SeD Radical: A probe for measurement of time variation of Fine Structure Constant ($\alpha$) and Proton to Electron Mass Ratio ($\mu$)

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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 through the Breit-Pauli operator. The relevant spectroscopic data are evaluated using Murrell-Sorbie fit to the potential energy surfaces. The spin-orbit splitting ($\omega_f$) between the two multiplets is similar in magnitude with the harmonic frequency ($\omega_c$) 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 SeD radical can be a plausible experimental candidate for measuring variation in $\alpha$ and $\mu$.

PACS numbers: 06.20.Jr, 33.20.Wr, 31.15.X-
that such a possibility is purely fortuitous as no such diatomic molecules exist. This limits the search for such diatomic molecules to cases where $\frac{\omega_f}{\omega_e}$ and $K$ is 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 et al. and others have recently proposed certain candidates as viable probes, such as CsH, MgH, CaH$^+$ [10, 11], Cl$_2^+$, IrC, HFF$^+$ [12, 13], NH$^+$ [15, 17], SiBr [18]. Out of these few do not have permanent dipole moment ($\mu$) and hence it may be considered as similar to the trapping of NH or CaH molecules in magneto-inversion. Laboratory experiment wise SeD is very similar to the microwave observations made on NH$_3$. Branch stars are probable sites to look for SeD due to the richness 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 $\alpha$ and $\mu$. Although NH$_3$ and other C-H compounds are astrophysically abundant, 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 potentially important complementarity to the microwave observations made on NH$_3$ inversion. Laboratory experiment wise SeD is very similar to the trapping of NH or CaH molecules in magneto-optical traps [2, 10] and hence it may be considered as a possible candidate for fundamental test. Chemically, SeD is an open shell molecule with one unpaired electron ($S = \frac{1}{2}$) in its $\pi$ orbital with a $\pi^3$ configuration. The first excited state $A^2\Sigma^+$ is well separated (about 30, 460 cm$^{-1}$) with the ground state $X^2\Pi$. For linear molecule under spin-orbit coupling (SOC) the electronic states can be expressed as $\Omega = |\Lambda + \Sigma\rangle$, where, $\Lambda$ and $\Sigma$ are the orbital and spin angular momentum. Under SOC splitting the $X^2\Pi$ state will split into $2\Pi_{\frac{3}{2}}$ and $2\Pi_{\frac{1}{2}}$ for $\Lambda = 1, \Sigma = \pm \frac{1}{2}$ and there is no split for $A^2\Sigma^+$ because of $\Lambda = 0, \Sigma = \pm \frac{1}{2}$. According to the Hund’s rule for more than half filled ($\pi^3$ 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. RO-VIBRONIC ENERGY LEVELS IN SELENIUM DEUTERIDE

The total Hamiltonian can be expressed as,

$$H = H_{Vib} + H_{SO} + H_{Rot}$$  (4)

for a $^2\Pi$ state the terms on the right hand side of the equation represents 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 upto first order term in $(v + \frac{1}{2})$ is,

$$E_{Vib}(v) = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2\omega_e\chi_e$$  (5)

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

$$H_{SO} = A_v\Lambda\Sigma$$  (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 co-workers [21] (expanded upto the first order of $(v + \frac{1}{2})$ term)

$$A_v = A_0, A_0, (v + \frac{1}{2})$$  (7)

Therefore the spin-orbit Hamiltonian becomes,

$$H_{SO} = A_v\Lambda\Sigma - \alpha_A(v + \frac{1}{2})\Lambda\Sigma$$  (8)

