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Enhanced sensitivity to the time variation of the fine-structure constant and m_p/m_e in diatomic molecules: A closer examination of silicon monobromide

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Recently it was pointed out that transition frequencies in certain diatomic molecules have an enhanced sensitivity to variations in the fine-structure constant α and the proton-to-electron mass ratio m_p/m_e due to a near cancellation between the fine structure and vibrational interval in a ground electronic multiplet [V. V. Flambaum and M. G. Kozlov, Phys. Rev. Lett. **99**, 150801 (2007)]. One such molecule possessing this favorable quality is silicon monobromide. Here we take a closer examination of SiBr as a candidate for detecting variations in α and m_p/m_e. We analyze the rovibronic spectrum by employing the most accurate experimental data available in the literature and perform *ab initio* calculations to determine the precise dependence of the spectrum on variations in α. Furthermore, we calculate the natural linewidths of the rovibronic levels, which place a fundamental limit on the accuracy to which variations may be determined.

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I. INTRODUCTION

Theories unifying gravity with other interactions suggest the possibility of spatial and temporal variation of fundamental physical constants, such as the fine-structure constant, $\alpha = e^2/\hbar c$, and the proton-to-electron mass ratio, $\mu = m_p/m_e$ [1]. The search for such variation has received considerable interest in recent years and is being conducted using a wide variety of methods [2,3]. Some major directions of this research include the analysis of high-resolution spectroscopy of quasar absorption systems [4–6], frequency comparison of atomic clocks over extended periods of time [7–9], and nuclear methods, including the study of nucleosynthesis, α and β decay, and the Oklo natural reactor [10–15].

Precision molecular spectroscopy is a new and promising direction of searching for variations in fundamental constants. Molecular spectra are sensitive to both μ and α, and by measuring close-lying levels, great enhancement of relative variation may be observed [3,16,17]. In particular, diatomic molecules that have a near cancellation between hyperfine structure and rotational intervals or between fine structure and vibrational intervals are of interest in the context of such an enhancement. A number of such molecules have been proposed, e.g., Cs_2 [18], CaH, MgH, CaH^+ [19,20], Cl_2^+, IrC, HfF^+, SiBr, LaS, LuO, and others [21].

In this paper, we conduct a detailed study of one of the molecular candidates suggested by Flambaum and Kozlov [21], namely, silicon monobromide. To this end, it is useful to start by briefly recapitulating some of the main concepts put forth by these authors. We consider a diatomic molecule with an electronic ground state composed of a fine-structure multiplet. Taking the vibrational energy spacing of the multiplet as ω_e in the harmonic approximation, and the fine-structure (spin-orbit) energy spacing between two multiplet states as ω_f, the energy associated with a transition between the multiplet states reads

$$\omega = \omega_f - v\omega_e,$$

where v represents the change in the number of vibrational quanta for the transition.

The fine-structure and vibrational energies have different sensitivities to variations in α and μ. In particular, ω_f is sensitive to variations in the fine-structure constant, scaling as $\omega_f \sim \alpha^2$, while being almost insensitive to variations in μ. On the other hand, ω_e is sensitive to variations in the proton-to-electron mass ratio, scaling as $\omega_e \sim \mu^{-1/2}$, while being insensitive to variations in α. It follows that ω is sensitive to variations in both α and μ, with a corresponding variation for fractional variations in α and μ given by

$$\delta\omega = 2\omega_f \frac{\delta\alpha}{\alpha} + \frac{v}{2}\omega_e \frac{\delta\mu}{\mu}.$$

For a number of molecules there exist transitions having a near cancellation between fine-structure and vibrational energies, i.e., $\omega_f \approx v\omega_e$. In such cases, the fractional variation of ω may then be written

$$\frac{\delta\omega}{\omega} \approx K\left(2\frac{\delta\alpha}{\alpha} + \frac{1}{2}\frac{\delta\mu}{\mu}\right),$$

where $K = \omega_f/\omega$ is an enhancement factor. Large values of K are suggestive of favorable cases for experimentally detecting a signal from variations in α or μ. As discussed in Ref. [21], however, it is also necessary to consider the size of the absolute shift $\delta\omega$ and compare this to experimental limitations on measuring ω itself; one such notable limitation is the natural linewidth and intensity of the transition.

The diatomic molecule SiBr has a $^2\Pi_r$ electronic ground state with fine-structure and vibrational spacing similar to about 1 cm^{-1} ($\omega_f \approx \omega_e \approx 420\ \mathrm{cm}^{-1}$). This is comparable to the rotational constant B_e, and thus ω may be reduced further by a suitable choice of rotational levels. In this paper we examine the rovibronic spectrum of SiBr by employing the most accurate experimental spectroscopic data for SiBr available in the literature, namely, that of Bosser *et al.* [22]. Furthermore we perform *ab initio* molecular calculations with the purpose of (i) determining the precise dependence of the spectrum on α, and (ii) obtaining values for the natural linewidths of the pertinent levels. As in Ref. [21], we still conclude that dedicated measurements are required to determine precise values of transition frequencies and find the best transitions for the search of variation in α and μ; the aim of this work is to entice experimental progress in this direction.

At the risk of being overly prudent, we discuss our convention used throughout concerning units, applicable to the above expressions as well. We choose to work with atomic units ($\hbar = e = m_e = 1$), and thus an expression such as δX indicates a variation in X when expressed in atomic units (this is not a trivial remark: for instance, when expressed in atomic units the speed of light $c = 1/\alpha$ certainly varies with a variation of α; however, *by definition* the speed of light does not change if expressed in SI units). Throughout this paper we will find it useful to express energy values in the spectroscopically familiar units of cm^{-1}; one should interpret this merely as a conversion from the atomic unit of energy, 1 a.u. $= 2.194\,746\,25 \times 10^5$ cm^{-1}. In the end we will only be concerned with variations of dimensionless quantities [1], such as the ratio of two frequencies, and for these expressions ambiguity surrounding units is nonexistent.

