$\mathcal{P}, \mathcal{T}$-odd energy shifts of the ^{173}YbOH molecule

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The energy shift in molecular spectra due to interaction of the nuclear magnetic quadrupole moment (M) with electrons is equal to $\delta E_M = MW_M P_M$ where W_M is a constant determined by the electronic structure of the molecule and P_M is a dimensionless constant. We extended the method for calculation of parity nonconservation effects in triatomic molecules developed in Ref. [A. Petrov and A. Zakharova, Phys. Rev. A **105**, L050801 (2022)] to the case of P_M constant and applied it to ^{173}YbOH in the first excited $v = 1$ bending mode. Results of our calculations are required for extraction of the M value from the YbOH experiment.

I. INTRODUCTION

A search for the electron electric dipole moment (eEDM), nuclear magnetic quadrupole moments (MQMs), and other $\mathcal{P},\mathcal{T}$-odd ($\mathcal{P}$ is the space parity and $\mathcal{T}$ is the time reversal) properties remains one of the key tests of the standard model of electroweak interactions and its most important extensions [1–4]. The best constraints on eEDM were obtained in experiments with diatomic molecules YbF [5], HfF$^+$ [6], and ThO [7].

The statistical accuracy of experiments on heavy-atom molecules may be significantly (by several orders of magnitude) enhanced by cooling and trapping the molecules in magneto-optical and/or dipole traps due to increased coherence time. Also the analysis of systematics is of utmost importance since it is what finally determines the accuracy limit of the measurement. Previously it was shown that due to existence of Ω-doublet levels the experiments for searching of the $\mathcal{P}, \mathcal{T}$-odd effects on ThO [7–12] or HfF$^+$ [6,13] are very robust against a number of systematics. Now it is clear that a large part of the great success with HfF$^+$ and ThO is due to its Ω-doubling structure. Therefore, further success in the search for the eEDM is also associated with the use of laser-cooled linear triatomic molecules like YbOH and RaOH [14–16]. In case of the triatomic molecules, the role of Ω doublets used in the diatomic (like ThO and HfF$^+$) molecular experiments is taken over by the l doublets of the excited $v = 1$ bending (distorting linear configuration) vibrational modes. The main advantage of YbOH and RaOH as compared to YbF and RaF is that the former due to bending vibrational structure has close levels of opposite parity l doublets.

Any eEDM experiment searches for an eEDM[1] induced Stark shift

$$\delta E_e = d_e E_{\text{eff}} P, \tag{1}$$

where d_e is the value of the electron electric dipole moment; E_{eff} is the *effective electric field* acting on the electron in the molecule, which is the subject of molecular calculations [17–21]; and P is the polarization of the molecule by the external electric field. In our Letter [22] we have shown that the l-doubling structure is, in general, different from Ω doubling, and the P value tends to approach half of the maximum value for molecules with Hund's case b and in particular for the YbOH molecule.

In turn nuclei with spin $I > 1/2$ gain a $\mathcal{P},\mathcal{T}$-odd-induced MQM that similarly to eEDM interacts with an unpaired electron spin. Measuring MQMs with the use of molecules may provide improved limits on the strength of $\mathcal{P},\mathcal{T}$-odd nuclear forces; on the proton, neutron, and quark EDMs; on the quark chromo-EDMs; and on the QCD θ term and CP-violating quark interactions [23,24].

The scheme of measuring MQMs with the use of molecules is essentially the same as for the eEDM. The energy shift in molecular spectra is equal to

$$\delta E_M = MW_M P_M, \tag{2}$$

where M is the value of the MQM, W_M (similarly to E_{eff}) is determined by the electronic structure of the molecule, and P_M (similarly to P) is the dimensionless constant (polarization). The W_M constant for ^{173}YbOH was calculated in Ref. [25]. To extract $M = \delta E_M / W_M P_M$ from the measured shift δE_M, one needs to know both W_M and P_M values. Strictly speaking,

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[1]Together with eEDM one always needs to consider scalar $\mathcal{P},\mathcal{T}$-odd electron-nuclear interaction, since its influence on the spectrum of molecules is identical to eEDM. For brevity, only the influence of eEDM is mentioned in the present paper.

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nuclei with spin $I \geqslant 1/2$ gain a Schiff moment that similarly to the MQM contributes to nuclear spin dependent $\mathcal{P},\mathcal{T}$-odd energy shift. In the current paper we consider only the MQM which is enhanced in the deformed nucleus of ^{173}Yb [25].

