intense laser allows for a larger beam waist and thus for a longer interaction time.

Indeed, measurements of absolute frequencies must ultimately be referenced to the primary frequency standard, which is based on the hyperfine ground-state splitting in cesium. The comparison of the measured transition frequencies in the optical domain (hundreds of THz) to the microwave cesium frequency standard (around 9 GHz) was a significant technical challenge in the past. However, the development of optical frequency combs (OFC) has allowed to bridge this

four-orders-of-magnitude gap directly, leading to measurements of unprecedented precision [111,112]. Nowadays OFCs are commercially available in the visible-to-near-IR (VIS-to-NIR) region but remain challenging in the mid IR. Similarly, narrow-linewidth laser sources, which are the other fundamental ingredient for high-resolution spectroscopy and a mature technology in the VIS-to-NIR, are still in their infancy in the MIR.

One possible approach to the absolute determination of MIR frequency is based on a two-step strategy. An OFC transfers the primary frequency standard to the NIR, then difference-frequency generation (DFG) from two sources, which are both referenced directly to the comb, provides light in the MIR. For this to be possible, the DFG pump and signal lasers must fall in the OFC coverage range and their frequencies must be locked to the nearest teeth of the comb. This leads to a very narrow idler linewidth, only limited by the excess phase noise between the two comb teeth due to the propagation of the repetition rate phase-noise to the optical frequencies. The first comb-assisted DFG sources have been used to measure the frequency of some CO₂ transitions around 4.3 μm by cavity-enhanced saturated-absorption spectroscopy, achieving an uncertainty of 800 Hz in the absolute frequencies (1.1×10^{-11} relative precision) [113]. Similar approaches have been adopted by other groups [114] covering different MIR spectral ranges. Further, if the free-running short-term stability of at least one of the DFG pumping lasers is better than the comb's, this scheme can be improved: the n/m excess phase noise between the n th and m th tooth to which the pump and signal lasers are locked can be canceled out using a direct digital synthesizer [115]. With this approach, absolutely-linked idler radiation between 4 and 4.5 μm with 10 Hz intrinsic linewidths (1 kHz integrated linewidth over 1 ms), has been demonstrated [116]. Entirely analogous is the generation of OFC-referenced MIR radiation using optical parametric oscillators (OPOs) [117–119].

An alternative approach consists in down-converting a visible or NIR OFC directly to the MIR [120], either by using a DFG processes [121–126] or an OPO [127–130]. DFG MIR combs benefit from being offset free, because of the perfect cancelation of any carrier-envelope phase offset that may be present in the original frequency comb [131]. The typical total average power of a DFG OFC is in the order of a few mW, which results in extremely low power per tooth. Therefore the application of DFG OFCs as sources for direct high-resolution spectroscopy is not common. In OPO MIR combs, the optical cavity is highly reflective for idler wavelengths, and matched in length to the pump (usually a mode-locked fiber laser) repetition rate. Methods for controlling the offset frequency and mode spacing of the frequency comb have also been demonstrated [130]. These combs yield an average W-level power, but their main drawbacks are the additional complexity given by the OPO cavity, the relatively limited oscillation spectral range, and the need for complex techniques for phase stabilization of both signal and idler outputs.

It is noteworthy that the limited availability of suitable nonlinear crystals often seriously restricts the possible choices for pump/signal/idler combination, according to the transparency range of the material or to the phase-matching requirements. For these reasons, many of the cited DFG and OPO combs fall in the 2.5–4.5 μm range, where PPLN crystals are transparent. Moreover, a proper choice of the poling period allows for quasi-phase-matching with Nd:YAG lasers at 1.064 μm , which is often convenient due to their high stability and power levels. It is more difficult to access the region above 5 μm , where PPLN crystals are not transparent. Here, other crystals are commercially available (AgGaSe, AgGaS₂, GaSe, ZnSeP₂), but present low conversion efficiencies and their transparency ranges and phase-matching requirements strongly limit the choice of pump, signal and idler sources. Some non-commercial crystal can be used, such as CdSeP₂ or the orientation-patterned (OP)-GaAs or -GaP. These crystals are characterized by high conversion efficiencies (at the level of PPLN or higher). Bulk crystals like CdSeP₂ allow for a wide spectral coverage, while OP-crystals are more selective according to the patterning period.

A third approach consists in the use of a relatively high-power MIR laser, emitting at the desired frequency, stabilized over some narrow spectral feature (high-finesse optical resonator, sub-Doppler molecular transition, narrow-linewidth optical reference, for instance) that is, in turn, referenced to a frequency standard. Researchers at LPL in Paris, for example, stabilized CO₂ lasers on a Fabry–Perot cavity filled with OsO₄ to achieve a 10-Hz-level linewidth, a 0.1 Hz stability over 100 s and a reproducibility up to 10 Hz [132]. Then, to determine the absolute frequency of their laser, they produced sum frequency (SF) radiation in a AgGaS₂ crystal of the CO₂ laser and a visible laser that is referred to an OFC. The SF radiation is also visible and can be measured against the same OFC [133].