II. ROVIBRONIC ENERGY LEVELS IN HUND'S CASE *a* DIATOMICS

We consider an electronic multiplet of a diatomic molecule described by Hund's case *a* [23]. In Hund's case *a*, the electronic orbital angular momentum $\mathbf{L}$ is strongly coupled to the internuclear axis (chosen to be the z axis in a molecule-fixed frame), which is to say that Λ, the eigenvalue of L_z, remains a good quantum number. Furthermore, the spin angular momentum $\mathbf{S}$ is strongly coupled to the internuclear axis by way of the spin-orbit interaction, and thus Σ, the eigenvalue of S_z, also remains a good quantum number.

Initially we neglect the spin-orbit interaction, in which case we may write the vibronic energies T_{ev} of a given electronic multiplet in terms of conventional spectroscopic constants,

$$T_{ev} = T_e + \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2, \tag{1}$$

where v is the vibrational quantum number, and terms beyond second order in $(v+\frac{1}{2})$ are omitted. The constant T_e is the energy relative to the ground-state multiplet; as we will only be concerned with the ground-state multiplet, we may set $T_e = 0$. Constants ω_e and $\omega_e x_e$ represent the harmonic vibrational energy and the first correction due to anharmonicity, respectively.

Next we consider the effective spin-orbit interaction. As $\mathbf{L}$ is strongly coupled to the internuclear (z) axis, the spin-orbit interaction takes the simple form [24]

$$H_{\mathrm{so}} = A_v L_z S_z. \tag{2}$$

The spin-orbit factor A_v here depends on the vibrational state and to the first order in $(v+\frac{1}{2})$ may be written as

$$A_v = A_e - \alpha_{Ae}\left(v+\frac{1}{2}\right). \tag{3}$$

Finally, we consider the energy associated with rotation, taking the effective rotational Hamiltonian for the Hund's intermediate case $a-b$ as in Ref. [24],

$$H_{\mathrm{rot}} = B_v N^2, \tag{4}$$

where $\mathbf{N} = \mathbf{J} - \mathbf{S}$, and $\mathbf{J}$ being the total angular momentum excluding nuclear spin. We now introduce the operators $J^{\pm} = J_x \pm i J_y$, and similar for $S^{\pm}$, where x and y correspond to the molecule-fixed axes perpendicular to the internuclear axis. With these operators we expand N^2 as

$$\begin{aligned} N^2 &= J^2 + S^2 - 2\mathbf{J}\cdot\mathbf{S} \\ &= J^2 + S^2 - 2S_z^2 - 2L_zS_z - (J^+S^- + J^-S^+), \end{aligned} \tag{5}$$

where we have used $J_z - L_z - S_z = 0$ with the physical reasoning that the molecule rotates about an axis perpendicular to the internuclear axis. In the expressions to follow, we neglect the small v dependence of B_v and use $B_v = B_e$. For the Hund's case *a* limit, where Σ is assumed to be a good quantum number, the term in parentheses in Eq. (5) may be dropped as it involves the raising and lowering operators $S^{\pm}$.

We now consider the energy levels specific to a Π doublet, such as the ground electronic state of SiBr. The appropriate basis for Hund's case *a* is $|JM,\Lambda\Sigma\rangle$, where M is the eigenvalue of J_Z, Z being a space-fixed axis. In this basis, the doubly degenerate $^2\Pi_{1/2}$ state is represented by $|JM,\pm1,\mp\frac{1}{2}\rangle$ and the doubly degenerate $^2\Pi_{3/2}$ state represented by $|JM,\pm1,\pm\frac{1}{2}\rangle$. The angular-momentum quantum number J is necessarily a half-integer, with limitations $J \geqslant 1/2$ and $J \geqslant 3/2$ for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states, respectively. In terms of the spectroscopic constants introduced above, the energy levels are then given by

$$\begin{aligned} E_{vJ} &= \pm\frac{1}{2}(A_e - 2B_e) + \left(\omega_e \mp \frac{1}{2}\alpha_{Ae}\right)\left(v+\frac{1}{2}\right) \\ &\quad - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + B_e\left(J+\frac{1}{2}\right)^2, \end{aligned} \tag{6}$$

where the top (bottom) sign corresponds to the $^2\Pi_{3/2}$ ($^2\Pi_{1/2}$) levels. As discussed in Ref. [24], α_{Ae} may be regarded as the difference in the harmonic vibrational energies of the doublet levels when considered independently, i.e., $\alpha_{Ae} = \omega_e^{(1/2)} - \omega_e^{(3/2)}$; this interpretation is consistent with Eq. (6).

It will be useful to separate the energy given by Eq. (6) into J-independent and J-dependent parts,

$$E_{vJ} = G_v + F_J,$$

where $F_J = B_e(J+\frac{1}{2})^2$. We will refer to these as the vibronic and rotational energies, respectively. Note that with this nomenclature, the energy contribution $\mp B_e$ of Eq. (6) is associated with the vibronic energy, despite arising from the rotational Hamiltonian, Eq. (4). We further note that with this choice of separation, only the expression for the vibronic part depends on the particular doublet state ($^2\Pi_{3/2}$ or $^2\Pi_{1/2}$). The total energies, E_{vJ}, will be referred to as the rovibronic energies.

It is briefly noted here that certain additional terms, such as those associated with the spin-rotation interaction, lambda-doubling, and the hyperfine interaction, have intentionally been neglected in this section. These contributions are typically small, though for large J some of these terms may have a sizable effect.

