Hyperfine Structure of the First Rotational Level in H_2, D_2 and HD Molecules and the Deuteron Quadrupole Moment

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We perform the four-body calculation of the hyperfine structure in the first rotational state $J = 1$ of the H_2, D_2, and HD molecules and determine the accurate value for the deuteron electric quadrupole moment $Q_d = 0.285\,699(15)(18)$ fm^2 in significant disagreement with former spectroscopic determinations. Our results for the hyperfine parameters agree very well with the currently most accurate molecular-beam magnetic resonance measurement performed several decades ago by N.F. Ramsey and coworkers. They also indicate the significance of previously neglected nonadiabatic effects. Moreover, a very good agreement with the recent calculation of Q_d based on the chiral effective field theory, although much less accurate, indicates the importance of the spin dependence of nucleon interactions in the accurate description of nuclei.

Precise atomic and molecular spectroscopy provides information on the nuclear electromagnetic moments important for testing theories of nuclear interactions [1–5] or even for searching for new physics [6]. This, however, requires a thorough understanding of the variety of interparticle interactions in atoms and molecules. For instance, the proton mean square charge radius has been extracted with unprecedented accuracy from the muonic hydrogen Lamb shift [7] only after careful analysis of all the important quantum electrodynamical effects. A similar determination has recently been performed for the alpha particle from the corresponding measurement in muonic helium [8]. Regarding nuclear magnetic moments, the direct measurement in a Penning trap was performed only for the proton [9], while magnetic moments of heavier stable nuclei have been determined by the nuclear magnetic resonance or the atomic hyperfine splitting measurements. Accordingly, the currently most accurate magnetic moments of deuteron and triton were determined by combining the nuclear magnetic resonance measurements with precise calculations of the molecular shielding factor [10]. Concerning the determination of nuclear magnetic moments from the hyperfine splitting, their accurate calculation is particularly difficult due to a large contribution from the not-well-known spin-dependent nuclear structure. The widely accepted Bohr-Weisskopf correction only partially accounts for the nuclear effects [11]. A clear indication of this problem is a strong and still unexplained discrepancy for the Zemach radius of ^{6}Li between the nuclear model value [12] and the result based on the spectroscopic data of the lithium atom [13], which has recently been confirmed by independent measurements and calculations in the Li$^+$ ion [14, 15].

In this work we investigate the electric quadrupole moment Q_d of the deuteron on the basis of the hyperfine splitting in HD and D_2 molecules. The total electron spin of such a two-electron system is zero, and the strengths of all couplings among nuclear spins and the rotational angular momentum are of the same order of magnitude. Therefore, Q_d can be extracted from the molecular hyperfine splitting with an accuracy that is limited only by the measurement uncertainty provided that sufficiently accurate theoretical calculations with all significant contributions are available.

The recent determinations of $Q_d = 0.285\,98(3)$ fm^2 [16] and $Q_d = 0.285\,783(30)$ fm^2 [17] considered to be the most accurate value to date [18], neglect or underestimate nonadiabatic effects, i.e. the effects beyond the commonly employed Born-Oppenheimer (BO) approximation. Indeed, these results disagree with the recommended value reported in this work (see Eq. (24)) obtained in the nonadiabatic approach, i.e. without separation of nuclear and electronic motions.

In the following we describe shortly the theory of the molecular hyperfine splitting, its accurate calculations with nonadiabatic wave functions, and the determination of Q_d from the measurements by Ramsey and coworkers. Henceforth, we use the original notation by Ramsey [19, 20].

Hyperfine Hamiltonian.—There are three angular momenta in the ground electronic state of the heteronuclear HD molecule, which all couple to each other—the proton spin $\vec{I}_p$, that of the deuteron $\vec{I}_d$, and the rotational angular momentum $\vec{J}$. The effective Hamiltonian describing these interactions reads

$$\begin{aligned} H_{\rm hfs} = & -c_p\,\vec{I}_p\cdot\vec{J} - c_d\,\vec{I}_d\cdot\vec{J} \\ & + \frac{5\,d_1}{(2\,J-1)(2\,J+3)}\bigg[\frac{3}{2}\,(\vec{I}_p\cdot\vec{J})\,(\vec{I}_d\cdot\vec{J}) \\ & \qquad + \frac{3}{2}\,(\vec{I}_d\cdot\vec{J})\,(\vec{I}_p\cdot\vec{J}) - (\vec{I}_p\cdot\vec{I}_d)\,\vec{J}^{\,2}\bigg] \\ & + \frac{5\,d_2}{(2\,J-1)(2\,J+3)}\bigg[3\,(\vec{I}_d\cdot\vec{J})^2 \\ & \qquad + \frac{3}{2}\,(\vec{I}_d\cdot\vec{J}) - \vec{I}_d^{\,2}\,\vec{J}^{\,2}\bigg]. \end{aligned} \tag{1}$$

