Chiral Molecules as Sensitive Probes for Direct Detection of $\mathcal{P}$-Odd Cosmic Fields

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Potential advantages of chiral molecules for a sensitive search for parity violating cosmic fields are highlighted. Such fields are invoked in different models for cold dark matter or in the Lorentz-invariance violating standard model extensions and thus are signatures of physics beyond the standard model. The sensitivity of a 20-year-old experiment with the molecule CHBrClF to pseudovector cosmic fields as characterized by the parameter $|b_0^e|$ is estimated to be $\mathcal{O}(10^{-12}\ \mathrm{GeV})$ employing *ab initio* calculations. This allows us to project the sensitivity of future experiments with favorable choices of chiral heavy-elemental molecular probes to be $\mathcal{O}(10^{-17}\ \mathrm{GeV})$, which will be an improvement of the present best limits by at least two orders of magnitude.

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Introduction.—The nature of dark matter (DM), the existence of which is invoked to explain the cosmological motion of visible matter, is considered to be one of the biggest unsolved problems of modern physics (see, e.g., Ref. [1]). Among the various DM theories, the cold DM (CDM) variant appears to provide a simple explanation for a wealth of astrophysical observations [2]. Up to now, however, the constituents of CDM are unknown and can range from macroscopic objects such as black holes to new particles like weakly interacting massive particles (WIMPs), axions, sterile neutrinos, or dark photons (see, e.g., Refs. [3–5]).

The model of CDM has also several shortcomings [6–11]. In order to overcome some of these, so-called fuzzy CDM models, which assume CDM to consist of ultra light particles with masses of $m_\phi \sim 1 \times 10^{-22}\ \mathrm{eV/c^2}$, were proposed [12,13].

CDM can consist of different types of bosons (an overview can be found, e.g., in Ref. [14]). Among those, we focus in the following on pseudoscalar and pseudovector particles as they are a source of direct parity ($\mathcal{P}$) violation. Other DM candidates that are potential sources for $\mathcal{P}$-odd interactions with a hypothetical neutrino background [15] are discussed elsewhere [16,17].

Pseudoscalar cosmic fields behave as axion fields, which were originally proposed [18–20] as a solution to the so-called strong $\mathcal{CP}$-problem [21], i.e., the apparently missing violation under combined charge conjugation $\mathcal{C}$ and $\mathcal{P}$ in quantum chromodynamics (QCD) although there is a free parameter in QCD that can account for such a violation. The window to search for such particles can be restricted to a defined parameter space, like for the QCD axion (see, e.g., [22]) which has to solve the strong $\mathcal{CP}$ problem, or can be large as for axionic particles that are not bound to solve the strong $\mathcal{CP}$ problem. The latter are often referred to as axionlike particles (ALPs). *Pseudovector* cosmic fields are important for models such as dark photons [23,24] and also appear as sources of local Lorentz invariance violation in the standard model extension (SME) [25].

In the last decade many proposals for new experiments and improved bounds on pseudoscalar CDM appeared, some of which employ atomic spectroscopy (see, e.g., [26–31]). Among the latter, direct measurement of $\mathcal{P}$ violation with modern atomic precision spectroscopy [29,32] provided strict limits on static $\mathcal{P}$-odd cosmic field interactions, where effects of these cosmic fields adds to $\mathcal{P}$-violating effects stemming from electroweak electron-nucleus interactions mediated by the Z^0 boson.

It is well known that such $\mathcal{P}$-odd effects are strongly enhanced in chiral molecules, as the chiral arrangement of the nuclei leads to helicity in the electron cloud (see, e.g., Refs. [33,34]). Such $\mathcal{P}$-odd effects can be measured as energy difference between enantiomers of chiral molecules or as resonance frequency differences between the two nonidentical mirror-image molecules [35,36]. As frequency shifts can be measured very accurately, this appears to be a particularly promising tool to search for $\mathcal{P}$-odd cosmic field interactions (for recent reviews on molecular $\mathcal{P}$ violation, see [33,34,37–41]). In the following we show advantages of the use of chiral molecules to search for

$\mathcal{P}$-odd cosmic field interactions. We estimate the sensitivity on cosmic $\mathcal{P}$ violation of a 20-year-old experiment [42] with the chiral methane derivative CHBrClF [43,44] and discuss the prospects of modern experiments with chiral molecules.