The YbOH molecule is a promising system for experiments looking for nonconservation effects such as eEDM and nuclear MQM [16,22]. For eEDM search experiments, the spinless common ^{174}Yb isotope would be ideal, while for MQM searches, the ^{173}Yb isotope with nuclear spin $I = 5/2$ has to be used. In Ref. [22] we have developed the method for calculation of the polarization P. The aim of the present paper is to extend the method to P_M and apply it to the ground rotational level of the first excited $v = 1$ bending vibrational mode of the ^{173}YbOH molecule. Previously P_M was calculated in diatomics [26–28].

Since both eEDM and MQM contribute to the measured energy splitting of the molecular ^{173}YbOH spectra one needs to find a way to distinguish these two contributions. It is possible due to the different dependence of P and P_M (E_{eff} and W_M are the same for all hyperfine levels) on the hyperfine level of the molecule. Then, performing the measurements on two (at least) different hyperfine levels (provided P and P_M are known) allows one to distinguish between the eEDM and MQM contributions. Therefore calculation of the P for ^{173}YbOH is also performed in the paper.

II. METHOD

For the purpose of the present paper we present our Hamiltonian as

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_{\text{mol}} + \hat{\mathbf{H}}_{\text{hfs}} + \hat{\mathbf{H}}_{\text{ext}}, \tag{3}$$

where $\hat{\mathbf{H}}_{\text{mol}}$ is the molecular Hamiltonian as it is described in Ref. [22],

$$\hat{\mathbf{H}}_{\text{hfs}} = g_{\text{H}}\mathbf{I}^{\text{H}} \sum_a \left(\frac{\boldsymbol{\alpha}_a \times \boldsymbol{r}_{2a}}{r_{2a}^3} \right) + g_{\text{Yb}}\mu_N \mathbf{I}^{\text{Yb}} \sum_a \left(\frac{\boldsymbol{\alpha}_a \times \boldsymbol{r}_{1a}}{r_{1a}{}^3} \right)$$
$$- e^2 \sum_q (-1)^q \hat{Q}_q^2(\mathbf{I}^{\text{Yb}}) \sum_a \sqrt{\frac{2\pi}{5}} \frac{Y_{2q}(\theta_{1a}, \phi_{1a})}{r_{1a}{}^3} \tag{4}$$

is the hyperfine interaction of electrons with Yb and H nuclei, g_{Yb} and g_{H} are the g factors of the ytterbium and hydrogen nuclei, $\boldsymbol{\alpha}_a$ are the Dirac matrices for the ath electron, $\boldsymbol{r}_{1a}$ and $\boldsymbol{r}_{2a}$ are their radius vectors in the coordinate system centered on the Yb and H nuclei, $\hat{Q}_q^2(\mathbf{I}^{\text{Yb}})$ is the quadrupole moment operator for the ^{173}Yb nucleus, index a enumerates (as in all equations below) electrons of YbOH,

$$\hat{\mathbf{H}}_{\text{ext}} = -\mathbf{D} \cdot \mathbf{E} \tag{5}$$

describes the interaction of the molecule with the external electric field, and $\mathbf{D}$ is the dipole moment operator.

Wave functions were obtained by numerical diagonalization of the Hamiltonian (3) over the basis set of the electronic-rotational-vibrational wave functions:

$$\Psi_{\Omega m\omega} P_{lm}(\theta) \Theta_{M_J,\omega}^J(\alpha, \beta) U_{M_I^{\text{H}}}^{\text{H}} U_{M_I^{\text{Yb}}}^{\text{Yb}}. \tag{6}$$

Here $\Theta_{M_J,\omega}^J(\alpha, \beta) = \sqrt{(2J+1)/4\pi} D_{M_J,\omega}^J(\alpha, \beta, \gamma = 0)$ is the rotational wave function, $U_{M_I^{\text{H}}}^{\text{H}}$ and $U_{M_I^{\text{Yb}}}^{\text{Yb}}$ are the hydrogen and ytterbium nuclear spin wave functions, M_J is the projection of

the molecular (electronic-rotational-vibrational) angular momentum $\hat{\mathbf{J}}$ on the laboratory axis, ω is the projection of the same momentum on the z axis of the molecular frame, M_I^{H} and M_I^{Yb} are the projections of the nuclear angular momenta of hydrogen and ytterbium on the laboratory axis, $P_{lm}(\theta)$ is the associated Legendre polynomial, and $\Psi_{\Omega m\omega}$ is the electronic wave function (see Ref. [22] for details).