The above coefficients c_p, c_d, d_1, and d_2 are related, respectively, to the interactions between the following: the proton spin and molecular rotation, the deuteron spin and rotation, the proton and deuteron spins, and the electric quadrupole moment of the deuteron with the electric field gradient [21]. For homonuclear molecules with odd $\vec{J}$ the effective Hamiltonian takes a simplified form

$$H_{\rm hfs} = -\,c\,\vec{I}\cdot\vec{J} + \frac{5\,d}{(2\,J-1)(2\,J+3)} \times \left[3\,(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}\,(\vec{I}\cdot\vec{J}) - \vec{I}^{\,2}\,\vec{J}^{\,2}\right], \tag{2}$$

where the total nuclear spin $\vec{I} = \vec{I}_A + \vec{I}_B$ is equal to 1, and $c = c_p$, $d = d_1/2$ for H_2, and $c = c_d$, $d = d_1 - d_2$ for D_2. We will consider all these constants for the first rotational level $J = 1$ and $v = 0$ and present a short derivation of corresponding formulas followed by numerical calculations using explicitly correlated wave functions. Both the derivation and the calculations are performed in the nonadiabatic regime.

The general spin-orbit Hamiltonian is of the form

$$\delta H = \sum_{\alpha,\beta} \frac{e_\alpha\,e_\beta}{4\,\pi}\,\frac{1}{2\,r_{\alpha\beta}^3}\left[\frac{g_\alpha}{m_\alpha\,m_\beta}\,\vec{I}_\alpha\cdot\vec{r}_{\alpha\beta}\times\vec{p}_\beta - \frac{(g_\alpha-1)}{m_\alpha^2}\,\vec{I}_\alpha\cdot\vec{r}_{\alpha\beta}\times\vec{p}_\alpha\right], \tag{3}$$

where the indices α and β are for electrons and nuclei. The gyromagnetic factors

$$g_p = \frac{\mu_p}{\mu_N\,I_p} = 5.585\,695\ldots \tag{4}$$

$$g_d = \frac{\mu_d}{\mu_N\,I_d}\,\frac{m_d}{m_p} = 1.714\,025\ldots \tag{5}$$

are related to the magnetic moment of the proton $\mu_p = 2.792\,847\,344\,63(82)\,\mu_N$ and the deuteron $\mu_d = 0.857\,438\,2338(22)\,\mu_N$, respectively [22]. The g factor is a dimensionless quantity convenient for use in the magnetic moment formulas. In particular, the coupling of the nuclear spin $\vec{I}_A$ to the molecular rotation, using Eq. (3), is

$$\delta_A H = \vec{I}_A\cdot\vec{Q}_A \tag{6}$$

$$\vec{Q}_A = -\sum_b \frac{\alpha}{2\,r_{Ab}^3}\left[\frac{g_A}{m_A\,m_e}\,\vec{r}_{Ab}\times\vec{p}_b - \frac{(g_A-1)}{m_A^2}\,\vec{r}_{Ab}\times\vec{p}_A\right] + \frac{\alpha}{2\,r_{AB}^3}\left[\frac{g_A}{m_A\,m_B}\,\vec{r}_{AB}\times\vec{p}_B - \frac{(g_A-1)}{m_A^2}\,\vec{r}_{AB}\times\vec{p}_A\right] \tag{7}$$

and the spin-rotation coefficient is thus

$$c_A = \frac{1}{2}\,{\rm i}\,\epsilon^{ijk}\,\langle\phi^i|Q_A^j|\phi^k\rangle\,, \tag{8}$$

where ϕ^i is the wave function for the first rotational state with normalization $\langle\phi^i|\phi^i\rangle = 1$.

