SeD radical as a probe for the measurement of the time variation of the fine-structure constant α and proton-to-electron mass ratio μ

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Based on the spectroscopic constants derived from highly accurate potential-energy surfaces, the SeD radical is identified as a spectroscopic probe for measuring spatial and temporal variation of fundamental physical constants such as the fine-structure constant (denoted as $\alpha = \frac{e^2}{\hbar c}$) and the proton-to-electron mass ratio (denoted as $\mu = \frac{m_p}{m_e}$). The ground state of SeD ($X^2\Pi$), due to spin-orbit coupling, splits into two fine-structure multiplets $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$. The potential-energy surfaces of these spin-orbit components are derived from a state of the art electronic structure method, MRCI + Q inclusive of scalar relativistic effects with the spin-orbit effects accounted for through the Breit-Pauli operator. The relevant spectroscopic data are evaluated using a Murrel-Sorbie fit to the potential-energy surfaces. The spin-orbit splitting ω_f between the two multiplets is similar in magnitude with the harmonic frequency ω_e of the diatomic molecule. The amplification factor K derived from this theoretical method for this particular molecule can be as large as 350; on the lower side it can be about 34. The significantly large values of K indicate that the SeD radical can be a plausible experimental candidate for measuring variation in α and μ.

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I. INTRODUCTION

Spatial and temporal variation of the fundamental constants to some level points to the invalidation of Einstein's equivalence principle [1,2]. These include the coupling constant of electromagnetic interaction, usually called the fine-structure constant (denoted as $\alpha = \frac{e^2}{\hbar c}$) and the proton-to-electron mass ratio (denoted as $\mu = \frac{m_p}{m_e}$). Over vast space and time scales of the expanding universe these variations can be astrophysically measured and compared to the high-precision laboratory data [3]. Recent advances in computational methods and high-precision experimental techniques propelled researchers to propose different experiments as well as experimental candidates aimed at the determination of such variation in the last few decades [4,5]. High-precision trapped atom and molecular ion spectroscopy is one of the most promising approaches for measuring such space-time variation of the fundamental physical constants experimentally, as molecular spectroscopy is sensitive to both the dimensionless constants α and μ [6,7]. These spectroscopic techniques employ a diatomic molecule as a probe for measuring such variations in fundamental physical constants following the proposal put forward by Flambaum and Kozlov [8].

Diatomic molecules including radicals having nearly degenerate long-lived rotational and vibrational levels belonging to different electronic states are particularly sensitive to measure the variation in α and μ due to several orders of magnitude enhancement [8]. In case of a neutral or charged diatomic molecule having unpaired electrons with a ground-state fine-structure multiplet the transition frequency between the two multiplet states is given by

$$\omega = \omega_f - v\omega_e, \quad v = 1,2,3,4,\ldots \tag{1}$$

where ω_f is the magnitude of spacing between the multiplets (spin orbit), ω_e is the magnitude of vibrational spacing under harmonic approximation, and v is the vibrational quantum number [8]. The fine-structure interval ω_f holds the relation with α as $\omega_f \sim Z^2\alpha^2 E_H$, where Z is the nuclear charge and $E_H = \frac{m_e e^4}{\hbar^2}$. On the other hand ω_e is related to μ, which is given by $\omega_e \sim M_r^{-\frac{1}{2}}\mu^{-\frac{1}{2}}E_H$. Therefore ω is sensitive to the variation of both α and μ as given by the following equations:

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

On the other hand the fractional variation of ω may be written as [8]

$$\begin{aligned}\frac{\delta\omega}{\omega} &= \frac{1}{\omega}\left(2\omega_f\frac{\delta\alpha}{\alpha} + \frac{v}{2}\omega_e\frac{\delta\mu}{\mu}\right)\\ &= 2K\left(\frac{\delta\alpha}{\alpha} + \frac{1}{4}\frac{\delta\mu}{\mu}\right),\end{aligned} \tag{3}$$

where $K = \frac{\omega_f}{\omega_f - v\omega_e} = \frac{\omega_f}{\omega}$ [8] is known as the enhancement factor or the amplification factor. According to Flambaum and Kozlov a large value for K of a species hints at its potential candidacy as an experimental probe to gauge the variation in α and μ. Ideally diatomic molecules for which $\omega = 0$ would be the best possible probes for such a purpose. However, it turns out that such a possibility is purely fortuitous as no such diatomic molecules exist. This limits the search for such diatomic molecules to cases where $\frac{\omega_f}{\omega}$ and K are substantially large. Unfortunately there are very few molecules which obey this criterion. Therefore it is essential to identify molecular candidates on which both experiments can be performed and astrophysical observations can be made. Flambaum and others have recently proposed certain candidates as viable probes, such as Cs_2 [9], MgH, CaH^+ [10,11], Cl_2^+, IrC, HfF^+ [12–14], NH^+ [15–17], and SiBr [18]. Out of these, few do not have permanent dipole moments and are inactive to