III. ROVIBRONIC ENERGY LEVELS OF SILICON MONOBROMIDE

The ground electronic multiplet, $X^2\Pi_r$, of SiBr falls into the category of Hund's case a. Accurate spectroscopic constants for this doublet have been experimentally determined by Bosser *et al.* [22] and are presented in Table I. Figure 1(a) illustrates the potential energy curves for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states near minima, based on the data for isotopic species ^{28}Si^{79}Br; also displayed are the lowest few vibronic energy levels. Due to similarity in the magnitude of the A_e and ω_e constants, the $G_v^{(1/2)}$ level is quasidegenerate with the $G_{v-1}^{(3/2)}$ level for $v = 1,2,\ldots$. Figure 1(b) provides a magnification of the energy separation between these quasidegenerate levels.

Before proceeding we briefly discuss the accuracy of the experimental data in Table I. Explicit uncertainties are not provided for the constants, but indications from Ref. [22] suggest that the data are likely to be accurate to $\sim$0.1 cm^{-1}. For the illustrative purposes of this section, we will treat the data as exact; for deviations on the order of $\sim$0.1 cm^{-1}, the important qualitative features of the spectrum remain, and only minor modifications would be necessary.

As mentioned in the Introduction, we are interested in transitions having large enhancement factors, namely, the transitions between the quasidegenerate vibronic levels. We define the small energy difference between quasidegenerate vibronic levels as

$$\begin{aligned}\Delta G_v &\equiv G_{v-1}^{(3/2)} - G_v^{(1/2)}\\ &= A_e - \omega_e - 2B_e + v(2\omega_e x_e - \alpha_{Ae}).\end{aligned} \tag{7}$$

(It is noted that ΔG_v as defined here is not related to the usual spectroscopic $\Delta G_{1/2}, \Delta G_{3/2}, \ldots$) For the isotope ^{28}Si^{79}Br this reduces to

$$\Delta G_v = (-1.86 + 0.85v)\ \text{cm}^{-1}.$$

An interesting property of the ^{28}Si^{79}Br vibronic spectrum is that ΔG_v is negative for $v = 1,2$ and positive for $v \geqslant 3$. This is plainly seen in Fig. 1(b), where for the quasidegenerate levels described by $v = 1,2$, the $G_{v-1}^{(3/2)}$ energy (dashed red line) is below the $G_v^{(1/2)}$ energy (solid blue line), whereas the order is inverted for $v \geqslant 3$. This inversion arises due to the anharmonicity of the potentials, $\omega_e x_e$.

TABLE I. Spectroscopic constants for the $X^2\Pi_r$ ground doublet of SiBr. Theoretical values for ^{28}Si^{79}Br are calculated using the relativistic Fock space coupled cluster approach, described in Sec. V. Experimental data for isotope ^{28}Si^{79}Br are from Ref. [22], whereas data for isotope ^{28}Si^{81}Br are inferred using the appropriate dependence on reduced mass per spectroscopic constant along with the ratio of reduced masses of the two isotopic species, 1.0065044. All values in the table are in cm^{-1}.

	^{28}Si^{79}Br		^{28}Si^{81}Br
Constant	Theor.	Expt.	Expt.
A_e	419.54	422.61	422.61
ω_e	424.35	424.14	422.77
$\omega_e x_e$	1.32	1.41	1.40
α_{Ae}	2.26	1.97	1.96
B_e	0.1634	0.1671	0.1660

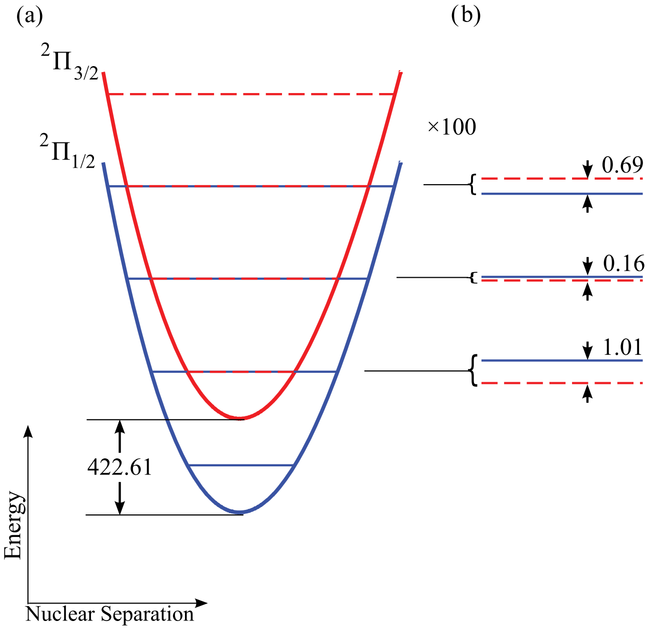

FIG. 1. (Color online) Potential energy curves and the lowest few vibronic energy levels for the $X^2\Pi_r$ ground doublet of ^{28}Si^{79}Br. (a) The lower blue and upper red curves represent the potential energy curves for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states, respectively, with the solid blue and dashed red horizontal lines illustrating the corresponding vibronic energy levels. (b) The energy separation between the quasidegenerate vibronic levels is magnified by a factor of 100. All energy differences are in cm^{-1}.

We now turn our attention to rotational energies. With our choice of separation for "vibronic" and "rotational" contributions to the total energy, the rotational energies are given by the same expression for both doublet states, i.e., $F_J^{(1/2)} = F_J^{(3/2)} = B_e(J + \frac{1}{2})^2$. We will concern ourselves only with single-photon transitions, from which the angular-momentum restriction $\Delta J = 0, \pm 1$ follows. For $\Delta J = 0$ transitions, there is no change in rotational energy, and the corresponding measured transition lines for all J may be blended, limiting the accuracy. For this reason, we focus on transitions with $\Delta J = \pm 1$. We define the difference in rotational energy encompassing both of these cases as

$$\Delta F_J^{\pm} \equiv F_{J\pm 1}^{(3/2)} - F_J^{(1/2)} = \begin{cases} 2B_e(J+1), \\ -2B_e J, \end{cases} \tag{8}$$

where ΔF_J^{+} and ΔF_J^{-} are restricted by $J \geqslant 1/2$ and $J \geqslant 5/2$, respectively. We note that ΔF_J^{+} is necessarily positive, whereas ΔF_J^{-} is necessarily negative.