Theory.—We write the *pseudoscalar* cosmic field as $\phi(t) = \phi_0 \cos(\omega_\phi t)$ (see, e.g., Ref. [32]), which is supposed to behave nonrelativistically $\hbar\omega_\phi \approx m_\phi c^2$. The interaction of electrons ψ_e with such pseudoscalar cosmic fields $\phi(t)$ can be described by the following Lagrangian density (see, e.g., [19,20])

$$\mathcal{L}^{\phi}_{\mathrm{ps}} = g_{\phi\bar{e}e}(\hbar c\partial_\mu\phi)\bar{\psi}_e\boldsymbol{\gamma}^\mu\boldsymbol{\gamma}^5\psi_e, \tag{1}$$

where $g_{\phi\bar{e}e}$ is a coupling constant of dimension GeV^{-1}. Here the 4×4 Dirac matrices are defined as

$$\boldsymbol{\gamma}^0 = \begin{pmatrix} \mathbf{1}_{2\times2} & \mathbf{0}_{2\times2} \\ \mathbf{0}_{2\times2} & -\mathbf{1}_{2\times2} \end{pmatrix}, \qquad \boldsymbol{\gamma}^k = \begin{pmatrix} \mathbf{0}_{2\times2} & \boldsymbol{\sigma}^k \\ -\boldsymbol{\sigma}^k & \mathbf{0}_{2\times2} \end{pmatrix}, \tag{2}$$

where $\boldsymbol{\sigma}^k$ are the Pauli spin matrices with upper indices $k = 1, 2, 3$. The index μ runs as $\mu = 0, 1, 2, 3$. We define $\boldsymbol{\gamma}^5 = \imath\boldsymbol{\gamma}^0\boldsymbol{\gamma}^1\boldsymbol{\gamma}^2\boldsymbol{\gamma}^3$ with $\imath = \sqrt{-1}$ being the imaginary unit. $\partial_\mu = (\partial/\partial x^\mu)$ is the first derivative with respect to the four-vector $x^\mu = (ct, x, y, z)$, and we use Einstein's sum convention here for convenience. The time derivative of the pseudoscalar field leads to the $\mathcal{P}$-odd one-electron Hamiltonian

$$\hat{h}_{\mathrm{ps}} = g_{\phi\bar{e}e}\sqrt{2(hc)^3\rho_{\mathrm{CDM}}}\sin(\omega_\phi t)\boldsymbol{\gamma}^5, \tag{3}$$

where $\rho_{\mathrm{CDM}} \approx [(\hbar\omega_\phi\phi_0)^2/2(hc)^3]$ is the CDM energy density, for which we assume all ALPs to comprise all of the CDM with a uniform density: $(hc)^3\rho_{\mathrm{CDM}} = (hc)^3 0.4\ \mathrm{GeV\,cm^{-3}} = 7.6\times10^{-4}\ \mathrm{eV}^4$ (see Ref. [45]).

Electronic interactions with *pseudovector* cosmic fields can be described by the Lagrangian density

$$\mathcal{L}^{b}_{\mathrm{pv}} = -b^e_\mu\bar{\psi}_e\boldsymbol{\gamma}^\mu\boldsymbol{\gamma}^5\psi_e, \tag{4}$$

which appears, e.g., in the SME (for details see Refs. [25,46]). The $\mathcal{P}$ nonconserving one-electron interaction Hamiltonian for the temporal component $\mu = 0$ is

$$\hat{h}_{\mathrm{pv}} = b^e_0(t)\boldsymbol{\gamma}^5, \tag{5}$$

where the field can be static $b^e_0(t) = b^e_0$ or dynamic $b^e_0(t) = b^e_0\sin(\omega_b t)$. Here b^e_0 is the interaction strength of the timelike component of the field with the electrons.