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microwave spectroscopy. Although SiBr is relevant, its harmonic stretching frequency falls out of the infrared spectroscopy window. It is imperative to identify new candidates as this would enrich the gamut of probes so that more systematic analysis can be conducted. In this paper we identify selenium deuteride (SeD) as a potential candidate for experimentally probing the variation of fundamental physical constants and perform detailed theoretical study on that particular molecule to find variation in transition frequency upon a given change in α and μ. Although NH_3 and other C-H compounds are astrophysically abundant, the SeD radical is yet to be observed. However, asymptotic giant branch stars are probable sites to look for SeD due to the abundance of s-process isotopes and freely available deuterium in the cooler portion of the universe. The added advantage would be the cooler temperature for good IR observation which can be a potentially important complementarity to the microwave observations made on NH_3 inversion. With regard to laboratory experiments SeD is very similar to the trapping of NH or CaH molecules in magneto-optical traps [2,19] and hence it may be considered as a possible candidate for a fundamental test. Chemically, SeD is an open shell molecule with one unpaired electron ($S = \frac{1}{2}$) in its π orbital with a π^3 configuration. The first excited state $A^2\Sigma^+$ is well separated (about 30 460 cm^{-1}) with the ground state $X^2\Pi$. For a linear molecule under spin-orbit coupling (SOC) the electronic states can be expressed as $\Omega = |\Lambda + \Sigma|$, where Λ and Σ are the orbital and spin angular momenta. Under SOC splitting the $X^2\Pi$ state will split into $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$ for $\Lambda = 1$ and $\Sigma = \pm\frac{1}{2}$ and there is no split for $A^2\Sigma^+$ because of $\Lambda = 0$ and $\Sigma = \frac{1}{2}$. According to Hund's rule for a more than half filled shell (π^3 electronic configuration) $^2\Pi_{\frac{3}{2}}$ is energetically lower than $^2\Pi_{\frac{1}{2}}$. The fine-structure and vibrational spacings of the $X^2\Pi$ state are similar in magnitude ($\omega_f \approx v\omega_e, v = 1$) [20].

II. ROVIBRONIC ENERGY LEVELS IN SELENIUM DEUTERIDE

The total Hamiltonian can be expressed as

$$\boldsymbol{H} = \boldsymbol{H}_{\text{vib}} + \boldsymbol{H}_{\text{SO}} + \boldsymbol{H}_{\text{rot}}, \tag{4}$$

and for a $^2\Pi$ state the terms on the right-hand side of the equation represent the vibronic Hamiltonian, spin-orbit interaction Hamiltonian, and rotational Hamiltonian, respectively. The vibronic energy (in cm^{-1}) of a given electronic state in an anharmonic oscillator approximation taking up to the first-order term in $(v + \frac{1}{2})$ is

$$E_{\text{vib}}(v) = \left(v + \tfrac{1}{2}\right)\omega_e - \left(v + \tfrac{1}{2}\right)^2\omega_e\chi_e, \tag{5}$$

where ω_e and $\omega_e\chi_e$ are the harmonic vibrational frequency and first correction due to anharmonicity, respectively. Now, for the case of spin-orbit interaction the orbital angular momentum ($\boldsymbol{L}$) and spin angular momentum ($\boldsymbol{S}$) are strongly coupled to the internuclear axis. If we denote the axial component of $\boldsymbol{L}$ and $\boldsymbol{S}$ as $\boldsymbol{\Lambda}$ and $\boldsymbol{\Sigma}$ the spin-orbit coupling Hamiltonian will be

$$\boldsymbol{H}_{\text{SO}} = A_v\boldsymbol{\Lambda}\cdot\boldsymbol{\Sigma}, \tag{6}$$

where A_v is the spin-orbit coupling constant. A_v depends on the vibrational quantum number as per the following relation derived by Brown and Watson [21] [expanded up to the first order of the $(v + \frac{1}{2})$ term]:

$$A_v = A_e - \alpha_{A_e}\left(v + \tfrac{1}{2}\right). \tag{7}$$

Therefore the spin-orbit Hamiltonian becomes

$$\boldsymbol{H}_{\text{SO}} = A_e\boldsymbol{\Lambda}\cdot\boldsymbol{\Sigma} - \alpha_{A_e}\left(v + \tfrac{1}{2}\right)\boldsymbol{\Lambda}\cdot\boldsymbol{\Sigma}. \tag{8}$$

In a molecular system rotation, vibration and electronic interactions influence one another. For the rovibrational electronic spectra of a diatomic molecule, the different angular momenta, i.e., electron spin angular momentum ($\boldsymbol{S}$), electron orbital angular momentum ($\boldsymbol{L}$), and angular momentum of nuclear rotation ($\boldsymbol{R}$), can couple in various ways to form the resultant angular momentum $\boldsymbol{J}$. These types of coupling are described by Hund's coupling cases. The ground-state electronic multiplet, $X^2\Pi$, of SeD falls into the category of the Hund's case (a) type of diatomic molecule where electronic orbital angular momentum $\boldsymbol{L}$ is weakly coupled with the nuclear rotation and strongly coupled with the internuclear axis by electrostatic force, i.e., $|\frac{A_e}{B_e}| \ll 1$. Spin angular momentum ($\boldsymbol{S}$) is strongly coupled to orbital angular momentum ($\boldsymbol{L}$) by spin-orbit coupling. The electronic angular momentum for a rotating diatomic molecule is defined as $\boldsymbol{\Omega} = \boldsymbol{\Lambda} + \boldsymbol{\Sigma}$ (where $\boldsymbol{\Lambda}$ and $\boldsymbol{\Sigma}$ are the axial components of $\boldsymbol{L}$ and $\boldsymbol{S}$). Angular momentum of the rotating nuclei (R) is coupled to Ω to form total angular momentum $\boldsymbol{J} = \boldsymbol{\Omega} + \boldsymbol{R}$. After neglecting the centrifugal force terms in the rotational energy in Hund's case (a) [22], the rotational Hamiltonian will be that of the asymmetric top with $\boldsymbol{\Omega}$ as the angular momentum about the internuclear axis. The effective Hamiltonian in Hund's case (a) is