The nuclear spin-spin direct interaction can be effectively written as

$$\delta H = I_A^i\,I_B^j\,Q_{AB}^{ij} \tag{9}$$

$$Q_{AB}^{ij} = \frac{g_A\,g_B}{4\,m_A\,m_B}\,\frac{\alpha}{r_{AB}^3}\left(\delta^{ij} - 3\,\frac{r_{AB}^i\,r_{AB}^j}{r_{AB}^2}\right) \tag{10}$$

and the corresponding d_1 coefficient is

$$d_1 = -\frac{1}{5}\,\langle\phi^i|Q_{AB}^{ij}|\phi^j\rangle \tag{11}$$

The omitted part of the spin-spin interaction, proportional to $\delta^3(r_{AB})$, is negligibly small.

The interaction of a particle with the charge e, possessing the electric quadrupole moment Q^{ij} with the gradient of the electric field, is given by

$$\delta H = -\,\frac{e}{6}\,Q^{ij}\,\partial_j E^i\,. \tag{12}$$

For a particle with a definite spin $I \geq 1$, the Q^{ij}, as a traceless and symmetric tensor, can be expressed in terms of a single scalar electric quadrupole moment Q defined by

$$Q^{ij} = \frac{Q}{I\,(2I-1)}\left(\frac{3}{2}\,I^i\,I^j + \frac{3}{2}I^j\,I^i - \delta^{ij}\,\vec{I}^2\right). \tag{13}$$

Referring to Eq. (1), the Ramsey's constant d_2 becomes (in atomic units)

$$d_2 = -\alpha^2\,\frac{Q\,q}{10\,\lambda^2}, \tag{14}$$

where

$$q = \left\langle\phi^i\left|\frac{\partial^2 V}{\partial r_A^i\,\partial r_A^j} - \frac{\delta^{ij}}{3}\,\frac{\partial^2 V}{\partial r_A^k\,\partial r_A^k}\right|\phi^j\right\rangle \tag{15}$$

is the electric field gradient at the nucleus A, V is the Coulomb potential of Eq. (18), and λ is the reduced Compton wavelength of the electron.

Numerical calculations.—The nonadiabatic wave function Ψ is obtained from the variational principle with the following nonrelativistic Hamiltonian for the hydrogen molecule

$$H = T + V\,, \tag{16}$$

where (in atomic units)

$$T = \frac{\vec{p}_A^{\,2}}{2\,m_A} + \frac{\vec{p}_B^{\,2}}{2\,m_B} + \frac{\vec{p}_1^{\,2}}{2} + \frac{\vec{p}_2^{\,2}}{2}\,, \tag{17}$$

$$V = \frac{1}{r_{AB}} - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}}\,. \tag{18}$$

Here, indices A, B and 1, 2 denote nuclei and electrons, respectively. The nuclear masses are those currently recommended by CODATA [22]. The wave function Ψ depends on four particle coordinates $\Psi = \Psi(\vec{r}_A, \vec{r}_B, \vec{r}_1, \vec{r}_2)$. In the center of mass frame the total momentum vanishes $\vec{p}_A + \vec{p}_B + \vec{p}_1 + \vec{p}_2 = 0$, and thus we may assume that the wave function Ψ depends only on the coordinate differences.

In the variational approach the wave function is represented as a linear combination

$$\Psi = \sum_k^N c_k\,\psi_k(\vec{r}_A, \vec{r}_B, \vec{r}_1, \vec{r}_2)\,, \tag{19}$$

of properly symmetrized basis functions

$$\psi_k = (1 \pm P_{A\leftrightarrow B})\,(1 + P_{1\leftrightarrow 2})\,\phi_k(\vec{r}_A, \vec{r}_B, \vec{r}_1, \vec{r}_2), \qquad (20)$$

where $P_{i\leftrightarrow j}$ is the particle exchange operator. In the $J = 1$ state of H_2 and D_2 the wave function is antisymmetric with respect to the exchange of nuclear spatial variables and symmetric in electronic spatial variables, whereas in the heteronuclear HD molecule, only electronic symmetry is imposed, and both (nuclear) symmetric and antisymmetric basis functions are employed. For $J = 1$ the functions ϕ_k in Eq. (20) are the nonadiabatic explicitly correlated Gaussians (naECG) of the form

$$\phi_k^i = r^i\, r_{AB}^n \qquad (21)$$
$$\times e^{-a_{k,1}\, r_{AB}^2 - a_{k,2}\, r_{A1}^2 - a_{k,3}\, r_{A2}^2 - a_{k,4}\, r_{B1}^2 - a_{k,5}\, r_{B2}^2 - a_{k,6}\, r_{12}^2},$$