The operators corresponding to $\mathcal{P}$-odd electronic interactions with cosmic fields shown above are proportional to $\boldsymbol{\gamma}^5$. The electronic expectation value of $\langle\boldsymbol{\gamma}^5\rangle$ can be expanded in orders of the fine structure constant α giving in leading order:

$$\langle\boldsymbol{\gamma}^5\rangle \approx \alpha\langle\vec{\boldsymbol{\sigma}}\cdot\hat{\vec{p}}\rangle, \tag{6}$$

where $\hat{\vec{p}}$ is the electronic linear momentum operator. As $\vec{\boldsymbol{\sigma}}\cdot\hat{\vec{p}}$ is an imaginary, electron-spin dependent operator, this expectation value vanishes in the strict electrostatic limit, but it can become nonzero when spin-orbit coupling $\hat{H}_{\mathrm{so}}$ is accounted for, similarly to the situation for $\mathcal{P}$ violation in chiral molecules due to weak neutral currents [47,48]. Furthermore, it is obvious from Eq. (6) that $\langle\boldsymbol{\gamma}^5\rangle$ depends on the helicity of the electron cloud. Thus, $\langle\boldsymbol{\gamma}^5\rangle$ can be nonzero in a chiral molecule, in which the electrons move in a $\mathcal{P}$-noninvariant potential caused by the chiral arrangement of the nuclei, whereas in a nonchiral molecule or in an atom $\langle\boldsymbol{\gamma}^5\rangle$ vanishes in the absence of additional $\mathcal{P}$-odd forces.

It can be shown from perturbation theory that for systems containing two heavy main group elements with nuclear charge numbers Z_A and Z_B the following scaling relation holds in lowest order:

$$\langle\boldsymbol{\gamma}^5\rangle_{\mathrm{mol}} \sim c_1\alpha^5 Z_A^2 Z_B^2 + c_2\alpha^3 Z_A^2 + c_3\alpha^3 Z_B^2. \tag{7}$$

Here the factor $\alpha^2 Z_B^2$ in the first term emerges from spin-orbit coupling. The constants c_1, c_2, and c_3 are dependent on the electronic structure and we can expect that $|c_{2,3}| \ll |c_1|$. A detailed derivation together with evidence from numerical studies of several chiral molecules will be provided in a separate publication [49]. From this it can be deduced that contributions at the nuclear center dominate the electronic expectation value of $\boldsymbol{\gamma}^5$ and let it behave similarly to nuclear-spin independent electroweak electron-nucleon current interactions described by the one-electron Hamiltonian

$$\hat{h}_{\mathrm{ew}} = \frac{G_F}{2\sqrt{2}}\sum_{A=1}^{N_{\mathrm{nuc}}} Q_{W,A}\rho_A(\vec{r})\boldsymbol{\gamma}^5 \tag{8}$$

with G_F being Fermi's constant, $Q_{W,A}$ being the weak nuclear charge of nucleus A with nuclear density distribution $\rho_A(\vec{r})$ and the sum running over all N_{nuc} nuclei. In a previous study the electronic expectation value of $\boldsymbol{\gamma}^5$ was discussed as possible total molecular chirality measure [50], but we refer to the critical discussion in Ref. [51] on the utility of pseudoscalar functions as chirality measures.

Thus, molecular experiments that aim to test $\mathcal{P}$ violation due to weak interactions can also be used for searches of $\mathcal{P}$-violating cosmic fields with a comparable sensitivity.