$$\boldsymbol{H}_{\text{rot}} = |B_v|\boldsymbol{R}^2, \tag{9}$$

where B_v is the rotational constant. Hund's case (a) is a good representation when $A_e\Lambda$ is much greater than B_vJ, where A_e is the spin-orbit coupling constant. The rotational energy is given by

$$E_{\text{rot}}(J) = B_v[J(J+1) - \Omega^2]. \tag{10}$$

B_v is dependent on the vibrational quantum number v. Expanding the rotational constant up to the first order of the $(v + \frac{1}{2})$ term, where α_e is the rotation-vibration coupling constant,

$$B_v = B_e - \alpha_e\left(v + \tfrac{1}{2}\right). \tag{11}$$

Therefore the final form of the rotational energy can be written as

$$\begin{aligned} E_{\text{rot}}(J) = {} & B_e[J(J+1) - \Omega^2] \\ & - \alpha_e[J(J+1) - \Omega^2]\left(v + \tfrac{1}{2}\right). \end{aligned} \tag{12}$$

Now, since the spin-orbit coupling and the vibronic energy are large compared to the rotational energy, the total energy of the Hamiltonian will clearly be the sum of the individual energies and can be expanded in terms of spectroscopic constants by

$$\begin{aligned} E(v,J) = {} & \pm\tfrac{1}{2}\left[A_e - \alpha_{A_e}\left(v + \tfrac{1}{2}\right)\right] + \left(v + \tfrac{1}{2}\right)\omega_e \\ & - \left(v + \tfrac{1}{2}\right)^2\omega_e\chi_e + B_e[J(J+1) - \Omega^2] \\ & - \alpha_e[J(J+1) - \Omega^2]\left(v + \tfrac{1}{2}\right). \end{aligned} \tag{13}$$

Here the top and bottom sign denote the $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$ states, respectively. α_{A_e} may be represented as the difference of the harmonic frequencies of $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$ states when considered independently [21]. The total energy can be separated into the summation of J dependent and the J independent parts:

$$E(v,J) = G(v) + F_v(J), \tag{14}$$

where

$$G(v) = \pm\tfrac{1}{2}A_e - B_e\Omega^2 + \left(\omega_e \mp \tfrac{1}{2}\alpha_{A_e} + \alpha_{A_e}\Omega^2\right)\left(v+\tfrac{1}{2}\right) - \left(v+\tfrac{1}{2}\right)^2\omega_e\chi_e, \tag{15}$$

$$F_v(J) = B_e[J(J+1)] - \alpha_e[J(J+1)]\left(v+\tfrac{1}{2}\right). \tag{16}$$

Separating the energy in terms of J dependency allows us to pick up vibrational levels belonging to different spin-orbit coupled electronic states having similar energy. As a further refinement to the energy level difference, J belonging to the same or different vibrational levels can be chosen as per the experimental requirements.

III. COMPUTATIONAL DETAILS

The ground electronic state $X^2\Pi$ of the selenium deuteride radical is thoroughly studied in this paper. The ground-state electronic configuration of $X^2\Pi$ SeD is $(3s_{\mathrm{Se}})^2(3p_{z\,\mathrm{Se}} + 1s_{\mathrm{H}})^2(3p_{\pi\,\mathrm{Se}})^2(3p_{\pi\,\mathrm{Se}})^1$. If one electron is transferred from the $(3p_{z\,\mathrm{Se}} + 1s_{\mathrm{H}})$ orbital to $(3p_{\pi\,\mathrm{Se}})$ the first excited state $^2\Sigma^+$ is formed with the configuration $(3s_{\mathrm{Se}})^2(3p_{z\,\mathrm{Se}} + 1s_H)^2(3p_{\pi\,\mathrm{Se}})^2(3p_{\pi\,\mathrm{Se}})^2$. The theoretical characterization of potential-energy curves for the ground state and the first excited state over an extended internuclear separation until dissociation requires the account of both static and dynamic correlation effects. In this study for the ground state, these effects have been included by the use of state-averaged complete active space self consistent field theory (SA-CASSCF) [23,24] calculation on each doublet spin symmetry followed by single and double electron excitation on top of zeroth-order multireference wave function (MRCISD: Multi Reference Configurational Interaction Singles and Doubles). The SA-CASSCF step involved the two states of symmetry $B_1(\Pi_x)$ and $B_2(\Pi_y)$ in the C_{2V} point group representation, and the symmetries in the parentheses are the corresponding ones in the $C_{\infty V}$ point group. The active space consists the distribution of seven electrons over five orbitals [CAS(7,5)]. Since single and double electron excitation on top of the CAS wave function is computationally very demanding, the configuration state function (CSF) with coefficients greater than 0.01 only are included to construct the new zeroth-order configuration interaction (CI) space. A further reduction of the dimension of the CI wave function has been made with the Internally Contracted Multi-Reference Configuration Interaction Singles and Doubles (IC-MRCISD) approach [25,26] by restricting the core occupation to $(7A_1,3B_1,3B_2,1A_2)$ where A and B denote the symmetries of the irreducible representation in C_{2V} point group symmetry.