where $\vec{r}$ (or r^i) is the factor representing the angular momentum $J = 1$, and is either $\vec{r}_{AB}$, $\vec{r}_{A1}$, $\vec{r}_{A2}$, $\vec{r}_{B1}$, $\vec{r}_{B2}$ or $\vec{r}_{12}$. The nonlinear a_k parameters are optimized individually for each basis function ϕ_k. The powers n of the internuclear coordinate r_{AB}, needed to represent accurately the vibrational part of the wave function, are restricted to even integers and are generated randomly for each basis function from the log-normal distribution within the limited 0-80 range. Moreover, the number of basis functions with the particular prefactor $\vec{r}\, r_{AB}^n$ is subject to additional discrete optimization. As a result, the nonrelativistic energy reaches an accuracy of about 10^{-11} (see Table I).

Hyperfine parameters.—The hyperfine parameters for the hydrogen molecule isotopologues obtained with the above wave function are presented in Table I. The numerical convergence for the spin-orbit couplings c_p and c_d is relatively slow, and the resulting numerical uncertainties are not negligible. Most importantly, their difference from BO values fits within the uncertainties, which indicates that the estimation of the magnitude of nonadiabatic effects by the ratio of the electron mass to the nuclear reduced mass is correct. Moreover, the nonadiabatic and BO values are, within uncertainties, in agreement with the Ramsey measurements.

In contrast, the numerical convergence of d_1 and q parameters is very fast, and the corresponding inaccuracy is negligible compared to the uncertainty due to unknown higher order relativistic and QED effects. Again, the difference with BO values is consistent with the estimate of nonadiabatic effects, represented as an inaccuracy of the BO values. We also note that the nonadiabatic d_1 for HD agrees with Ramsey's measurements up to its uncertainty, while for H_2 it fits within $1.2\,\sigma$. Regarding the q parameter, the fast numerical convergence of the gradient of the electric field enables six significant digits to be quoted. Our recommended nonadiabatic value of

$$q = 0.335\,230\,7(7) \text{ a.u.} \qquad (22)$$

obtained for D_2 will be used in the next paragraph for the determination of the deuteron quadrupole moment Q_d. We note that this value differs by $0.000\,6$ a.u. from the $q = 0.334\,66$ a.u obtained in the pioneering nonadiabatic calculations by Bishop and Cheung [30]. This difference is relatively large and shows that the former results in [30] are not accurate enough to draw definite conclusions about the magnitude of the nonadiabatic effects.

The quadrupole moment of deuteron.—Q_d can be determined most accurately from the coupling constant d measured by the molecular-beam magnetic resonance method of Code and Ramsey [26] for D_2 in the first rotational level. We obtain d_2 from the difference $d_2 = d_1 - d$ of calculated d_1 and measured d. Finally, we evaluate the quadrupole moment from

$$Q_d = -\frac{d_2}{2\,Ry\,c}\,\frac{10\,\lambda^2}{\alpha^2\,q} \qquad (23)$$

obtaining the recommended value of

$$Q_d = 0.285\,699(15)(18) \text{ fm}^2. \qquad (24)$$

The results of such calculations are summarized in Table II. A comparison with literature data reported within the last fifty years is presented in Table II and Fig 1. The first uncertainty assigned to our Q_d is due to unknown higher order relativistic and QED corrections to q, which are estimated by a relative factor α^2. The second uncertainty comes from the measurement of d, while numerical uncertainties are negligible. We should mention that the second order magnetic dipole interaction, being also a kind of relativistic correction, leads to the pseudoquadrupole effect estimated by Ramsey to be of about 10^{-5} [31] and this contribution is included in our α^2 uncertainty.