In this calculation functions with $\omega - m = \Omega = \pm 1/2, l = 0$–$30$, $m = 0, \pm 1, \pm 2$, and $J = 1/2, 3/2, 5/2$ (as in Ref. [22]) were included to the basis set (6). Note that the ground mode $v = 0$ corresponds to $m = 0$, the first excited bending mode $v = 1$ corresponds to $m = \pm 1$, the second excited bending mode has states with $m = 0, \pm 2$, etc.

Provided that the *electronic-vibrational* matrix elements are known, the matrix elements of $\hat{\mathbf{H}}$ between states in the basis set (6) can be calculated with help of angular momentum algebra [22,29] in the same way as for the diatomic molecules [30]. Matrix elements required to calculate $\hat{\mathbf{H}}_{\text{mol}}$, $\hat{\mathbf{H}}_{\text{ext}}$, and hyperfine interaction associated with the hydrogen nucleus were taken from Ref. [22].

Matrix elements required to calculate hyperfine interaction with the ytterbium nucleus are

$$A_{\parallel} = \frac{g_{\text{Yb}}}{\Omega} \langle \Psi_{\Omega m\omega} P_{lm} | \sum_a \left(\frac{\boldsymbol{\alpha}_a \times \boldsymbol{r}_{1a}}{r_{1a}^3} \right)_z | \Psi_{\Omega m\omega} P_{l'm} \rangle$$
$$= -1929\delta_{ll'} \text{ MHz}, \tag{7}$$

$$A_{\perp} = g_{\text{Yb}} \langle \Psi_{\Omega=1/2m\omega} P_{lm} | \sum_a \left(\frac{\boldsymbol{\alpha}_a \times \boldsymbol{r}_{1a}}{r_{1a}^3} \right)_+ | \Psi_{\Omega=-1/2m\omega-1} P_{l'm} \rangle$$
$$= -1856\delta_{ll'} \text{ MHz}, \tag{8}$$

$$e^2 Q q_0 = \langle \Psi_{\Omega m\omega} P_{lm} |$$
$$\times e^2 \sum_q (-1)^q \hat{Q}_q^2(\mathbf{I}^{\text{Yb}}) \sum_a \sqrt{\frac{2\pi}{5}} \frac{Y_{2q}(\theta_{1a}, \phi_{1a})}{r_{1a}^3}$$
$$|\Psi_{\Omega m\omega} P_{l'm} \rangle = 3319\delta_{ll'} \text{ MHz} \tag{9}$$

from Ref. [31]. Following Ref. [22] we neglect the θ dependence of the above matrix elements.