The molecular orbitals constructing the CSFs are the natural orbitals which are obtained by diagonalization of the state-averaged (B_1 and B_2 states in C_{2v} point group symmetry) density matrix. Douglas-Kroll contracted correlation consistent Dunning's VnZ-DK ($n = 3-5$) [27,28] basis sets, employed for both the atoms, used in the expansion of the natural orbital. The second-order Douglas-Kroll-Hess Hamiltonian has been used for all MRCI and CASSCF computations to account for the scalar relativistic effects [29,30].

In the next step, the major focus is to determine the spin-orbit coupling. Technically spin-orbit contribution is computed using two steps: first, the SO Hamiltonian is added in a fashion of general first-order perturbation procedure to the electronic Hamiltonian to construct the total Hamiltonian of the form $\boldsymbol{H} = \boldsymbol{H}_{\mathrm{el}} + \boldsymbol{H}_{\mathrm{SO}}$. The spin-orbit matrix elements $\boldsymbol{H}_{\mathrm{SO}}$ are calculated between the internal configurations (i.e., no electron in the external orbitals) $^2\Pi(^2B_1)$ and $^2\Pi(^2B_2)$ with the spin-orbit full Breit-Pauli (BP) [31] operator of the form

$$\boldsymbol{H}_{\mathrm{SO}} = \frac{1}{2m^2c^2}\left[\sum_i\sum_\alpha \frac{Z_\alpha e^2}{r_{i\alpha}^3}\boldsymbol{I}_{i\alpha}\cdot\boldsymbol{S}_i - \sum_i\sum_\alpha \frac{e^2}{r_{ij}^3}\boldsymbol{I}_{ij}\cdot(\boldsymbol{S}_i + 2\boldsymbol{S}_j)\right], \tag{17}$$

which contains both one and two electron terms. Here $\boldsymbol{I}$ and $\boldsymbol{S}$ are orbital and spin angular momentum operators and i and α denote electron and nucleus, respectively.

In the next step, the $\boldsymbol{H} = \boldsymbol{H}_{\mathrm{el}} + \boldsymbol{H}_{\mathrm{SO}}$ matrix is diagonalized in the basis of SA-CASSCF/IC-MRCISD(7,5) wave functions to yield the desired spin-orbit splitting directly.

In order to improve the level of description this spin-orbit splitting is added as *a posteriori* correction to the corresponding MRCI + Q energy at each internuclear separation, where +Q denotes the quadruple excitation corrected by Davidson's method [32,33].These calculations have been carried out with the MOLPRO [34] suite of programs.

IV. THE POTENTIAL-ENERGY FUNCTION

Among the functions that were proposed to fit the analytical potential-energy functions (APEFs) of diatomic molecules, the Murrel-Sorbie (MS) potential-energy function seems to be the best one [35–40]. The interaction potential energies of many neutral and cationic diatomic molecules can be accurately reproduced by this function and have been used to deduce APEFs for many molecules [35–40]. The general form of the MS function is given by [41]

$$V(\rho) = -D_e\left(1 + \sum_{i=1}^{n} a_i\rho^i\right)\exp(-a_1\rho). \tag{18}$$

Usually, satisfactory results can be obtained when $n = 3$. In order to get accurate data, the following form of MS function is used [41,42]:

$$V(\rho) = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho), \tag{19}$$

where $\rho = R - R_e$ is the interatomic distance, R_e is the equilibrium distance, and D_e is the dissociation energy. The quadratic (f_2), cubic (f_3), and quatric (f_4) force constants can be derived by the MS function and then the spectroscopic parameters harmonic frequency (ω_e), anharmonicity factor ($\omega_e\chi_e$), rotational constant (B_e), and vibration-rotation coupling constant (α_e) can be calculated by the following relations:

$$f_2 = D_e\left(a_1^2 - 2a_2\right), \tag{20}$$

$$f_3 = 6D_e\left(a_1a_2 - a_3 - \frac{a_1^3}{3}\right), \tag{21}$$

$$f_4 = D_e a_1^4 - 6f_2a_1^2 - 4f_3a_1, \tag{22}$$

$$B_e = \frac{h}{8\pi^2 c\mu R_e^2}, \tag{23}$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2 mc^2}}, \tag{24}$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(\frac{f_3R_e}{3f_2} + 1\right), \tag{25}$$

$$\omega_e\chi_e = \frac{B_e}{8}\left[-\frac{f_4R_e^2}{f_2} + 15\left(1 + \frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right]. \tag{26}$$

Once these parameters are obtained from the calculation, it is straightforward to calculate the amplification factor for our purpose.