This nonadiabatic Q_d is in agreement with our BO value [23], the relative uncertainty of which was estimated by the ratio of the electron mass to the nuclear reduced mass. It is in significant disagreement, though, with the recent most accurate determination by Pavanello *et al.* [17] and Jóźwiak *et al.* [16] (see Table II and Fig 1). It is in agreement, however, with the revised result by Bishop, quoted in 1983 by Ericson *et al.* [3], which served for a long time as a reference value for Q_d. A comparison of our result with recent literature data indicates the significance of nonadiabatic effects and also draws

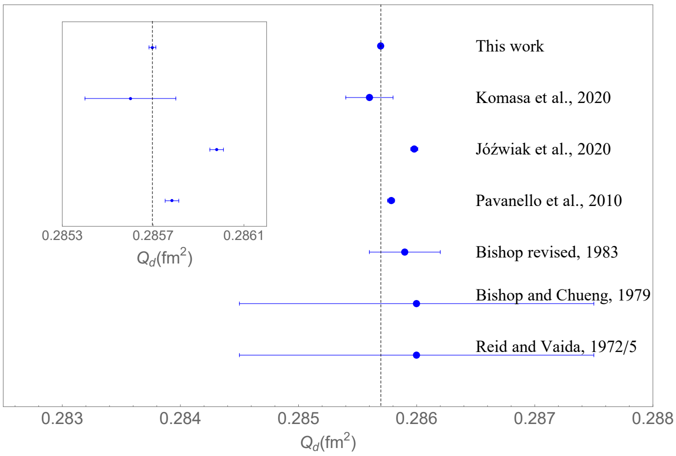

FIG. 1. Comparison of literature data for Q_d.

TABLE I. Convergence of the nonrelativistic energy E (in a.u.), hyperfine splitting parameters (in kHz), and the electric field gradient q (in a.u.) calculated using naECG wave functions for the first rotational level $(v, J) = (0, 1)$. The extrapolated nonadiabatic results (NA) are compared to the Born-Oppenheimer (BO) values [23] and with the results of measurements by Ramsey *et al.* [24–26]. The NA values do not include here the uncertainties due to omitted relativistic and QED effects, which can be estimated by the relative factor of $\alpha^2 \approx 5 \times 10^{-5}$, where α is the fine structure constant.

H_2

Basis	E	c_p	$d = d_1/2$
512	$-1.163\,485\,167\,695$	$112.393\,16$	$57.643\,938\,904\,75$
1024	$-1.163\,485\,172\,061$	$113.889\,80$	$57.643\,937\,929\,23$
1536	$-1.163\,485\,172\,209$	$113.904\,33$	$57.643\,937\,899\,30$
2048	$-1.163\,485\,172\,287$	$113.911\,88$	$57.643\,937\,895\,69$
NA	$-1.163\,485\,172\,314\,0(1)^a$	$113.920(8)$	$57.643\,937\,891(6)$
BO, [23]		$114.00(12)$	$57.69(6)$
NA − BO		$-0.08(12)$	$-0.05(6)$
Measured, [24]		$113.904(30)$	$57.671(24)$

HD

Basis	E	c_p	c_d	d_1	q
512	$-1.165\,065\,367\,519$	$83.740\,0$	$13.281\,98$	$17.761\,872\,179\,98$	$0.334\,510\,892$
1024	$-1.165\,065\,376\,045$	$85.446\,7$	$13.146\,42$	$17.761\,872\,391\,72$	$0.334\,493\,539$
1536	$-1.165\,065\,376\,735$	$85.550\,6$	$13.135\,55$	$17.761\,872\,423\,13$	$0.334\,492\,630$
2048	$-1.165\,065\,376\,858$	$85.598\,6$	$13.126\,23$	$17.761\,872\,410\,33$	$0.334\,491\,813$
NA	$-1.165\,065\,376\,941\,65(3)^a$	$85.63(4)$	$13.117(9)$	$17.761\,872\,414(13)$	$0.334\,491\,0(8)$
BO, [23]		$85.675(60)$	$13.132(9)$	$17.773(12)$	$0.334\,7(3)$
NA − BO		$-0.04(7)$	$-0.014(14)$	$-0.012(12)$	$-0.000\,2(3)$
Measured, [25]		$85.600(18)$	$13.122(11)$	$17.761(12)$	

D_2

Basis	E	c_d	d_1	q
512	$-1.166\,896\,428\,705$	$8.723\,72$	$2.737\,626\,131\,22$	$0.335\,240\,662$
1024	$-1.166\,896\,432\,071$	$8.763\,77$	$2.737\,626\,043\,01$	$0.335\,233\,684$
1536	$-1.166\,896\,432\,230$	$8.765\,41$	$2.737\,626\,038\,04$	$0.335\,232\,171$
2048	$-1.166\,896\,432\,323$	$8.766\,20$	$2.737\,626\,037\,75$	$0.335\,231\,377$
NA	$-1.166\,896\,432\,359\,76(4)^a$	$8.767\,4(10)$	$2.737\,626\,037\,4(12)$	$0.335\,230\,7(7)$
BO, [23]		$8.770(5)$	$2.739(2)$	$0.335\,35(18)$
NA − BO		$-0.003(5)$	$-0.002(2)$	$-0.000\,12(18)$
Measured, [26]		$8.768(3)$		