Results and discussion.—In the following we estimate the expected sensitivity of experiments with chiral molecules to $\mathcal{P}$-odd cosmic field interactions as characterized by the b^e_0 parameter from an experiment with CHBrClF reported by Daussy *et al.* [42]. In this experiment the C-F stretching fundamental vibration (ν_4) in enantioenriched samples of CHBrClF was studied by high-resolution infrared spectroscopy. We are interested in the $\mathcal{P}$-violating splittings of the vibrational resonance frequency induced by cosmic fields interacting through $\langle\boldsymbol{\gamma}^5\rangle$.

Our calculations for CHBrClF, which are described in more detail in a separate publication [49], were carried out

following Ref. [52], which utilized the separable anharmonic adiabatic approximation framework as described in Ref. [53]. Parity-violating molecular properties were computed on the level of two-component zeroth order regular approximation complex generalized Kohn-Sham (ZORA-CGKS) (see Refs. [54–56]) employing the exchange correlation functional B3LYP[57–60]. We reuse electronic densities and Kohn-Sham orbitals as well as vibrational wave functions determined in Ref. [52]. With these, electronic expectation values of $\boldsymbol{\gamma}^5 = \sum_i \boldsymbol{\gamma}_i^5$, with index i running over all electrons in the system, and of the nuclear-spin independent electroweak electron-nucleon current interaction term induced by $\hat{H}_{\mathrm{ew}} = \sum_i \hat{h}_{\mathrm{ew}}(i)$ were calculated with our ZORA property toolbox approach outlined in Ref. [56]. Vibrational corrections of the properties were computed as described in Ref. [52].

The (negative) result of the experimental test for a $\mathcal{P}$-violating frequency shift reported in Ref. [42] is $|\Delta\nu| = 9.4 \pm 5.1 \pm 12.7$ Hz, where ± 5.1 Hz is the statistical uncertainty and ± 12.7 Hz the systematic error.

The expectation values of $\boldsymbol{\gamma}^5$ for the ground and first excited vibrational states along the C-F stretching mode of (*S*)-CHBrClF are computed to be

$$\langle v_4 = 0|\boldsymbol{\gamma}^5|v_4 = 0\rangle = -8.28 \times 10^{-9}, \tag{9}$$

$$\langle v_4 = 1|\boldsymbol{\gamma}^5|v_4 = 1\rangle = -7.91 \times 10^{-9}. \tag{10}$$

This leads to an estimate for the splitting between the two enantiomers of CHBrClF due to the perturbation with $\boldsymbol{\gamma}^5$ for the transition between the vibrational ground and first excited states of v_4 of

$$\begin{aligned}\Delta_{(R,S)}\langle\boldsymbol{\gamma}^5\rangle &= 2(\langle v_4 = 1|\boldsymbol{\gamma}^5|v_4 = 1\rangle - \langle v_4 = 0|\boldsymbol{\gamma}^5|v_4 = 0\rangle) \\ &\approx 7.4 \times 10^{-10}.\end{aligned} \tag{11}$$

We define the dimensionless reduced normal coordinate q_r, which describes the collective motion of the nuclei in vibrational mode r. As we discuss in more detail in Ref. [49] nonseparable anharmonic effects can play a prominent role for the C-F stretching mode in CHBrClF as effects characterized by the first and second derivatives with respect to q_4 can be expected to be of the same order as those characterized by first derivatives with respect to $q_{r\neq 4}$. This can best be seen from a plot of $\langle\boldsymbol{\gamma}^5\rangle$ on one-dimensional cuts along all modes (see Fig. 1). Therein the weak dependence of $\langle\boldsymbol{\gamma}^5\rangle$ on q_4 in comparison to the pronounced dependence on other modes stands out. Therefore, we can expect that multimode effects have the potential to change even the sign of the predicted value of $\Delta_{(R,S)}\langle\boldsymbol{\gamma}^5\rangle$ and, thus, it is not possible to provide a robust theoretical value for $\langle\boldsymbol{\gamma}^5\rangle$ for the C-F stretching mode, but we give rather the order of magnitude, which is $\Delta_{(R,S)}\langle\boldsymbol{\gamma}^5\rangle \sim \mathcal{O}(10^{-10})$. The sensitivity of this experiment to b_0^e is found to be of the order