V. RESULT AND DISCUSSION

The three lowest states of the selenium deuteride radical $X^2\Pi, {}^2\Pi_{\frac{3}{2}}$, and ${}^2\Pi_{\frac{1}{2}}$ are least-square fitted to the Murrel-Sorbie function to get the parameters a_1, a_2, a_3, R_e and D_e of the corresponding states. By using the parameters in the respective equations the spectroscopic parameters are evaluated for the most abundant isotopes of Se, i.e., ^{80}Se for the ^{80}SeD molecule with different correlation consistent Dunning's basis sets. The potential-energy surfaces at the MRCI + Q/a-V5Z-DK for the states $X^2\Pi, {}^2\Pi_{\frac{3}{2}}$, and ${}^2\Pi_{\frac{1}{2}}$ of ^{80}SeD are shown in Fig. 1. The plotted potential-energy curves are smooth and show no presence of unphysical kinks along the whole surface.

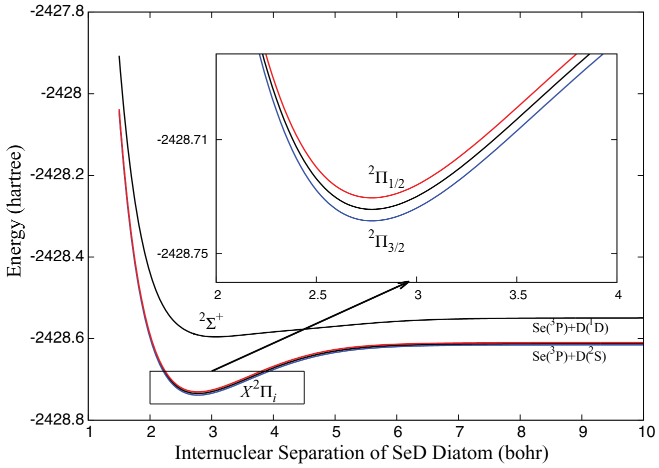

FIG. 1. (Color online) The PESs of the ground state $X^2\Pi$ and the first excited state $A^2\Sigma^+$ of the SeD radical and partly magnified PESs of the SOC split states ${}^2\Pi_{\frac{3}{2}}$ and ${}^2\Pi_{\frac{1}{2}}$ near equilibrium separation R_e (inset) at the MRCI + Q/a-V5Z-DK level of theory.

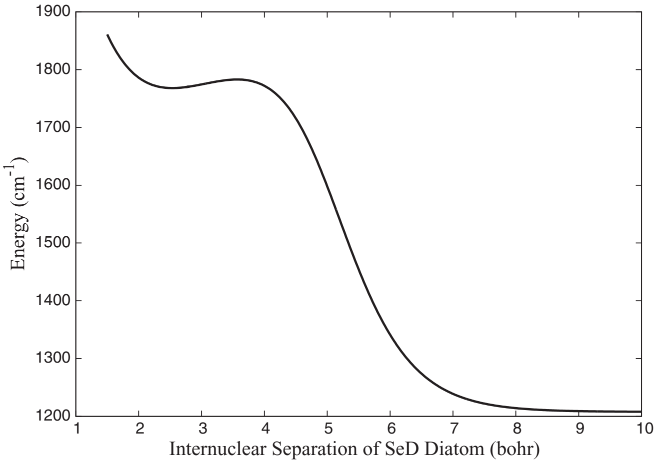

FIG. 2. The curve for the vertical transition energy of the SeD $X^2\Pi_{\frac{3}{2}\rightarrow\frac{1}{2}}$ transition energy (in cm^{-1}) versus the internuclear separation at the MRCI + Q/a-V5Z-DK level of theory.

The variation of spin-orbit energy difference between the two spin-orbit components $X^2\Pi_{\frac{3}{2}}$ and ${}^2\Pi_{\frac{1}{2}}$ with the change in internuclear separation between Se and D is presented in Fig. 2. This energy interval can be regarded as the vertical transition energy from $X^2\Pi_{\frac{3}{2}}$ to ${}^2\Pi_{\frac{1}{2}}$ which is determined by the SOC splitting of the ground electronic state $X^2\Pi$. Increasing the interatomic separation from the equilibrium distance 2.776 bohr, the curve exhibits a little increase (12 cm^{-1}) up to 3.56 bohr and then a gradual decrease is observed to about 1207.91 cm^{-1} at 10 bohr. The curve shows that the SOC between $X^2\Pi_{\frac{3}{2}}$ and ${}^2\Pi_{\frac{1}{2}}$ is lower than 1780 cm^{-1} at all internuclear separations, which supports the perturbative treatment of SOC in this case.

Relevant spectroscopic parameters such as harmonic frequency (ω_e), anharmonicity factor ($\omega_e\chi_e$), rotational constant (B_e), and vibration-rotation coupling constant (α_e) along with equilibrium bond length and spin-orbit coupling (SOC) are tabulated with different electron correlation consistent Dunning's basis sets in Table I.