[a] This is a reference energy obtained from explicitly correlated exponential functions [27–29]

attention to the need for the correct use of the BO potential, as the above mentioned results [16, 17, 23] differ from each other due to different potentials used to average the q parameter. To verify our result, we used the obtained value of Q_d to evaluate the d_2 parameter for the HD molecule in a $J = 1$ state, and we achieved a perfect agreement with d_2 as measured by Ramsey *et al.* [25] (see Table II).

Summary.—The deuteron quadrupole moment Q_d is determined with the highest accuracy among all nuclei in the periodic table [18]. This accurate result can be used not only in precise atomic and molecular structure calculations but also can serve as a benchmark for the nuclear structure theory. Indeed, for a long time, Q_d could not be reproduced by any modern potential model (see e.g. [3] and references therein). It was not until very recently very recently Filin *et al.* [32] reported $Q_d = 0.285\,4^{+38}_{-17}$ fm^2 obtained from chiral effective field theory (χEFT), which is in very good agreement with our result. This agreement opens the possibility of better understanding the spin-dependent nuclear structure effects in atomic spectra, particularly in muonic deuterium hyperfine splitting, where significant discrepancies with measurement [35] have been reported [36].

Apart from the deuteron quadrupole moment, by accounting for nonadiabatic effects, we obtained all the other hyperfine constants in very good agreement with Ramsey's molecular-beam magnetic resonance measurements (see Table I). However, current theory includes only the leading relativistic effects. Because the inclusion of higher order relativistic and QED corrections is certainly within reach, more accurate measurements are desirable. This may open new windows for high-precision tests of fundamental interactions on the molecular scale.

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TABLE II. Determination of the deuteron quadrupole moment (in fm^2) from D_2 hyperfine parameters and its verification for HD.

Quantity		Source
	D_2	
d	$25.241\,4(14)$ kHz	Code & Ramsey, 1971 [26]
d_1	$2.737\,626\,037\,4(12)$ kHz	This work, Eq. (11)
d_2	$-22.503\,8(14)$ kHz	$d_2 = d_1 - d$
q	$0.335\,230\,7(7)$ a.u.	This work, Eq. (15)
Q_d	$0.285\,699(15)(18)$[a]	This work, Eq. (23)
	$0.285\,4^{+38}_{-17}$[b]	Filin *et al.*, 2020 [32]
	$0.285\,98(3)$	Jóźwiak *et al.*, 2020 [16]
	$0.285\,6(2)$	Komasa *et al.*, 2020 [23]
	$0.285\,783(30)$	Pavanello *et al.*, 2010 [17]
	$0.285\,90(30)$	Bishop revisited, 1983, cited in [3]
	$0.286\,0(15)$	Bishop & Cheung, 1979 [30]
	$0.286\,0(15)$	Reid & Vaida, 1972/5 [33, 34]
	HD	
q	$0.334\,491\,0(8)$ a.u.	This work, Eq. (15)
d_2	$-22.454\,2(14)$[c] kHz	This work, Eq. (14)
d_2	$-22.454(6)$ kHz	Ramsey *et al.*, 1958 [25]
Diff.	$-0.000(6)$ kHz	

[a] The first uncertainty accounts for missing relativistic correction, the second one is due to the experimental uncertainty of d.

[b] Calculated in the framework of χEFT.

[c] This uncertainty comes from the experimental uncertainty in Q_d.

[1] F. M. Lev, E. Pace, and G. Salmè, Phys. Rev. Lett. **83**, 5250 (1999).

[2] R. Gilman and F. Gross, J. Phys. G **28**, R37 (2002).

[3] T. Ericson and M. Rosa-Clot, Nucl. Phys. A **405**, 497 (1983).

[4] E. Epelbaum, H.-W. Hammer, and Ulf-G. Meißner, Rev. Mod. Phys. **81**, 1773 (2009).

[5] A. A. Filin, V. Baru, E. Epelbaum, H. Krebs, D. Möller, and P. Reinert, Phys. Rev. Lett. **124**, 082501 (2020).