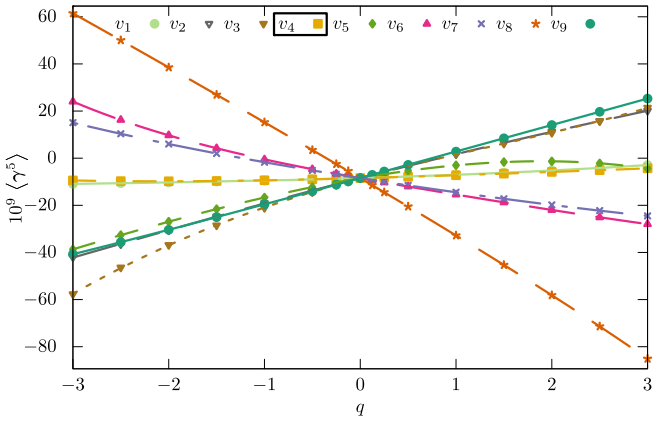

FIG. 1. Dependence of the expectation value of $\boldsymbol{\gamma}^5$ on the dimensionless reduced normal coordinates q of the nine different modes in (*S*)-CHBrClF computed at the level of ZORA-CGKS with the B3LYP functional and polynomial fits to $\langle\boldsymbol{\gamma}^5\rangle$ to fourth order (lines). The C-F stretching mode ν_4 was studied in the experiment in Ref. [42].

$$|b_0^e| \lesssim \left|\frac{12.7\ \mathrm{Hz}}{\mathcal{O}(10^{-10})}h\right| \sim \mathcal{O}(10^{-12}\ \mathrm{GeV}). \tag{12}$$

This sensitivity based on the 20-year-old experiment on CHBrClF is about two orders of magnitude inferior to the best limit from modern atomic experiments of 7×10^{-15} GeV so far [29]. An improvement in theory, most importantly by consideration of multimode effects [49,61] and additionally by calculations with more sophisticated electronic structure methods, would allow us to place a robust limit as we have highlighted in Ref. [49].

The sensitivity of the molecular experiment is supposed to be improvable by two orders of magnitude or better by a different experimental setup as discussed in Refs. [62–64], with Ref. [62] reporting also a slightly improved sensitivity of $|\Delta\nu| < 8$ Hz that was realized experimentally therein. The scaling behavior in Eq. (7) suggests that further sensitivity improvements are possible by selecting heavy-elemental chiral molecules. Electroweak $\mathcal{P}$-odd effects, which scale like $N_A Z_A^2 Z_B^2$ (with N_A being the number of neutrons of nucleus A), were estimated to give vibrational splittings that can become three orders of magnitude larger in well-chosen heavy-elemental molecules, such as CHAtFI or methyltrioxorhenium derivatives, when compared to CHBrClF [52,63]. Due to the missing N_A scaling, an enhancement by two orders of magnitude can thus be anticipated for $\Delta_{(R,S)}\langle\boldsymbol{\gamma}^5\rangle$. Furthermore, as indicated in Fig. 1 and highlighted in Ref. [49], the sensitivity is improvable by an order of magnitude by choice of a different vibrational transition. In case of CHBrClF, for instance, we may expect that the sensitivity of vibrational transitions involving the Br-F deformation mode or the lower-frequency H-deformation mode could be

larger by an order of magnitude in comparison to the C-F stretching mode (for a detailed discussion see Ref. [49]).