The experimentally observable quantity is the energy difference between two rovibronic levels; we define the energy difference between pertinent rovibronic levels as

$$\Delta E_{vJ}^{\pm} \equiv E_{v-1,J\pm 1}^{(3/2)} - E_{vJ}^{(1/2)} = \Delta G_v + \Delta F_J^{\pm}. \tag{9}$$

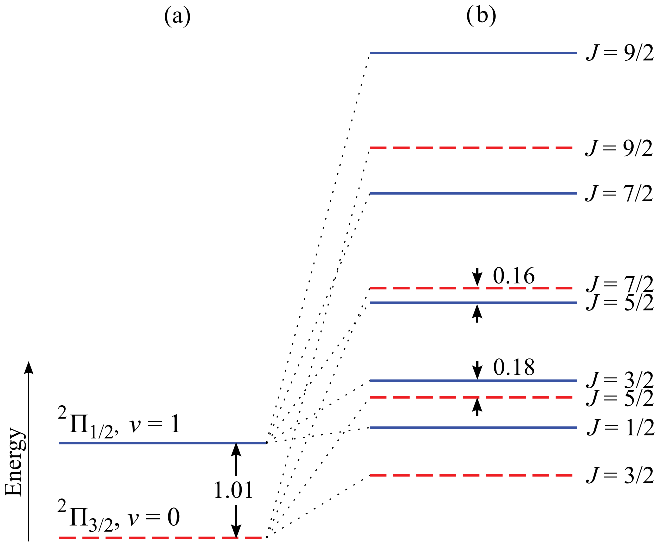

FIG. 2. (Color online) Rovibronic levels of ^{28}Si^{79}Br associated with the $^2\Pi_{1/2}, v = 1$ (solid blue lines) and $^2\Pi_{3/2}, v = 0$ (dashed red lines) quasidegenerate vibronic levels. Displayed are (a) the two vibronic levels and (b) all rovibronic levels for up to $J = 9/2$. All energy differences are in cm^{-1}.

To continue with our strategy of finding the largest enhancement factors, we look for specific transitions in which

$$\Delta E_{vJ}^{\pm} = \Delta G_v + \Delta F_J^{\pm} \approx 0. \tag{10}$$

As an example, we take the $v = 1$ vibronic energy difference of ^{28}Si^{79}Br, $\Delta G_1 = -1.01$ cm^{-1}. As ΔG_1 is negative, we require ΔF_J^+ in Eq. (10) and may subsequently solve for J,

$$J \approx -\frac{\Delta G_1}{2B_e} - 1 = 2.02,$$

which indicates that two appropriate choices for J are $J = 3/2$ and $J = 5/2$, with corresponding values of ΔE_{vJ}^+

$$\begin{aligned}\Delta E_{1,3/2}^+ &= -0.18\,\text{cm}^{-1},\\ \Delta E_{1,5/2}^+ &= +0.16\,\text{cm}^{-1}.\end{aligned} \tag{11}$$

Figure 2 displays the rovibronic spectrum arising from the $G_1^{(1/2)}$ ($^2\Pi_{1/2}, v = 1$) and $G_0^{(3/2)}$ ($^2\Pi_{3/2}, v = 0$) quasidegenerate vibronic levels for ^{28}Si^{79}Br. The energy differences corresponding to $\Delta E_{1,3/2}^+$ and $\Delta E_{1,5/2}^+$ are also displayed. One can resolve the absolute values appearing in Fig. 2 with the signed values appearing in Eq. (11) by noting that if the $E_{v-1,J\pm1}^{(3/2)}$ (red dashed line) is above the $E_{vJ}^{(1/2)}$ level (solid blue line), then the sign of $\Delta E_{vJ}^{\pm}$ is positive; if the order of the levels is opposite, the sign of $\Delta E_{vJ}^{\pm}$ is negative. The particular sign of $\Delta E_{vJ}^{\pm}$ is important from the viewpoint of variations of $\Delta E_{vJ}^{\pm}$ with respect to variations of α and μ, as discussed in the following section.

IV. VARIATIONS OF THE ROVIBRONIC TRANSITION FREQUENCIES WITH RESPECT TO VARIATIONS OF α AND μ

In this section we consider variation of the energy difference $\Delta E_{vJ}^{\pm}$ with respect to variations of α and μ. The constants A_e and ω_e are orders of magnitude larger than the other spectroscopic constants used to describe $\Delta E_{vJ}^{\pm}$; furthermore A_e is only sensitive to variations in α while ω_e is only sensitive to variations in μ. Consequently, to a first approximation, we can estimate the variation $\delta(\Delta E_{vJ}^{\pm})$ by variations of A_e and ω_e,

$$\delta(\Delta E_{vJ}^{\pm}) \cong \delta A_e - \delta\omega_e.$$

The spin-orbit constant A_e embodies the major relativistic correction to the energy spectrum of the doublet and to the lowest order scales as α^2. Thus, if we assume higher-order relativistic corrections to be negligible, we may write

$$\delta A_e = 2A_e\frac{\delta\alpha}{\alpha}.$$

The harmonic vibrational energy ω_e is insensitive to relativistic corrections, though it is proportional to $M_{\text{red}}^{-1/2}$, where M_{red} is the reduced nuclear mass, and as such is sensitive to μ. The proton and neutron masses, as well as nuclear binding energies, are all proportional to the quantum chromodynamics scale Λ_{QCD} (see, e.g., Refs. [25,26]). It follows that the nuclear masses and, further, the reduced nuclear mass are also proportional to Λ_{QCD}. We conclude that $\delta M_{\text{red}}/M_{\text{red}} = \delta m_p/m_p = \delta\mu/\mu$, where the last equality holds for atomic units. The constant ω_e then varies with μ as