The lack of tunability and limited spectral coverage of gas lasers, however, severely limits the range of molecules that can be studied. It is mainly for this reason that the introduction of Quantum Cascade Lasers (QCLs) has revolutionized the field of MIR spectroscopy. They allow for continuous tunability over tens of wavenumbers and a complete coverage, by design, of the MIR spectral range from 4 to 20 μm , at least [134]. Moreover, their output power has been demonstrated to reach the W level [135]. In 2007, the frequency of a free-running QCL around 4.3 μm was absolutely referenced to a comb operating between 500 and 1100 nm by SFG of the QCL radiation with the fundamental of a Nd:YAG in a PPLN crystal [136,137]. Analysis of the noise features showed that QCLs have very narrow intrinsic linewidths [138–140]. This observation triggered a series of improvements in stabilization of the QCL chip temperature and driving current. Thereafter, the frequency of QCLs was locked to a sub-Doppler transition [141], to MIR Fabry–Perot cavities [142,143], to a OsO₄-stabilized CO₂ laser [144], to a crystalline whispering gallery mode microresonator [145], and to a NIR ultra-low expansion reference cavity after up-conversion by SFG [146] as references. A linewidth as narrow as 10 Hz with a relative stability in the 10^{-14} range at 1 s, and

a relative accuracy of 3×10^{-12} , was demonstrated [144]. Phase locking of QCLs to OFCs has been done with the various up- and down-conversion strategies described above [131,146–148], and via optical injection locking [149], thereby allowing also for the narrowing of the linewidth ranging from tens of kHz down to a few hundreds of Hz. The most spectacular result to date was reported by LPL group (sub-Hz linewidth) by locking a QCL at $10.3 \mu\text{m}$ to an OFC, which is itself stabilised to a remote NIR ultra-stable frequency reference via an optical fibre [150].

At these levels of precision, the issue of dissemination of the primary frequency standard becomes of paramount importance. Standard OFCs are actively stabilized against a 10-MHz quartz-oscillator disciplined by a Rb-GPS (Global Positioning System) clock. The GPS stability and the quartz oscillator phase noise limit the comb stability to parts in 10^{13} in 1 s and the absolute accuracy to the 10^{-12} level [151]. To overcome this limit, the primary frequency standard is now delivered to some laboratories by the national metrological institutes directly via fiber link, improving by more than four orders of magnitude the resolution of satellite transfer techniques [152]. Among these, are the PTB in Germany, the LNE-SYRTE in France, the INRIM in Italy, the AGH in Poland, and the NPL in the UK, transferring the accuracy and resolution of their atomic clocks for hundreds of kilometers. Frequency instability of 3×10^{-19} over 1000 s were measured, with ultimate accuracies on the frequency transfer of parts in 10^{19} (1000 s integration time) [153]. In fact, it was thanks to a fiber link from LNE-SYRTE that at LPL it was possible to measure the absolute accuracy of a QCL at the 10^{-14} level [150].

5. Perspectives

With precision measurements on atoms reaching a total uncertainty of parts in 10^{18} [3], the gap with the precision of molecular measurements is about three orders of magnitude. The main reason for this poor performance is arguably that molecular samples on which one wants to do spectroscopy are much warmer, at the mK level at best, corresponding to velocities of the order of the meter per second, depending on the molecular mass. This constrains the interaction time with laser light to the millisecond range, assuming a laser beam waists of the order of the millimeter, which is optimistic in the case of a two-photon process required for sub-Doppler spectroscopy. One can push this limit with a Ramsey interrogation scheme, either in a beam [9–11] or building a fountain [154]. Yet this comes at the cost of lower number densities, larger setups, and, thus, worse control on stray fields. Therefore, the development of a second-stage cooling method is currently one of the biggest challenges in the field. One of the most promising proposals is sympathetic cooling, which is based on the conceptually simple idea of bringing cold molecules into thermal contact with a bath containing ultracold atoms. So far, sympathetic cooling has been

successfully accomplished for ions [155,156] and some neutral atoms [157,158], but not for neutral molecules.

Another challenge in the field is the extension of cooling and highly sensitive detection techniques to complex, polyatomic molecules. Presently, cooling these systems to a few kelvin and forming slow-moving beams would vastly extend the range of molecules that can be brought under control to enable high-precision measurements.

Finally, MIR sources present a twofold challenge: on one side, extending their spectral coverage to the entire MIR window from 3 to 25 μm allows to bring accurate frequency metrology methods to almost all molecules; on the other side, improving the light source stability and accuracy to the 10^{-15} level, at least, is required for many of the experiments described above. In this regard, the recent results with ultra-narrow, fiber-link-referenced MIR sources have just provided a major improvement.

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Disclosure statement

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