III. RESULTS AND DISCUSSIONS

In Fig. 1 the calculated polarizations P and P_M, as well as ratio P/P_M for the lowest $N = 1$ rotational level of the first excited $v = 1$ bending vibrational mode of ^{173}YbOH for the external electric field $E = 150$ V/cm, are presented as a bar chart for clarity. Within the M_F manifolds the levels are ordered by the energy value. Here $M_F = M_J + M_I^{\text{H}} + M_I^{\text{Yb}}$ is the projection of the total molecular (electronic-rotational-vibrational-nuclear spins) angular momentum $\mathbf{F}$ on the laboratory axis. Numerical data for Fig. 1 are given in Table S1 in Supplemental Material [32]. There are 24 levels for $M_F = 1/2$, 22 levels for $M_F = 3/2$, 16 levels for $M_F = 5/2$, eight levels for $M_F = 7/2$, and two levels for $M_F = 9/2$. As an example, in Fig. 2 the calculated P and P_M for $M_F = 1/2$ as functions of the external electric field are presented. Electric field $E = 150$ V/cm ensures almost saturated values for P and P_M. Calculations showed that all levels have polarizations $P < 0.65$ and $P_M < 0.15$. Energy levels for all M_F values
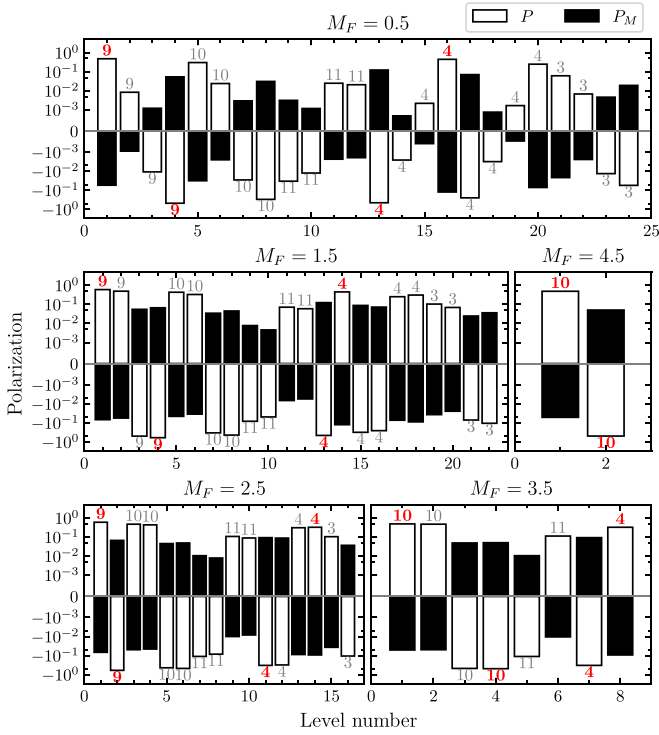
FIG. 1. The calculated polarizations P and P_M and ratio P/P_M. The abscissa numbering the states by increasing energy. Calculations were performed for electric field $E = 150$ V/cm. For levels suggested for experiment the P/P_M values are marked by red (bold style).

as functions of the external electric field are presented in Fig. 3. Numerical data for Fig. 3 are given in Table S2 in Supplemental Material [32].

Since MQM induced energy shift is proportional to P_M [see Eq. (2)] for MQM searches the levels with large P_M values are preferred. Beyond this, to distinguish eEDM and MQM contributions, the levels with different P/P_M ratios have to be used. For the levels satisfying these conditions the P/P_M
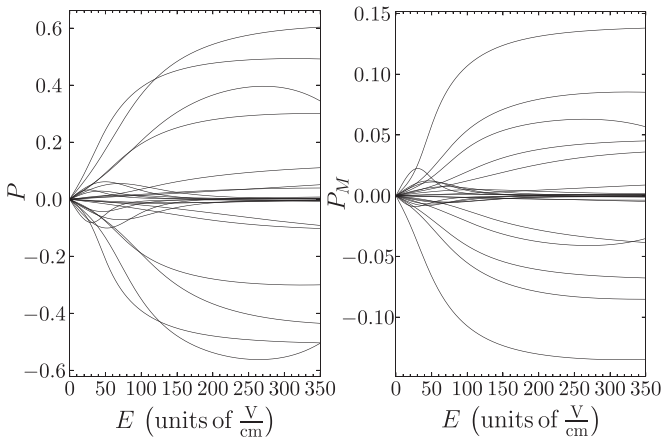