It is evident from Table I that the predicted equilibrium bond lengths of SeD using MRCI at different basis sets reveal almost no discernible variation from quadruple zeta quality basis sets to quintuple zeta basis sets and are less than 0.0001 Å. The estimated R_e is also in excellent agreement with the previously measured bond lengths of SeD (1.4640 Å) from laser magnetic resonance based experiments [21]. We find that the deviation at MRCI/a-V5Z-DK is less than 0.005 Å. Moreover, the estimated spectroscopic constants also show excellent convergence at better quality basis sets. In general theoretically estimated spectroscopic constants also exhibit excellent agrement with the experimentally determined values. However, for ω_e, we find that the agrement between the experimental and theoretical values can be termed satisfactory at best. Decades ago, Brown and Watson determined the band origin of the SeD vibrational spectrum to be 1677.05 cm^{-1} [21]. Using the equation $\nu_0 = \omega_e - 2\omega_e\chi_e$, where ν_0 is the fundamental vibrational band origin, the ω_e is estimated to be 1719.75 cm^{-1} [21]. In contrast, the ω_e predicted from the Murrel-Sorbie fit to the MRCI potential-energy surface

TABLE I. Spectroscopic parameters derived for the most abundant isotope ^{80}SeD (μ=1.9645891 a.u) from Murrel-Sorbie curve fitting with different Dunning's basis sets with the spin-orbit coupling at equilibrium.

Basis	Electronic state	R_e (Å)	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	D_e (eV)	A_e (cm^{-1})
a-VTZ-DK	$X^2\Pi$	1.4711	1754.20	22.598	3.9621	0.0732	3.284	−1759.72
	$^2\Pi_{\frac{3}{2}}$	1.4711	1750.08	22.429	3.9621	0.0736	3.318	
	$^2\Pi_{\frac{1}{2}}$	1.4711	1758.64	22.783	3.9621	0.0729	3.251	
VQZ-DK	$X^2\Pi$	1.4689	1769.06	22.576	3.9735	0.0724	3.328	−1768.01
	$^2\Pi_{\frac{3}{2}}$	1.4689	1764.85	22.402	3.9735	0.0727	3.362	
	$^2\Pi_{\frac{1}{2}}$	1.4689	1773.54	22.765	3.9735	0.0721	3.295	
a-VQZ-DK	$X^2\Pi$	1.4689	1764.39	22.588	3.9735	0.0732	3.338	−1767.81
	$^2\Pi_{\frac{3}{2}}$	1.4689	1760.41	22.426	3.9735	0.0735	3.372	
	$^2\Pi_{\frac{1}{2}}$	1.4689	1768.66	22.762	3.9735	0.0728	3.304	
V5Z-DK	$X^2\Pi$	1.4689	1766.88	22.441	3.9735	0.0724	3.347	−1770.26
	$^2\Pi_{\frac{3}{2}}$	1.4689	1762.79	22.273	3.9735	0.0728	3.313	
	$^2\Pi_{\frac{1}{2}}$	1.4689	1771.27	22.623	3.9735	0.0721	3.313	
a-V5Z-DK	$X^2\Pi$	1.4689	1765.11	22.442	3.9735	0.0727	3.353	−1770.26
	$^2\Pi_{\frac{3}{2}}$	1.4689	1761.11	22.280	3.9735	0.0730	3.387	
	$^2\Pi_{\frac{1}{2}}$	1.4689	1769.41	22.618	3.9735	0.0724	3.319	
	Electronic state	R_e (Å)	ν_0[1] (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	De (eV)	A_e (cm^{-1})
Expt.	$X^2\Pi$	1.4640	1677.05	21.35	4.0031	0.07985		−1762.696
	$^2\Pi_{\frac{3}{2}}$							
	$^2\Pi_{\frac{1}{2}}$							

predicts a ω_e of 1765.11 cm^{-1}. Harmonic frequency derived numerically by determining the second derivative of energy with respect to nuclei displacement about the equilibrium geometry is predicted to be 1712.12 cm^{-1}. We have checked also the ω_e with other reliable electronic structure methods such as coupled cluster singles and doubles (CCSD) [43–45] and coupled cluster singles and doubles with perturbative triples corrections [CCSD(T)] [46] with electron correlation consistent Dunning's basis sets. These methods can provide accurate estimates for harmonic frequencies (ω_e) as at equilibrium bond length if the system under consideration can be well approximated through a single determinant wave function. All of these values for harmonic frequencies are reported in Table II. The amplification factor K is dependent on the harmonic frequency. Hence using different harmonic frequencies we get a wide ranging spread for the amplification factor as shown in Table II. The amplification factor can be as high as 1070. If we use only theoretical estimates the maximum amplification factor can be 350. On the lower side it can be 34. Even if we consider the lowest amplification factor we can safely conclude that this molecule can be an effective probe for measuring space-time variation of fundamental constants.