$$\delta\omega_e = -\frac{1}{2}\omega_e\frac{\delta\mu}{\mu}.$$

Combining the above equations yields

$$\delta(\Delta E_{vJ}^{\pm}) \cong 2A_e\frac{\delta\alpha}{\alpha} + \frac{1}{2}\omega_e\frac{\delta\mu}{\mu} \cong 2A_e\left(\frac{\delta\alpha}{\alpha} + \frac{1}{4}\frac{\delta\mu}{\mu}\right), \tag{12}$$

where in the last expression we used the fact that $A_e \cong \omega_e$. Evidently the transitions $\Delta E_{vJ}^{\pm}$ are sensitive to variations in the combined constant $\alpha\mu^{1/4}$ (the term in parentheses is equivalent to the fractional variation $\delta\rho/\rho$, where $\rho = \alpha\mu^{1/4}$).

As discussed in the Introduction, the variation $\delta(\Delta E_{vJ}^{\pm})$ is dependent on our choice of unit system, namely, atomic units. To remove dependence on the unit system, we consider variations of dimensionless quantities, such as the ratio of two transition energies. In the present setup, we may consider the ratio of two transition energies within the same doublet rovibronic spectrum. Equating ω_1 and ω_2 to two separate transition energies $\Delta E_{vJ}^{\pm}$, the variation of the dimensionless ratio ω_1/ω_2 is given by

$$\frac{\delta(\omega_1/\omega_2)}{(\omega_1/\omega_2)} = \frac{\delta\omega_1}{\omega_1} - \frac{\delta\omega_2}{\omega_2} \cong \left(\frac{1}{\omega_1} - \frac{1}{\omega_2}\right)2A_e\left(\frac{\delta\alpha}{\alpha} + \frac{1}{4}\frac{\delta\mu}{\mu}\right).$$

The sensitivity to variations in $\alpha\mu^{1/4}$ is maximized by selecting transitions which have small values of ω_1 and ω_2 and which additionally differ in sign.

Alternatively, one may measure the ratios $(|\omega_1| + |\omega_2|)/\omega_r$ and $(|\omega_1| - |\omega_2|)/\omega_r$, where ω_r is some reference energy. This is similar to what has been done with atomic dysprosium (in which case ω_1 and ω_2 are defined by different isotopic species) [27,28]. Noting that in the present case $\omega_1 + \omega_2$ is sensitive to variations in $\alpha\mu^{1/4}$ whereas $\omega_1 - \omega_2$ is not, it follows that whether $|\omega_1| \pm |\omega_2|$ is sensitive to variations in $\alpha\mu^{1/4}$ depends on the relative signs of ω_1 and ω_2. In particular, given opposite signs of ω_1 and ω_2, the difference

$|\omega_1| - |\omega_2|$ is sensitive to variations in $\alpha\mu^{1/4}$; an immediate benefit of this choice is that systematic effects (e.g., constant frequency shifts) can presumably be controlled or eliminated to a large extent by taking the difference. Dependence of the reference energy on the variation of the fundamental constants may be neglected if there is no relative enhancement (cancellation of different contributions) there. This is the case for the Cs hyperfine standard and any other hyperfine transition (calculated in Ref. [29]) and for practically any other transition in SiBr.

The preceding expressions of this section are approximate relations. In the remainder of this section, we present more precise formulas. In particular, we include contributions from variations in the additional spectroscopic constants $\omega_e x_e$, α_{Ae}, and B_e and, further, we use *ab initio* calculations to determine the precise dependence of the variations of the constants with variations of α. En route to calculating the variations of the constants with respect to α, we obtain values for the constants themselves, which are presented in Table I alongside the experimental data. We note an impressive agreement between our computed constants and the experimental constants. In particular, the primary constants A_e and ω_e agree to better than 1%, and we feel that this is indicative of the accuracy of our computed variations of the constants with respect to α presented below. A brief discussion of the computational method is provided in the following section.

From our calculations we obtain the following relations for variations of the constants with respect to variations of α only:

$$\frac{\delta A_e}{A_e} = 2.019\frac{\delta\alpha}{\alpha}, \quad \frac{\delta\alpha_{Ae}}{\alpha_{Ae}} = 1.927\frac{\delta\alpha}{\alpha}, \\ \frac{\delta\omega_e}{\omega_e} = -4.5\times10^{-3}\frac{\delta\alpha}{\alpha}, \tag{13}$$

and variations in constants $\omega_e x_e$ and B_e with respect to variations in α give negligible contribution.

For variations with respect to μ, we make use of analytical formulas, using the appropriate dependence of the constants on the reduced mass. In particular, we have the following relations for variations of the constants with respect to variations of μ only:

$$\frac{\delta\omega_e}{\omega_e} = -\frac{1}{2}\frac{\delta\mu}{\mu}, \quad \frac{\delta\alpha_{Ae}}{\alpha_{Ae}} = -\frac{1}{2}\frac{\delta\mu}{\mu}, \\ \frac{\delta(\omega_e x_e)}{\omega_e x_e} = -\frac{\delta\mu}{\mu}, \quad \frac{\delta B_e}{B_e} = -\frac{\delta\mu}{\mu}, \tag{14}$$

and no variation in A_e with respect to variations in μ.