Thus we can estimate that in future $\mathcal{P}$-violation experiments with chiral molecules the sensitivity of the 1999 experiment can be improved by at least five orders of magnitude down to 10^{-17} GeV, i.e., an improvement of the actual best limit by at least two orders of magnitude. This renders experiments with suitably chosen chiral molecules sensitive probes for physics beyond the standard model.

To exploit its full potential, however, a measurement of cosmic $\mathcal{P}$ violation on the background of the larger electroweak frequency splittings would become necessary, which makes additional demands on accuracy of the accompanying computational approaches or calls for experimental schemes to disentangle these two contributions for instance by measuring isotope-dependent electroweak frequency splittings.

The experiment discussed above is sensitive to *oscillating* $\mathcal{P}$-odd interactions of electrons as well. We can exploit the fact that the experiment was performed over a time span of ten days with a well defined set of measurements on each day. In the following we estimate expected sensitivities for this kind of experiments to oscillating pseudoscalar and pseudovector cosmic fields. As CHBrClF is not an optimal choice, we do not aim to determine the best possible limit from the actual experiment but rather highlight the applicability of such a type of experiment for the direct detection of oscillating pseudovector cosmic fields.

The measured frequency shift due to electronic interactions with ALP fields is proportional to

$$g_{\phi\bar{e}e}\sqrt{2(hc)^3\rho_{\mathrm{CDM}}} \sim 4\times 10^{-20}\ \mathrm{GeV}^2 g_{\phi\bar{e}e}. \tag{13}$$

For *pseudoscalar* cosmic fields, measurements of the time derivative of the ALP field as well as the spatial derivatives are sensitive to the same parameter $g_{\phi\bar{e}e}$. Thus, it would require static bounds on the order of 10^{-30} GeV (i.e., a precision of 10^{-17} Hz in the CHBrClF experiment) to be competitive with spin precession experiments that set limits of $|g_{\phi\bar{e}e}| < 10^{-7}\ \mathrm{GeV}^{-1}$ (see Refs. [31,65]). This appears not to be achievable with experiments available today that follow this approach for chiral molecules.

Chiral molecules, however, are directly sensitive to the timelike component of oscillating *pseudovector* cosmic fields, which is not favorably accessible in spin precession experiments. In the following we discuss briefly the expected sensitivity on b_0^e of oscillating fields that can in principle be obtained from available experiments with chiral molecules.

To obtain a rough estimate for the sensitivity to b_0^e in dependence of ω_b due to the sinusoidal behavior of $b_0^e(t)$ we assume that the sensitivity is decreasing for larger frequencies with $\sin(\omega_b t_{\mathrm{tot}}) \approx \omega_b t_{\mathrm{tot}}$. Furthermore we can expect that the experimental uncertainty increases with resulting shorter interrogation times for larger ω_b as

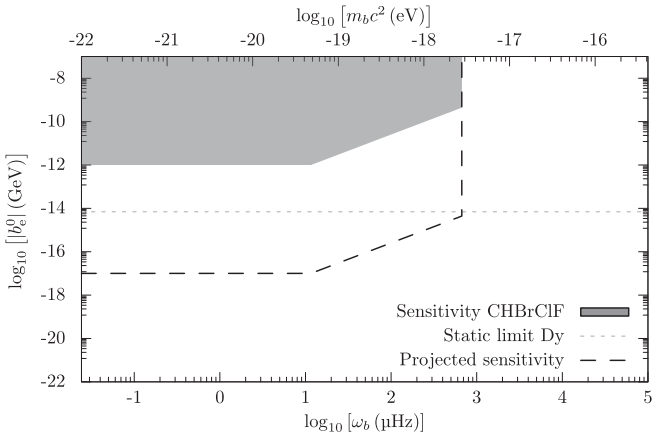

FIG. 2. Sensitivity on electron couplings with the timelike component of pseudovector cosmic fields b_0^e in dependence of the CDM pseudovector oscillation frequency ω_b from a 20-year-old experiment with CHBrClF[42] (gray area) compared to the actual best static limit on b_0^e from the Dy experiment (see Ref. [29], dashed light gray line). The projected sensitivity (dashed black line) indicated for modern experiments with chiral molecules assumes an improvement in sensitivity of five orders of magnitude compared to the CHBrClF experiment of 1999 (see text).