Since from Table II the spin-orbit coupling constant A_e and harmonic frequency ω_e are very similar in magnitude for the SeD radical in its ground-state electronic multiplet $X^2\Pi_i$, $G(v+1)^{\frac{3}{2}}$ is quasidegenerate with the $G(v)^{\frac{1}{2}}$ level for $v = 0,1,2,3,\ldots$. As mentioned in the introduction, for measuring space-time variation of fundamental physical constants, we have to have a large value of amplification factor (K) for the transition between quasidegenerate vibronic levels. The energy difference between the quasidegenerate vibronic levels can be expressed as

$$\begin{aligned}\Delta G(v) &\equiv G(v)^{\frac{1}{2}} - G(v+1)^{\frac{3}{2}},\\ &= -A_e - \omega_e + 2B_e - 2\alpha_e\\ &\quad + (2\omega_e\chi_e + \alpha_{A_e})(v+1).\end{aligned} \tag{27}$$

TABLE II. Amplification factor K predicted at different levels of theory with the experimental SOC.

Isotope	Electronic state	Level of theory	ω_e[2] (cm^{-1})	A_e or ω_f[3] (cm^{-1})	Amplification factor $K = \frac{\omega_f}{\omega_f - v\omega_e}$
^{80}SeD	$^2\Pi$	CCSD/a-VQZ-DK	1761.04	−1762.696	1064.42
^{80}SeD	$^2\Pi$	CCSD(T)/a-VQZ-DK	1738.05	−1762.696	71.52
^{80}SeD	$^2\Pi$	MRCI/a-VQZ-DK	1712.12	−1762.696	34.85
^{80}SeD	$^2\Pi$	Expt. [21]	1719.75	−1762.696	41.04

TABLE III. Difference between quasidegenerate vibronic states for the most abundant four isotopes of SeD with increasing vibrational quantum number.

Isotope	$\Delta G(v)$ (cm^{-1})	$\Delta G(v=0)$ (cm^{-1})	$\Delta G(v=1)$ (cm^{-1})	$\Delta G(v=2)$ (cm^{-1})
^{77}SeD	$11.85+36.62(v+1)$	48.47	85.09	121.71
^{79}SeD	$12.54+36.59(v+1)$	49.13	85.72	122.31
^{80}SeD	$12.84+35.58(v+1)$	49.40	83.98	119.57
^{82}SeD	$13.34+35.58(v+1)$	49.89	86.44	122.99

For the most abundant four isotopes of SeD at the MRCI + Q/a-V5Z-DK level of theory, the change of $\Delta G(v)$ is tabulated in Table III. $\Delta G(v)$ is positive for all vibrational levels and increases with the vibrational quantum number due to anharmonicity. For $v = 0$ the vibrational levels of the two states become closest to each other.

Since for $v = 0$ the vibrational levels of the two states come within 50 cm^{-1}, rotational states with J value from the two states interact significantly with each other. Rotational energies of both the doublet states are expressed with the same expression, i.e., $F_v(J)^{(\frac{1}{2})} = F_v(J)^{(\frac{3}{2})} = B_e[J(J+1) - \alpha_e J(J+1)(v+\frac{1}{2})]$. Therefore the energy associated with the microwave transition is $\Delta F_v(J) = F_v(J)^{(\frac{1}{2})} - F_v(J)^{(\frac{3}{2})}$. Now the selection rule for microwave transition is $\Delta F_v(J) = \pm 1$, i.e., $\Delta L + \Delta J = \pm 1$, which leads to two possibilities: one is $\Delta L = \pm 1, \Delta J = 0$ (only observed for the open shell molecule, which leads to Q-branch spectra) and another is $\Delta L = 0, \Delta J = \pm 1$ (which leads to P and R-branch spectra). So the overall selection rule for this kind of doublet species is $\Delta J = 0, \pm 1$. For $\Delta J = 0$ transitions, there is no change in the rotational energy, so we are considering only those transitions which follow the selection rule $\Delta J = \pm 1$. For $\Delta J = +1$, $\Delta F_{v=1}(J) = 2B_e(J+1) - \alpha_e J(J+1)(J+3)$ and, for $\Delta J = -1$, $\Delta F_{v=1}(J) = -2B_e J - \alpha_e J(J-2)$.

Now the transitions of interest are those which lead to $\Delta E(v,J) \approx 0$, i.e., $\Delta G(v) + \Delta F_v(J) \approx 0$. Since for $v = 1$ vibronic levels of the two doublet states come closest and $\Delta G(v=0)$ is a positive quantity ΔJ have to be -1. Therefore $\Delta G(v=0) + \Delta F_v(J) \approx 0$:

$$\begin{aligned}\Delta G(v=0) &= -\Delta F_v(J)\\ &= -[-2B_e J - \alpha_e J(J-2)]\\ &= 2B_e J + \alpha_e J(J-2).\end{aligned} \tag{28}$$

From the table of the spectroscopic parameters we notice the fact that $\alpha_e \ll B_e$ in magnitude and we neglect the term containing α_e to convert the equation into linear equation $\Delta G(v=0) = 2B_e J$ and solve for J, leading to

$$J = \frac{\Delta G(v=0)}{2B_e} = 6.21 \approx 6.$$

For open shell systems J is essentially a half integer; the two appropriate choices of J are $J = 6\frac{1}{2}$ and $5\frac{1}{2}$.