We consider as an example the two transition energies $\omega_1 = \Delta E^{+}_{1,5/2}$ and $\omega_2 = \Delta E^{+}_{1,3/2}$ [i.e., the transitions identified in Fig. 2(a)]. Using Eqs. (13) and (14), we find the variations in these transition energies to be

$$\delta\omega_1 = \delta\omega_2 = (851\ \text{cm}^{-1})\left(\frac{\delta\alpha}{\alpha} + 0.247\frac{\delta\mu}{\mu}\right).$$

The deviation of this expression from the less sophisticated expression, Eq. (12), is small and on the order of the accuracy of the computations. Note, however, that for transitions associated with a higher vibrational quantum number v, the deviations from Eq. (12) become more pronounced. For example, suppose the transition $\omega = \Delta E^{-}_{24,55.5}$ is found to be a convenient transition to probe [with Eqs. (7)–(9), $\omega = -0.01\ \text{cm}^{-1}$]; for this transition, we obtain

$$\delta\omega = (764\ \text{cm}^{-1})\left(\frac{\delta\alpha}{\alpha} + 0.196\frac{\delta\mu}{\mu}\right).$$

V. COMPUTATIONAL DETAILS OF $X^2\Pi_r$ ROVIBRONIC SPECTRUM

Fine-structure splitting is an inherently relativistic effect; hence, all the energy calculations employed the relativistic four-component molecular Dirac-Coulomb Hamiltonian

$$H_{\text{DC}} = \sum_i h_{\text{D}}(i) + \sum_{i<j}\frac{1}{r_{ij}},$$

where

$$h_{\text{D}}(i) = c\alpha_i\cdot\mathbf{p}_i + \beta_i c^2 + V_{\text{nuc}}(i).$$

Here h_{D} is the one-electron Dirac Hamiltonian, with V_{nuc} the nuclear attraction operator for the two nuclei considered, and takes into account the finite nucleus effect; α and β are the four-dimensional Dirac matrices; and the term $\sum_{i<j} 1/r_{ij}$ represents the repulsive Coulomb interaction between electrons.

As SiBr is an open-shell system with a single valence electron outside the closed shell, we employed the Fock space coupled cluster (FSCC) method with sectors (0,0) and (0,1) to account for electron correlation, where the closed-shell cation served as reference, and an electron was added in the (0,1) sector, with the model space composed of both $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ molecular orbitals to obtain the potential energy curves for the two states of interest.

An uncontracted aug-cc-pVTZ basis set was used for both atoms [30,31]; 37 electrons were correlated and virtual orbitals with energies above 35 a.u. were omitted. All the energy calculations were performed using the DIRAC program package [32], and the spectroscopic constants were obtained from the potential energy curves by solving the rotational-vibrational Schrödinger equation numerically using the program VIBROT [33]. The results are presented and compared with the experimental values in Table I.

To assess the dependence of the values of interest, A_e, ω_e, α_{A_e}, $\omega_e x_e$, and B_e, on the fine-structure constant, the calculations were carried out for different values of $x \equiv (\alpha/\alpha_0)^2 - 1$, α_0 being the present value of α, and the derivatives were obtained using numerical differentiation.

VI. COMPUTED LINEWIDTHS OF ROVIBRONIC LEVELS

The natural linewidths of the rovibronic levels place a fundamental limit on the accuracy to which a given transition frequency can be measured, and, therefore, also on the accuracy to which any variation in $\alpha\mu^{1/4}$ may be measured. In Ref. [21], rough estimates of the linewidths of the rovibronic levels were obtained for Π doublets; here we provide computed values for the SiBr molecule.

To obtain the linewidths, we require dipole matrix elements. We begin with the wave function $\Psi_{\gamma v}(\overline{q},R)$ representing the Born-Oppenheimer molecular solutions for a nonrotating molecule (see, e.g., Ref. [23]),

$$\Psi_{\gamma v}(\overline{q},R) = \psi_\gamma(\overline{q},R)\phi_{\gamma v}(R),$$

where R is the nuclear separation and $\overline{q}$ encapsulates all electronic space and spin coordinates. Here $\psi_\gamma(\overline{q},R)$ represents the electronic eigensolutions for a given nuclear separation R, and $\phi_{\gamma v}(R)$ represents the subsequent eigensolutions for the nuclear vibrational motion. The solutions are assumed to be orthogonal and normalized over the appropriate space, i.e.,

$$\int \psi^*_{\gamma'}(\overline{q},R)\psi_\gamma(\overline{q},R)\,d\overline{q} = \delta_{\gamma'\gamma},$$

$$\int \phi^*_{\gamma v'}(R)\phi_{\gamma v}(R)\,dR = \delta_{v'v}.$$

We may write the dipole operator in terms of electronic and nuclear contributions,

$$\mathbf{D}(\overline{q},R) = \mathbf{D}_e(\overline{q}) + \mathbf{D}_n(R).$$

Specifically, the electronic contribution $\mathbf{D}_e(\overline{q})$ is given by

$$\mathbf{D}_e(\overline{q}) = -\sum_i \mathbf{r}_i,$$

where $\mathbf{r}_i$ is the position vector of the ith electron ($\mathbf{r}_i \in \overline{q}$) and the summation runs over all electrons. The nuclear contribution $\mathbf{D}_n(R)$ is

$$\mathbf{D}_n(R) = \left(\frac{Z_B}{M_B} - \frac{Z_A}{M_A}\right) M_{\text{red}} R\hat{\mathbf{e}}_z,$$

where M_i and Z_i are the mass and atomic numbers of the nuclei $i = A,B$ and we have assumed the coordinate origin to be at the center of mass with the z axis aligned with the internuclear axis. A dipole matrix element between the Born-Oppenheimer wave functions reads

$$\begin{aligned}\langle\gamma'v'|\mathbf{D}|\gamma v\rangle &= \int\!\!\int \psi^*_{\gamma'}(\overline{q},R)\phi^*_{\gamma'v'}(R)[\mathbf{D}_e(\overline{q}) + \mathbf{D}_n(R)] \\ &\quad\times \psi_\gamma(\overline{q},R)\phi_{\gamma v}(R)\,d\overline{q}\,dR \\ &= \int \phi^*_{\gamma'v'}(R)\langle\gamma'|\mathbf{D}|\gamma\rangle\phi_{\gamma v}(R)\,dR, \qquad (15)\end{aligned}$$

where the R-dependent matrix element $\langle\gamma'|\mathbf{D}|\gamma\rangle$ represents the dipole matrix element for a given "clamped" nuclear separation R and is given by

$$\langle\gamma'|\mathbf{D}|\gamma\rangle \equiv \delta_{\gamma'\gamma}\mathbf{D}_n(R) + \int \psi^*_{\gamma'}(\overline{q},R)\mathbf{D}_e(\overline{q})\psi_\gamma(\overline{q},R)\,d\overline{q}.$$