In a molecular system rotation, vibration and electronic interactions influence one another. For the ro-vibrational electronic spectra of a diatomic molecule, the different angular momenta, i.e. electron spin angular momentum ($\vec{S}$), electron orbital angular momentum ($\vec{L}$) and angular momentum of nuclear rotation ($\vec{R}$) can couple in various ways to form the resultant angular momentum $\vec{J}$. These type of coupling are described by Hund’s coupling cases. The ground state electronic multiplet, $X^2\Pi, \Upsilon, of SeD falls into the category of Hund’s case (a) type of diatomic molecule where electronic orbital angular momentum $\vec{L}$ is weakly coupled with the nuclear rotation and strongly coupled with the inter nuclear axis by electrostatic force i.e. $|\frac{\lambda}{R^3}| << 1$. Spin angular momentum ($\vec{S}$) is strongly coupled to orbital angular momentum ($\vec{L}$) by spin orbit coupling. The electronic angular momentum for a rotating diatomic molecule is defined as $\Omega = \Lambda + \Sigma$ (Where $\Lambda$ and $\Sigma$ are the axial components of $\vec{L}$ and $\vec{S}$). Angular momentum of the rotating nuclei ($\vec{R}$) is coupled to $\Omega$ to form total angular momentum $\vec{J} = \Omega + \vec{R}$. After neglecting the centrifugal force terms the rotational energy in Hund’s case (a) [22], rotational Hamiltonian will be that of asymmetric top with $\Omega$ as the angular momentum about the internuclear axis. The effective Hamiltonian in case for Hund’s case (a) is

$$H_{Rot} = |B_v|R^2$$  (9)
where $B_r$ is the rotational constant. Hunds case (a) is a good representation when $A_r \Lambda$ is much greater than $B_r J$, where $A_r$ is the spin-orbit coupling constant. The rotational energy is given by,

$$E_{Rot}(J) = B_r[J(J + 1) - \Omega^2]$$

(10)

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

$$B_r = B_e - \alpha_e(v + \frac{1}{2})$$

(11)

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

$$E_{Rot}(J) = B_e[J(J + 1) - \Omega^2] - \alpha_e[J(J + 1) - \Omega^2](v + \frac{1}{2})$$

(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,

$$E(v, J) = \pm [A_e - A_{A_e}(v + \frac{1}{2})] + (v + \frac{1}{2})\omega_e$$

$$- (v + \frac{1}{2})^2\omega_e \chi_e + B_e[J(J + 1) - \Omega^2]$$

$$- \alpha_e[J(J + 1) - \Omega^2](v + \frac{1}{2})$$

(13)

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

$$E(v, J) = G(v) + F_v(J)$$

(14)

where,

$$G(v) = \pm \frac{1}{2} [A_e - B_e \Omega^2 + \omega_e \pm \frac{1}{2} \alpha_{A_e}]$$

$$+ \alpha_{A_e} \Omega^2(v + \frac{1}{2})$$

$$- (v + \frac{1}{2})^2\omega_e \chi_e$$

$$F_v(J) = B_e[J(J + 1)] - \alpha_e[J(J + 1)](v + \frac{1}{2})$$

(15)

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, $J$’s belonging to same or different vibrational levels can be chosen as per the experimental requirements.

### III. COMPUTATIONAL DETAILS

The ground electronic state $X^2\Pi$ of Selenium Deuteride radical is thoroughly studied in this paper. The ground state electronic configuration of $X^2\Pi$ SeD is $(3s_{Se})^2(3p_{zSe} + 1s_H)^2(3p_{\pi Se})^2(3p_{\pi Se})^1$. If one electron is transferred from $(3p_{zSe} + 1s_H)$ orbital to $(3p_{\pi Se})$ the first excited state $^2\Sigma^+$ is formed with the configuration $(3p_{zSe})^2(3p_{zSe} + 1s_H)^2(3p_{\pi Se})^2(3p_{\pi Se})^2$. The theoretical characterization of potential energy curves for the ground state and the first excited state over an extended inter nuclear separation until dissociation requires the account of both static and dynamic correlation effects. In this study for the ground state, these effects has been included by the use of state-averaged complete active space SCF(SA-CASSCF)[23, 24] calculation on each doublet spin symmetry (MRCISD). 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, the symmetries in the parenthesis are the corresponding one in the C$_{\infty v}$ point group. The active space consists the distribution of 7 electrons over 5 orbitals(CAS(7,5)). Since single and double electron excitation on top of CAS wave function is computationally very demanding, so Configuration State Function(CSF) with coefficients greater than 0.01 only are included to construct the new zero-order CI space. A further reduction of the dimension of the CI wavefunction has been made with internally contracted configuration interaction (IC-MRCISD) approach[25, 26] by restricting the core occupation to $(7A_1, 3B_1, 3B_2, 1A_2)$ where A and B denotes the symmetries of the irreducible representation in $C_{2v}$ point group symmetry.