$\sim\sqrt{\omega_b t_{\mathrm{tot}}}$ and we expect the experiment not to be sensitive to frequencies with $\omega_b t_{\mathrm{tot}} > n_{\mathrm{tot}}$, where n_{tot} is the total number of individual measurements. As CDM is supposed to be incoherent for small frequencies $\omega_b < 2\pi/t_{\mathrm{tot}}$ we can expect that b_0^e converges to the static limit. The experiment in Ref. [42] was performed on ten separate days with a total of 580 individual measurements. When assuming a continuous measurement campaign on each day of 58 subsequent measurements we have $t_{\mathrm{tot}} \approx 1\mathrm{d}$ and $n_{\mathrm{tot}} \approx 58$. In total we arrive at the sensitivities

$$b_0^e \lesssim \begin{cases} 10^{-12}\ \mathrm{GeV}, & \text{if } \frac{\omega_b}{2\pi} \leq 1.2\ \mu\mathrm{Hz} \\ (\omega_b t_{\mathrm{tot}})^{3/2} 10^{-12}\ \mathrm{GeV}, & \text{if } 1.2\ \mu\mathrm{Hz} < \frac{\omega_b}{2\pi} \leq 0.7\ \mathrm{mHz} \\ \infty, & \text{if } \frac{\omega_b}{2\pi} > 0.7\ \mathrm{mHz} \end{cases}. \tag{14}$$

The expected sensitivities on b_0^e in CHBrClF and future experiments in dependence on the pseudovector CDM oscillation frequency ω_b is shown in Fig. 2. It shall be noted that the region of ω_b to which the experiment is sensitive may be smaller or even extended depending on the actual timing of the measurements. However, robust bounds require an extended theoretical description and a rigorous statistical analysis of the actual datasets as was also discussed in Refs. [66–68].

Conclusion.—We have shown in this letter that $\mathcal{P}$-odd interactions of electrons with cosmic fields are strongly pronounced in chiral molecules. We could demonstrate that chiral molecules are suitable systems to tighten bounds on $\mathcal{P}$-odd electronic interactions of static pseudovector cosmic

fields that emerge, e.g., from the SME. By performing quasirelativistic calculations of expectation values of $\mathcal{P}$-odd cosmic field interactions in CHBrClF including vibrational corrections, we demonstrated that the C-F stretching mode is not a good choice to place robust limits on pseudovector cosmic fields as the effects are comparatively small and also difficult to predict due to pronounced multimode contributions. However, we estimated the sensitivity of this mode to the parameter b_0^e to be on the order of 10^{-12} GeV in a 20-year-old experiment. This sensitivity is inferior by two orders of magnitude to the actual best direct measurements drawn from modern atomic $\mathcal{P}$-violation experiments. We estimate the achievable sensitivity to $\mathcal{P}$-odd cosmic field interactions with modern high-resolution molecular spectroscopy on suitably chosen chiral molecules to be on the order of 10^{-17} GeV for static cosmic fields (see Fig. 2). This would be an improvement of the current best limit on b_0^e by two orders of magnitude. Furthermore, we discussed possibilities of direct detection of ultra light DM by studying oscillating parity violating potentials in chiral molecules. We have shown that without design of a fundamentally new experimental concept limits on electronic interactions of ultra light oscillating pseudovector particles b_0^e with frequencies of around $\omega_b \lesssim 10$ μHz could be pushed to about 10^{-17} GeV or better with modern experiments with chiral molecules. This corresponds to a direct detection of CDM masses below 10^{-19} eV/c^2 and thus can be interesting for fuzzy CDM searches.

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