[6] M. S. Safronova, D. Budker, D. DeMille, Derek F. Jackson Kimball, A. Derevianko, and C. W. Clark, Rev. Mod. Phys. **90**, 025008 (2018).

[7] R. Pohl, A. Antognini, F. Nez, F. D. Amaro, F. Biraben, J. M. R. Cardoso, D. S. Covita, A. Dax, S. Dhawan, L. M. P. Fernandes, et al., Nature **466**, 213 (2010).

[8] R. Pohl and coworkers (private communication).

[9] S. Sturm, F. Kohler, J. Zatorski, A. Wagner, Z. Harman, G. Werth, W. Quint, C. H. Keitel, and K. Blaum, Nature **506**, 467 (2014).

[10] M. Puchalski, J. Komasa, and K. Pachucki, Phys. Rev. A **92**, 020501(R) (2015).

[11] A. Bohr and V. F. Weisskopf, Phys. Rev. **77**, 94 (1950).

[12] V. A. Yerokhin, Phys. Rev. A **78**, 012513 (2008).

[13] M. Puchalski and K. Pachucki, Phys. Rev. Lett. **111**, 243001 (2013).

[14] H. Guan, S. Chen, X.-Q. Qi, S. Liang, W. Sun, P. Zhou, Y. Huang, P.-P. Zhang, Z.-X. Zhong, Z.-C. Yan, et al., Phys. Rev. A **102**, 030801(R) (2020).

[15] Xiao-Qiu Qi, Pei-Pei Zhang, Zong-Chao Yan, G.W.F. Drake, Zhen-Xiang Zhong, Ting-Yun Shi, Shao-Long Chen, Yao Huang, Hua Guan, and Ke-Lin Gao, Phys. Rev. Lett. **125**, 183002 (2020).

[16] H. Jóźwiak, H. Cybulski, and P. Wcisło, J. Quant. Spectrosc. Radiat. Transfer **253**, 107186 (2020).

[17] M. Pavanello, W.-C. Tung, and L. Adamowicz, Phys. Rev. A **81**, 042526 (2010).

[18] P. Pyykkö, Mol. Phys. **116**, 1328 (2018).

[19] N. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, 1956).

[20] N. F. Ramsey and H. R. Lewis, Phys. Rev. **108**, 1246 (1957).

[21] J. M. Brown and A. Carrington, *Rotational Spectroscopy of Diatomic Molecules*, Cambridge Molecular Science (Cambridge University Press, Cambridge, England, 2003).

[22] 2018 CODATA recommended values (2018),`https://physics.nist.gov/cuu/Constants`.

[23] J. Komasa, M. Puchalski, and K. Pachucki, Phys. Rev. A **102**, 012814 (2020).

[24] N. J. Harrick, R. G. Barnes, P. J. Bray, and N. F. Ramsey, Phys. Rev. **90**, 260 (1953).

[25] W. E. Quinn, J. M. Baker, J. T. LaTourrette, and N. F. Ramsey, Phys. Rev. **112**, 1929 (1958).

[26] R. F. Code and N. F. Ramsey, Phys. Rev. A **4**, 1945 (1971).

[27] K. Pachucki and J. Komasa, Phys. Chem. Chem. Phys. **20**, 247

(2018).
[28] K. Pachucki and J. Komasa, Phys. Chem. Chem. Phys. **20**, 26297 (2018).
[29] K. Pachucki and J. Komasa, Phys. Chem. Chem. Phys. **21**, 10272 (2019).
[30] D. M. Bishop and L. M. Cheung, Phys. Rev. A **20**, 381 (1979).
[31] N. F. Ramsey, Phys. Rev. **89**, 527 (1953).
[32] A. A. Filin, D. Möller, V. Baru, E. Epelbaum, H. Krebs, and P. Reinert, arXiv 2009.08911.
[33] R. V. Reid and M. L. Vaida, Phys. Rev. Lett. **29**, 494 (1972).
[34] R. V. Reid and M. L. Vaida, Phys. Rev. Lett. **34**, 1064 (1975).
[35] R. Pohl, F. Nez, L. M. P. Fernandes, F. D. Amaro, F. Biraben, J. M. R. Cardoso, D. S. Covita, A. Dax, S. Dhawan, M. Diepold, et al., Science **353**, 669 (2016).
[36] M. Kalinowski, K. Pachucki, and V. A. Yerokhin, Phys. Rev. A **98**, 062513 (2018).