The molecular orbitals constructing the CSF’s are the natural orbitals which are obtained by diagonalization of state-averaged $(B_1$ and $B_2$ state 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 natural orbital. The second-order Douglas-Kroll-Hess Hamiltonian has been used for all MRCl 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 $\hat{H} = \hat{H}_{el} + \hat{H}_{SO}$. The spin-orbit matrix elements $\hat{H}_{SO}$ 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)\textsuperscript{31} operator of the form

\begin{equation}
\hat{H}_{SO} = \frac{1}{2m^2e^2} \left[ \sum_i \sum_{\alpha} Z_{\alpha} c^2 \hat{I}_{\alpha i} \hat{S}_i - \sum_i \sum_{\alpha} e^2 \hat{I}_{\alpha i}(\hat{S}_i + 2\hat{S}_j) \right] \tag{17}
\end{equation}

which contains both one and two electron terms. Here \( \hat{I} \) and \( \hat{S} \) are orbital and spin angular momentum operators, \( i \) and \( \alpha \) denotes electron and nucleus respectively.

In the next step, \( \hat{H} = \hat{H}_{el} + \hat{H}_{SO} \) matrix is diagonalised in the basis of SA-CASSCF/IC-MRCISD(7,5) wavefunctions 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 Davidsons method\textsuperscript{32, 33}. These calculations have been carried out with the MOLPRO\textsuperscript{34} suite of programs.

**IV. THE POTENTIAL ENERGY FUNCTION**

Among the functions that was proposed to fit the Analytical Potential Energy Functions(APEF) of diatomic molecules, Murrel Sorbie (MS) potential energy function seems to be the best one\textsuperscript{35–40}. The interaction potential energies of many neutral and cationic diatomic molecules can be accurately reproduced by this function and has been used to deduce APEFs for many molecules\textsuperscript{35–40}. The general form of MS function is given by\textsuperscript{41}

\begin{equation}
V(\rho) = -D_e(1 + \sum_{i=1}^{n} a_i \rho^i) \exp(-a_1 \rho) \tag{18}
\end{equation}

Usually, satisfactory results can be obtained when \( n \) equals 3. In order to get accurate data, the following form of MS function is used\textsuperscript{11, 42}

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

where \( \rho = R - R_e \) is the inter atomic distance, \( R_e \) is the equilibrium distance and \( D_e \) is the dissociation energy. The quadratic(\( f_2 \)), cubic(\( f_3 \)) and quartic(\( f_4 \)) force constants can be derived by the M-S function and then spectroscopic parameters harmonic frequency (\( \omega_e \)), anharmonicity factor (\( \omega_e \chi_e \)) rotational constant(\( B_e \)) and vibration-rotation coupling constant (\( \alpha_e \)) can be calculated by the following relations,

\begin{align}
&f_2 = D_e(a_1^2 - 2a_2) \tag{20} \\
f_3 &= 6D_e(a_1 a_2 - a_3 - \frac{a_3^2}{2}) \tag{21} \\
f_4 &= D_e a_4 - 6f_2 a_1^2 - 4f_3 a_3 \tag{22} \\
B_e &= \frac{\hbar}{8\pi^2 e \mu R_e^2} \tag{23} \\
\omega_e &= \sqrt{\frac{f_2}{4\pi^2 e^2 \mu^2}} \tag{24} \\
\alpha_e &= -\frac{6B_e^2}{\omega_e}(\frac{f_2 R_e}{3f_2} + 1) \tag{25} \\
\omega_e \chi_e &= \frac{B_e}{8} \left[ -\frac{f_3 R_e^2}{f_2} + 15\left(1 + \frac{\omega_e \alpha_e}{6B_e^2}\right)^2 \right] \tag{26}
\end{align}