FIG. 2. Calculated polarizations P and P_M for the $M_F = 0.5$ of the lowest $N = 1$ rotational level of the first excited $v = 1$ bending vibrational mode of ^{173}YbOH as functions of the external electric field
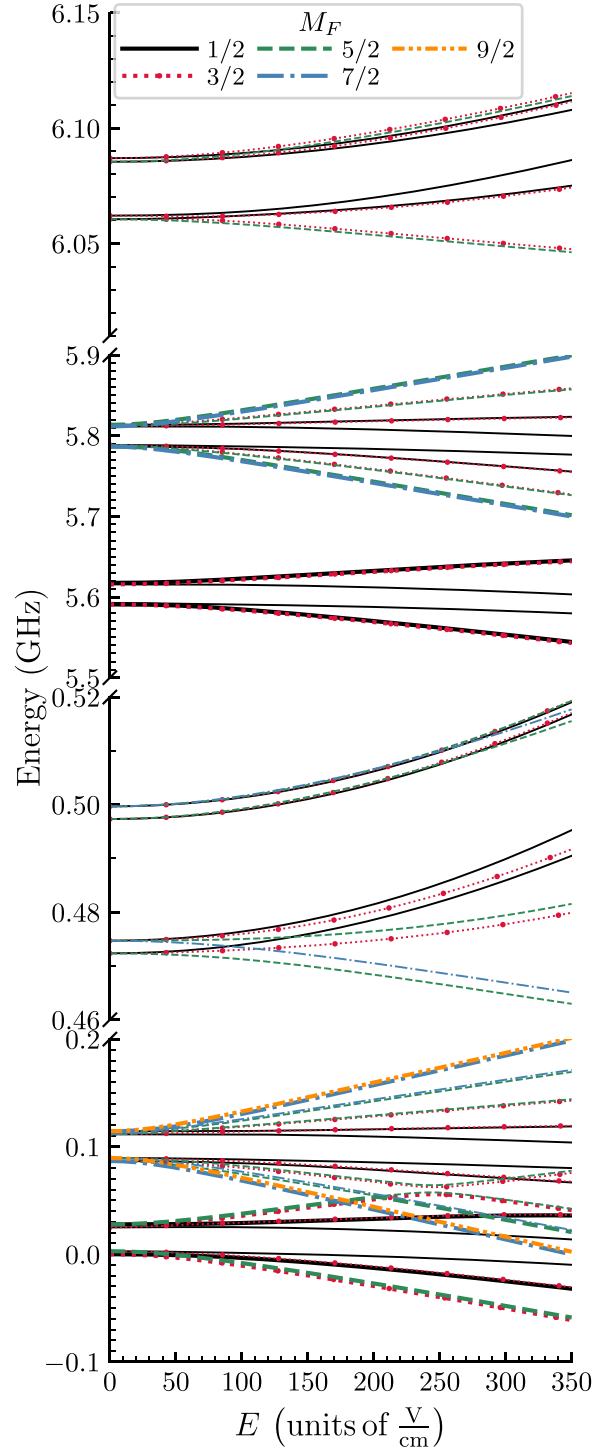

FIG. 3. The calculated energies of the lowest $N = 1$ rotational level of the first excited $v = 1$ bending vibrational mode of ^{173}YbOH as functions of the external electric field. Zero energy level corresponds to the the lowest energy of $N = 1$ states at zero electric field.

values are marked by red (bold style) in Fig. 1. In Fig. 3 the corresponding levels are marked by the bold style. These levels are the first, fourth, thirteenth, and sixteenth for $M_F = 0.5$; the first, fourth, thirteenth, and fourteenth for $M_F = 1.5$; the first, second, eleventh, and fourteenth for $M_F = 2.5$; the first,

fourth, seventh, and eighth for $M_F = 3.5$; and the first and second for $M_F = 4.5$ (the only levels for $M_F = 4.5$).

As an example of the proposed eEDM contribution exclusion scheme, let us consider the first and sixteenth levels of $M_F = 0.5$. For the first level we have $P = 0.4833$, $P_M = -0.0542$, and $|P/P_M| = 8.91$. Then the energy shift induced by eEDM and MQM is $\delta E^1 = \delta E_e^1 + \delta E_M^1 = 0.4833 d_e E_{\text{eff}} - 0.0542 M W_M$. For the 16th level we have $P = 0.4515$, $P_M = -0.1235$, and $|P/P_M| = 3.66$. The corresponding energy shift is $\delta E^{16} = \delta E_e^{16} + \delta E_M^{16} = 0.4515 d_e E_{\text{eff}} - 0.1235 M W_M$. Then we have $\delta E^1 - 1.07 \delta E^{16} \approx 0.078 M W_M$. So, we managed to exclude the contribution from the eEDM and can extract M (our final goal, W_M, is known from Ref. [25]) from the measured δE^1 and δE^{16}. If the ratios P/P_M for the considered levels were the same we would not be able to write an appropriate (depending only on M) linear combination of δE^1 and δE^{16}. Thus we should choose levels with different P/P_M ratios. Formally, it is enough to select two levels

(independently of whether they have the same M_F or not) with different P/P_M ratios to extract the M value. However, using three or more levels can help to improve statistics and check data (both experimental δE and calculated P and P_M) for consistency. Using only two levels in the experiment may not be practical, as the disentanglement of eEDM and MQM contributions is depending on the accuracy of the computed P and P_M values. We note also that our selection of the levels is only an example. On the basis of Fig. 1 one can select other appropriate levels for the MQM search.

Finally we calculated the polarizations P and P_M associated with eEDM and MQM energy shifts for the ^{173}YbOH molecule in the first excited bending mode. The levels most suitable for the MQM search are determined.

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[32] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevA.106.062806 for numerical data for Figs 1 and 3 in Excel file.