We are interested in dipole matrix elements between the vibronic states of a (Hund's case a) electronic multiplet. The relevant vibrational wave functions $\phi_{\gamma v}(R)$ are largely independent of the particular multiplet level; i.e., $\phi_{\gamma v}(R) \equiv \phi_v(R)$. Furthermore, the wave functions $\phi_v(R)$ are significant in magnitude only within a small region about the equilibrium nuclear separation $R = R_e$ [note that the Born-Oppenheimer approximation is rooted in the assumption that $\phi_v(R)$ varies more rapidly with R than $\psi_\gamma(\overline{q},R)$]. As such, we may expand $\langle\gamma'|\mathbf{D}|\gamma\rangle$ in the integrand of Eq. (15) about R_e; explicitly to the first order in $(R - R_e)$ this is

$$\langle\gamma'|\mathbf{D}|\gamma\rangle \cong \langle\gamma'|\mathbf{D}|\gamma\rangle\Big|_{R_e} + \frac{d\langle\gamma'|\mathbf{D}|\gamma\rangle}{dR}\Big|_{R_e}(R - R_e).$$

Subsequent evaluation of the integral gives

$$\begin{aligned}\langle\gamma'v'|\mathbf{D}|\gamma v\rangle &\cong \delta_{v'v}\langle\gamma'|\mathbf{D}|\gamma\rangle\Big|_{R_e} + \frac{d\langle\gamma'|\mathbf{D}|\gamma\rangle}{dR}\Big|_{R_e} \\ &\quad\times R_e\sqrt{\frac{B_e}{\omega_e}}(\sqrt{v}\,\delta_{v'+1,v} + \sqrt{v'}\,\delta_{v'-1,v}), \qquad (16)\end{aligned}$$

where we have assumed the vibrational wave functions $\phi_v(R)$ to be harmonic oscillator eigenfunctions.

The contribution to the natural linewidth for a given decay channel $\gamma v \rightarrow \gamma'v'$ is given by

$$\Gamma(\gamma v \rightarrow \gamma'v') = \frac{4\omega^3_{\gamma v,\gamma'v'}}{3c^3}|\langle\gamma'v'|\mathbf{D}|\gamma v\rangle|^2, \qquad (17)$$

where $\omega_{\gamma v,\gamma'v'}$ is the energy difference between the initial and final state, and we have summed over final rotational states. We neglect decay channels within a given vibronic level and between quasidegenerate vibronic levels for which the energy difference is small.

We begin by considering vibrational decay. Using the MOLPRO computational package [34], we calculated the diagonal matrix elements $\langle{}^2\Pi_{1/2}|\mathbf{D}|{}^2\Pi_{1/2}\rangle$ and $\langle{}^2\Pi_{3/2}|\mathbf{D}|{}^2\Pi_{3/2}\rangle$ at multiple nuclear separation distances R within the vicinity of R_e. With numerical differentiation and taking the experimental ratio $\sqrt{B_e/\omega_e} = 0.020$, we obtain the results

$$\left.\begin{array}{l}|\langle{}^2\Pi_{1/2},v-1|\mathbf{D}|{}^2\Pi_{1/2},v\rangle| \\ |\langle{}^2\Pi_{3/2},v-1|\mathbf{D}|{}^2\Pi_{3/2},v\rangle|\end{array}\right\} = 0.12\sqrt{v}\,\text{a.u.} \qquad (18)$$

The decay channel ${}^2\Pi_{3/2},v \rightarrow {}^2\Pi_{1/2},v$ is forbidden in the nonrelativistic limit, though it is opened up by spin-orbit mixing of the ${}^2\Pi_{1/2}$ state with the excited electronic ${}^2\Sigma_{1/2}$ state. Due to its purely relativistic origin, the corresponding dipole matrix element proves very difficult to obtain by computational methods. To circumvent the need for a direct computational value, we write the dipole matrix element as in Ref. [21],

$$|\langle{}^2\Pi_{3/2}|\mathbf{D}|{}^2\Pi_{1/2}\rangle| \cong \xi|\langle{}^2\Pi_{3/2}|\mathbf{D}|{}^2\Sigma_{1/2}\rangle|,$$

where ξ is the small parameter quantifying the spin-orbit mixing. We find from computation $|\langle{}^2\Pi_{3/2}|\mathbf{D}|{}^2\Sigma_{1/2}\rangle| \sim 0.1$ a.u., indicating that $|\langle{}^2\Pi_{3/2}|\mathbf{D}|{}^2\Pi_{1/2}\rangle|$ is appreciably smaller than the dipole matrix elements in Eqs. (18). Thus we conclude that neglect of the decay channel ${}^2\Pi_{3/2},v \rightarrow {}^2\Pi_{1/2},v$ is acceptable, because its contribution to linewidths will be overshadowed by the contribution from the vibrational decay.