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

**V. RESULT AND DISCUSSION**

| Basis       | Electronic State | \( R_e \) (\( \text{Å} \)) | \( \omega_e \) (\( \text{cm}^{-1} \)) | \( \omega_e \chi_e \) (\( \text{cm}^{-1} \)) | \( B_e \) (\( \text{cm}^{-1} \)) | \( \alpha_e \) (\( \text{cm}^{-1} \)) | \( A_e \) (\( \text{cm}^{-1} \)) |
|-------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| a-VTZ-DK    | \( \chi^2 \Pi \) | 1.4711           | 1754.20         | 22.598           | 3.9621          | 0.07327         | -1759.72        |
|             | \( ^1 \Pi_2 \)  | 1.4711           | 1750.08         | 22.429           | 3.9621          | 0.07360         |                  |
|             | \( ^3 \Pi_2 \)  | 1.4711           | 1758.64         | 22.783           | 3.9621          | 0.07270         |                  |
| VQZ-DK      | \( \chi^2 \Pi \) | 1.4698           | 1769.06         | 22.576           | 3.9735          | 0.07243         | -1768.01        |
|             | \( ^1 \Pi_2 \)  | 1.4698           | 1764.85         | 22.402           | 3.9735          | 0.07278         |                  |
|             | \( ^3 \Pi_2 \)  | 1.4698           | 1773.60         | 22.765           | 3.9735          | 0.07272         |                  |
|             | \( ^3 \Pi_4 \)  | 1.4698           | 1754.39         | 22.588           | 3.9735          | 0.07274         |                  |
|             | \( ^1 \Pi_4 \)  | 1.4698           | 1764.41         | 22.426           | 3.9735          | 0.07355         |                  |
| V5Z-DK      | \( \chi^2 \Pi \) | 1.4698           | 1766.88         | 22.441           | 3.9735          | 0.07243         | -1770.26        |
|             | \( ^1 \Pi_2 \)  | 1.4698           | 1762.79         | 22.273           | 3.9735          | 0.07285         |                  |
|             | \( ^3 \Pi_2 \)  | 1.4698           | 1771.27         | 22.623           | 3.9735          | 0.07273         |                  |
|             | \( ^3 \Pi_4 \)  | 1.4698           | 1765.11         | 22.442           | 3.9735          | 0.07278         |                  |
|             | \( ^1 \Pi_4 \)  | 1.4698           | 1761.11         | 22.280           | 3.9735          | 0.07300         |                  |
|             | \( ^3 \Pi_4 \)  | 1.4698           | 1769.41         | 22.618           | 3.9735          | 0.07274         |                  |

| Expt.       | \( \chi^2 \Pi \) | 1.4640           | 1677.05         | 21.35            | 4.00310         | 0.07985         | -1762.096       |
|             | \( ^1 \Pi_2 \)  | -                | -               | -                | -               | -               |                  |
|             | \( ^3 \Pi_2 \)  | -                | -               | -                | -               | -               |                  |

Three lowest states of Selenium Deuteride radical \( X^2 \Pi, ^2 \Pi_2 \) and \( ^2 \Pi_4 \) 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 into the respective equations the spectroscopic parameters are evaluated for the most abundant isotopes of Se i.e. $^{80}$Se for the SeD molecule with different correlation consistent with Dunning’s basis sets. The potential energy surfaces at the MRCI+Q/a-V5Z-DK for the states $X^2\Pi, ^2\Pi^\pm$ and $^2\Pi^\mp$ of SeD are shown in Fig. 1. The plotted potential energy curves are smooth and show no presence of unphysical kinks along the whole surface.

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

Relevant spectroscopic parameters such as, harmonic frequency $\omega_e$, anharmonicity factor ($\omega_e \chi_e$), rotational constant ($B_e$) and vibration-rotation coupling constant ($\alpha_e$), along with equilibrium bond length and Spin-Orbit Coupling(SOC) are tabulated with different electron correlation consistent Dunning’s basis set in Tab. 1.

It is evident from Table 1 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 is 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 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 agreement with the experimentally determined values. However for $\omega_e$, we find that the agreement between the experimental and theoretical value can be termed satisfactory at best.