Variation of rovibronic transition frequency with respect to variations of *α* and *μ*

The rovibrational energy difference between two electronic states can be expressed as

$$\begin{aligned}\Delta E_v(J) &= \Delta G(v) + \Delta F_v(J)\\ &= A_e - \omega_e - \alpha_e + 2B_e + v(2\omega_e\chi_e - \alpha_{A_e})\\ &\quad - 2B_e J - \alpha_e J(J-2).\end{aligned} \tag{29}$$

Thus, for the variation in energy difference $\Delta E_v(J)$ in terms of variation in α and μ can be expressed as

$$\begin{aligned}\delta E_v(J) &= \delta[A_e - \omega_e - \alpha_e + 2B_e + v\big(2\omega_e\chi_e - \alpha_{A_e}\big)\\ &\quad - 2B_e J - \alpha_e J(J-2)]\\ &= \delta(A_e - \omega_e).\end{aligned} \tag{30}$$

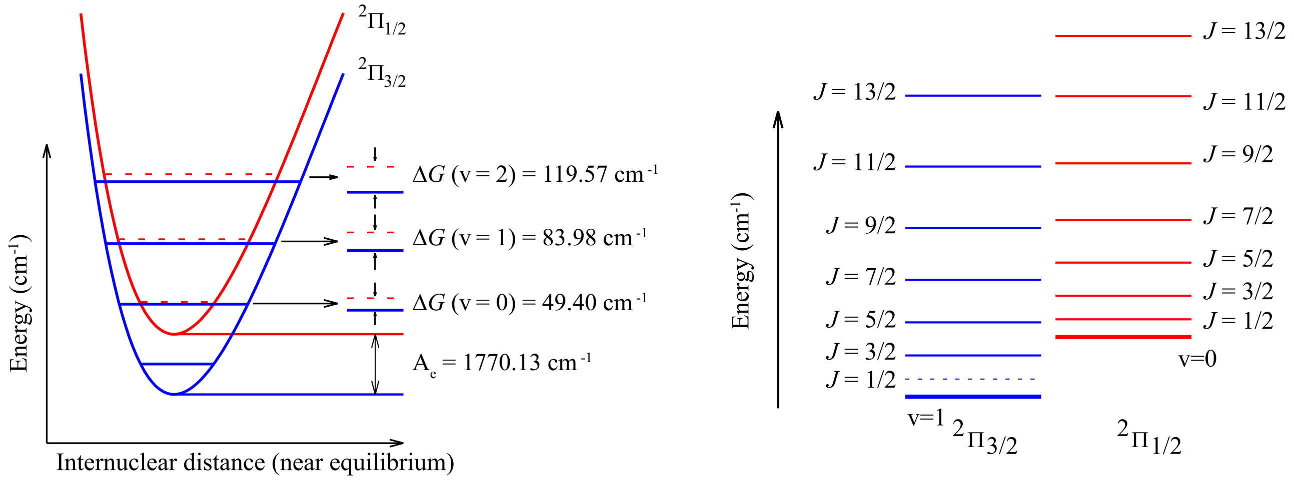

FIG. 3. (Color online) (Left) The magnitude of vibronic levels of the two doublet states of ^{80}SeD. The blue and red lines represent the ${}^2\Pi_{\frac{3}{2}}$ and ${}^2\Pi_{\frac{1}{2}}$ MRCI + Q/a-V5Z-DK levels of theory, respectively. (Right) Rotational levels of the two doublet states. The blue (solid) and red (dashed) lines represent ${}^2\Pi_{\frac{3}{2}}$ and ${}^2\Pi_{\frac{1}{2}}$. Since J is always $\geqslant \Omega$, for ${}^2\Pi_{\frac{3}{2}}$ the $J = \frac{1}{2}$ rotational level is not observed.

As other terms are negligible compared to A_e and ω_e they are neglected in Eq. (30). Now the spin-orbit constant A_e varies as $\sim Z^2\alpha^2 E_H$ and ω varies as $M_r^{-\frac{1}{2}}\mu^{-\frac{1}{2}}E_H$ as mentioned in the introduction, so overall variation in transition energy will be

$$\delta E_v(J) = \delta(A_e - \omega_e), \quad \cong 2A_e\left(\frac{\delta\alpha}{\alpha} + \frac{1}{4}\frac{\delta\mu}{\mu}\right), \\ = (3540 \ \ \mathrm{cm}^{-1})\left(\frac{\delta\alpha}{\alpha} + \frac{1}{4}\frac{\delta\mu}{\mu}\right). \qquad (31)$$

For SeD the values are shown in Fig. 3. Therefore a large enhancement factor may be obtained by proper choice of a molecular probe, in this case the SeD radical, which is likely to be found under certain astrophysical conditions like an asymptotic giant branch star.

VI. CONCLUSION

To summarize, for a SeD molecule, we have analyzed the sensitivity of the rovibronic spectrum to variations in the fundamental physical constants. We have found enhanced sensitivity for a number of low-frequency microwave transitions within $^2\Pi_{\frac{1}{2}}(v=0)$ and $^2\Pi_{\frac{3}{2}}(v=1)$ which may enhance the amplification factor up to the order of ~350. We acknowledge the fact that the data produced in the calculation should not be considered as accurate as microwave frequency because the error bar of the MRCISD + Q level of theory can be as large as $\sim 100\ \mathrm{cm}^{-1}$. Fairly accurate data can only be obtained from high-precision laboratory experiments, so experimental evidence is necessary on the molecule to confirm our findings.

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