As a specific example, we consider the natural linewidth of the ${}^2\Pi_{1/2},v = 1$ vibronic level. With Eqs. (17), we find

$$\Gamma({}^2\Pi_{1/2},v = 1) = 5.3 \times 10^{-17}\text{a.u.} = 0.35\,\text{Hz}.$$

We note that this is an order of magnitude larger than the estimate given in Ref. [21].

VII. CONCLUSION

Here we have extended upon Flambaum and Kozlov's work [21] by considering properties of silicon monobromide that make it a prospective candidate for detecting variations in the fine-structure constant α and the proton-to-electron mass ratio μ (in particular, variations in the combined constant $\alpha\mu^{1/4}$).

We have examined the rovibronic spectrum by employing the most accurate experimental data available in the literature, namely, that of Bosser *et al.* [22]. Furthermore, we present results of *ab initio* calculations for the precise dependence of the spectroscopic constants on variations in α. We additionally present calculated values for the natural linewidths of the rovibronic levels which place a fundamental limit on the accuracy to which variations in $\alpha\mu^{1/4}$ may be determined.

As in Ref. [21], we emphasize that dedicated measurements are necessary to find precise values for the transition frequencies and determine the best transitions. It is our hope that this work entices experimental progress in this direction.

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[1] J.-P. Uzan, Rev. Mod. Phys. **75**, 403 (2003).
[2] V. V. Flambaum, Int. J. Mod. Phys. A **22**, 4937 (2007).
[3] V. V. Flambaum, Eur. Phys. J. Sp. Top. **163**, 159 (2008).
[4] J. K. Webb, V. V. Flambaum, C. W. Churchill, M. J. Drinkwater, and J. D. Barrow, Phys. Rev. Lett. **82**, 884 (1999).
[5] J. K. Webb, M. T. Murphy, V. V. Flambaum, V. A. Dzuba, J. D. Barrow, C. W. Churchill, J. X. Prochaska, and A. M. Wolfe, Phys. Rev. Lett. **87**, 091301 (2001).
[6] M. T. Murphy, J. K. Webb, and V. V. Flambaum, Phys. Rev. Lett. **99**, 239001 (2007).
[7] J. D. Prestage, R. L. Tjoelker, and L. Maleki, Phys. Rev. Lett. **74**, 3511 (1995).
[8] T. M. Fortier *et al.*, Phys. Rev. Lett. **98**, 070801 (2007).
[9] Y. Sortais *et al.*, Phys. Scr. **2001**, 50 (2001).
[10] K. A. Olive and M. Pospelov, Phys. Rev. D **65**, 085044 (2002).
[11] K. A. Olive, M. Pospelov, Y.-Z. Qian, A. Coc, M. Cassé, and E. Vangioni-Flam, Phys. Rev. D **66**, 045022 (2002).
[12] S. K. Lamoreaux and J. R. Torgerson, Phys. Rev. D **69**, 121701 (2004).
[13] Y. Fujii, A. Iwamoto, T. Fukahori, T. Ohnuki, M. Nakagawa, H. Hidaka, Y. Oura, and P. Möller, Nucl. Phys. B **573**, 377 (2000).
[14] T. Damour and F. Dyson, Nucl. Phys. B **480**, 37 (1996).
[15] V. F. Dmitriev, V. V. Flambaum, and J. K. Webb, Phys. Rev. D **69**, 063506 (2004).
[16] C. Chin, V. V. Flambaum, and M. G. Kozlov, New J. Phys. **11**, 055048 (2009).
[17] M. T. Murphy, V. V. Flambaum, S. Muller, and C. Henkel, Science **320**, 1611 (2008).
[18] D. DeMille, S. Sainis, J. Sage, T. Bergeman, S. Kotochigova, and E. Tiesinga, Phys. Rev. Lett. **100**, 043202 (2008).
[19] M. Kajita, Phys. Rev. A **77**, 012511 (2008).
[20] M. Kajita and Y. Moriwaki, J. Phys. B **42**, 154022 (2009).
[21] V. V. Flambaum and M. G. Kozlov, Phys. Rev. Lett. **99**, 150801 (2007).
[22] G. Bosser, J. Lebreton, and J. Rostas, J. Chim. Phys. Phys. Chim. Biol. **78**, 787 (1981).
[23] H. W. Kroto, *Molecular Rotation Spectra* (Dover, Mineola, NY, 2003).
[24] J. M. Brown and J. K. G. Watson, J. Mol. Spectrosc. **65**, 65 (1977).
[25] V. V. Flambaum and E. V. Shuryak, Phys. Rev. D **65**, 103503 (2002).
[26] V. V. Flambaum and E. V. Shuryak, Phys. Rev. D **67**, 083507 (2003).
[27] A. Cingöz, A. Lapierre, A.-T. Nguyen, N. Leefer, D. Budker, S. K. Lamoreaux, and J. R. Torgerson, Phys. Rev. Lett. **98**, 040801 (2007).
[28] S. J. Ferrell, A. Cingöz, A. Lapierre, A.-T. Nguyen, N. Leefer, D. Budker, V. V. Flambaum, S. K. Lamoreaux, and J. R. Torgerson, Phys. Rev. A **76**, 062104 (2007).
[29] V. V. Flambaum and A. F. Tedesco, Phys. Rev. C **73**, 055501 (2006).
[30] D. E. Woon and T. H. Dunning, J. Chem. Phys. **98**, 1358 (1993).
[31] A. K. Wilson, D. E. Woon, K. A. Peterson, and T. H. Dunning, J. Chem. Phys. **110**, 7667 (1999).
[32] L. Visscher *et al.*, DIRAC, a relativistic *ab initio* electronic structure program, release DIRAC08 (2008), [http://dirac.chem.sdu.dk].
[33] G. Karlström, R. Lindh, and P.-A. Malmqvist *et al.*, Comp. Mat. Sci. **28**, 222 (2003).
[34] H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2009.1, a package of *ab initio* programs (2009), see [http://www.molpro.net].