Decades back Brown and co-workers have determined the band origin of SeD vibrationional spectrum to be 1677.05 cm$^{-1}$.$^{[21]}$ Using the equation $\nu_0 = \omega_e - 2\omega_e \chi_e$, where $\nu_0$ is the fundamental vibrational band origin the $\omega_e$ is estimated to be 1719.75 cm$^{-1}$.$^{[21]}$ On the contrary the $\omega_e$ predicted from the Murrel-Sorbie fit to the MRCI potential energy surface predicts a $\omega_e$ of 1765.11 cm$^{-1}$. Harmonic frequency derived numerically by determining the 2nd 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 $\omega_e$ with other reliable electronic structure methods such as coupled cluster singles and doubles (CCSD) and coupled cluster singles and doubles with perturbative Triples corrections (CCSD(T)) with electron correlation consistent dunning’s basis sets. These methods can provide accurate estimates for harmonic frequencies($\omega_e$) as at equilibrium bond length if the system under consideration can be well approximated through a single determinant wavefunction. All of these values for harmonic frequencies are reported in Table 1.

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 1. The amplification factor can be as high as 1070. If use only theoretical estimates the maximum amplification factor

![Image](image-url)
can be 350. On the lower side it can be 34. Even if we consider the lowest amplification factor one can safely conclude that this molecule can be an effective probe for measuring space-time variation of fundamental constants.

### TABLE II: Amplification factor (K) predicted at different level of theory with the experimental SOC

| Isotope  | Electronic State | Level of Theory | ∆G or ω/ cm | Amplification factor (K) | K × 100 |
|----------|------------------|----------------|-------------|--------------------------|---------|
| 68SeD    | 4H                | CCSD/a-VQZ-DK  | 1764.06     | 1762.69 ε               | 1064.42 |
| 70SeD    | 4H                | CCSD(T)/a-VQZ-DK | 1764.06     | 1762.69 ε              | 71.52  |
| 72SeD    | 4H                | MRCI+Q/a-VQZ-DK | 1762.69     | 1762.69 ε              | 34.64  |
| 76SeD    | 4H                | Exp. [21]      | 1738.75     | 1762.69 ε              | 41.94  |

Since from the above table, the spin-orbit coupling constant A_e and harmonic frequency ω_e are very similar in magnitude for SeD radical in its ground state electronic multiplet X^2Π\textsubscript{g}. G(v + 1)\hat{J} is quasi-degenerate with G(v)\hat{J} level for v = 0, 1, 2, 3, .... 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 quasi-degenerate vibronic levels. The energy difference between the quasi-degenerate vibronic levels can be expressed as,

\[ \Delta G(v) \equiv G(v)\hat{J} - G(v + 1)\hat{J} , \]

\[ = -A_e - \omega_e + 2B_e - 2\alpha_e + (2\omega_e\chi_e + \alpha_A_e)(v + 1) \] \hspace{1cm} (27)

For the most abundant four isotopes of SeD at the MRCI+Q/a-V5Z-DK level of theory, the change of ∆G(v) is tabulated in Table III. ∆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.

### TABLE III: Difference between quasi-degenerate vibronic states for the four most abundant isotope SeD with increasing vibrational quantum number.

| Isotope  | ∆G(v) \( \text{cm}^{-1} \) | ∆G(v = 0) \( \text{cm}^{-1} \) | ∆G(v = 1) \( \text{cm}^{-1} \) | ∆G(v = 2) \( \text{cm}^{-1} \) |
|----------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|    77SeD | 11.850+36.62(v + 1)         | 48.47                       | 85.09                       | 121.71                      |
|    79SeD | 12.540+36.59(v + 1)         | 49.13                       | 85.72                       | 122.31                      |
|    80SeD | 12.840+35.58(v + 1)         | 49.40                       | 83.98                       | 119.57                      |
|    82SeD | 13.340+35.58(v + 1)         | 49.89                       | 86.44                       | 122.99                      |

Since for v = 0 the vibrational levels of the two states come within a 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. \( F_e(J)\hat{J} = F_e(J)\hat{J} = F_e(J)\hat{J} + F_e(J)\hat{J} \). Therefore the energy associated with the microwave transition is \( \Delta F_e(J) = F_e(J)\hat{J} - F_e(J)\hat{J} \). Now the selection rule for microwave transition is \( \Delta F_e(J) = \pm 1 \) i.e. \( \Delta L = \Delta J = \pm 1 \), which leads to two possibility, one is \( \Delta L = \pm 1, \Delta J = 0 \) (only observed for 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 are no change in the rotational energy. So we are considering only those transitions which follow the selection rule \( \Delta J = \pm 1 \). For \( \Delta J = +1 \), \( \Delta F_{v=1}(J) = 2B_e(J + 1) - \alpha_e(J + 1)(J + 3) \) and for \( \Delta J = -1 \), \( \Delta F_{v=1}(J) = -2B_eJ - \alpha_e(J - 2) \).

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

\[ \Delta G(v = 0) = -\Delta F_e(J), \]

\[ = (-2B_eJ - \alpha_e(J - 2)), \]

\[ = 2B_eJ + \alpha_e(J - 2) \] \hspace{1cm} (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 \( \alpha_e \) to convert the equation into linear equation \( \Delta G(v = 0) \approx 2B_eJ \) 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 half integer, the two appropriate choices of J be \( J = 6\frac{1}{2} \) and \( J = 5\frac{1}{2} \).

### A. Variation of ro-vibronic transition frequency with respect to variations of α and µ:

The ro-vibrational energy difference between two electronic states can be expressed as,

\[ \Delta E_e(J) = \Delta G(v) + \Delta F_e(J), \]

\[ = A_e - \omega_e - \alpha_e + 2B_e + \nu(2\omega_e\chi_e - \alpha_A_e) - 2B_eJ - \alpha_e(J - 2) \] \hspace{1cm} (29)

So for the variation in energy difference \( \Delta E_e(J) \) in terms of variation in \( \alpha \) and \( \mu \) can be expressed as,

\[ \delta E_e(J) = \delta(A_e - \omega_e - \alpha_e + 2B_e + \nu(2\omega_e\chi_e - \alpha_A_e) - 2B_eJ - \alpha_e(J - 2)), \]

\[ = \delta(A_e - \omega_e) \] \hspace{1cm} (30)

As other terms are negligible compared to \( A_e \) and \( \omega_e \) they are neglected in equation (30). Now the spin-orbit constant \( A_e \) varies as \( \sim Z^2\alpha^2E_H \) and \( \omega_e \) varies as
Inter nuclear distance (near equilibrium)

\[ \Delta G(v = 2) = 119.57 \text{ cm}^{-1} \]
\[ \Delta G(v = 1) = 83.98 \text{ cm}^{-1} \]
\[ \Delta G(v = 0) = 49.40 \text{ cm}^{-1} \]

\[ A_e = 1770.13 \text{ cm}^{-1} \]

\[ J \leq \Omega \text{ so for } ^2\Pi \frac{3}{2}, J = \frac{1}{2} \text{ rotational level is not observed.} \]

\[ M_e \frac{-\mu}{2} E_H \text{ as mentioned in the introduction so overall variation in transition energy will be,} \]
\[ \delta E_v(J) = \delta(A_e - \omega_e), \]
\[ \cong 2A_e \left( \frac{\delta \alpha}{\alpha} + \frac{1}{4} \frac{\delta \mu}{\mu} \right), \]
\[ = 3540 \text{ cm}^{-1} \left( \frac{\delta \alpha}{\alpha} + \frac{1}{4} \frac{\delta \mu}{\mu} \right) \] (32)

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 AGB star.

VI. CONCLUSION

To summarize, for SeD molecule, we have analyzed the sensitivity of the ro-vibronic spectrum to variations in the fundamental physical constants. We have found enhanced sensitivity for a number of low frequency microwave transition 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 \(\sim 350\). 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 \(\sim 100 \text{ cm}^{-1}\). Fairly accurate data can only be obtained from high precision laboratory experiments. So, experimental evidence is necessary on the molecule to confirm our findings.

VII. ACKNOWLEDGMENTS

G.G and A.S acknowledge the Council of Scientific and Industrial research (CSIR) India for a their Research Fel-

lowship. A.P would like to thank CEFIPRA (Project No. IFC/4705-3/2012/3025) for financial support.
