Spectroscopy of Rubidium atoms in solid matrices of rare gases: experimental results and theoretical analysis

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We present an experimental and theoretical investigation of the spectroscopy of dilute alkali atoms in a solid matrix of inert gases at cryogenic temperatures, specifically Rubidium atoms in a solid Argon or Neon matrix, and related aspects of the interaction energies between the alkali atoms and the atoms of the solid matrix. The system considered is relevant for matrix isolation spectroscopy, and it is at the basis of a recently proposed detector of cosmological axions, exploiting magnetic-type transitions between Zeeman sublevels of alkali atoms in a magnetic field, tuned to the axion mass, assumed in the meV range. Axions are one of the supposed constituents of the dark matter (DM) of the Universe. This spectroscopy can be also relevant for experimental search of new physics beyond the Standard Model, in particular the search of violations of time-reversal or parity-charge-conjugation (CP) symmetry. In order to efficiently resolve the axion-induced transition in alkali doped solid matrices, it is necessary to reduce as much as possible the spectral linewidth of the electronic transitions involved. The theoretical investigation presented in this paper aims to evaluate the inhomogeneous contribution to the linewidth due to the alkali-matrix interactions (Coulomb/exchange and dispersion), and to compare the theoretical results with our experimental measurements of spectra of dilute Rubidium atoms in Argon and Neon solid matrix. The comparison of the expected or measured spectral linewidths will be essential for selecting the most appropriate combination of alkali atoms and matrix inert elements to be used in the axion detection scheme. It is finally suggested that dilute Lithium atoms diffused in a cold parahydrogen solid matrix could be an excellent system on which the proposed detector could be based.

I. INTRODUCTION

Matrix Isolation Spectroscopy of alkali atoms in solid matrices of inert gases at cryogenic temperatures is a widely used spectroscopic technique in several fields of research. The atoms are trapped in fixed positions inside the solid matrix, and thus their mutual interactions are strongly reduced, as well as their interaction with the matrix atoms or molecules. In the cases we consider in this paper, relevant for DM search, all atoms or molecules considered have not permanent dipole moments, and thermal effects are also strongly reduced by the use of cryogenic temperatures (some Kelvin) [1–3].

Matrix Isolation Spectroscopy of atoms or molecules has recently been proposed also for investigating new physics beyond the Standard Model with atoms and molecules, such as search for time-reversal or CP symmetry violations, electric dipole moment of standard-model particles, as well as DM [4–7].

Cosmological axions are supposed to be one of the possible constituents of the DM of the Universe, whose composition is still unknown [8]. Axions were initially introduced by Peccei and Quinn in order to solve the strong CP problem in quantum chromodynamics [9,10], and are assumed to interact very weakly with ordinary matter. Successively, it was proposed that they could be one of the possible constituents of DM [11], and Sikivie proposed that they could induce magnetic-type transitions between atomic Zeeman sub-levels, yielding possibility of their indirect detection [12]. It is thus of fundamental importance to envisage possible mechanisms, and relative experiments, to detect these particles. Several possibilities have been recently proposed; for a review, see for example [13,14,15].

Recently, possible detection schemes for cosmological axions in the meV energy range, based on electron transitions between Zeeman-shifted levels of dilute alkali or oxygen atoms [20], or their ionization [21], embedded in
a solid matrix of inert gases at cryogenic temperatures \[22\], have been proposed.

The basic idea is illustrated in Fig. 1: \( a \) and \( b \) denote two Zeeman sublevels of the alkali atom, with energy \( E_a \) and \( E_b \), respectively; \( \Delta E = E_b - E_a \) is their energy separation, that can be varied through the external magnetic field \( B \). \( \Delta E \) is tuned to the axion mass \( m_a \), that is unknown, but supposed of the order of some meV. The absorption of the axion by the alkali atom induces a transition from the Zeeman sublevel \( a \) to the sublevel \( b \). Then, the atomic excitation can be detected exploiting a laser field that brings the atom from \( b \) to an electronic excited state \( c \), or, alternatively, bringing the atomic electron to the conduction band of the solid matrix where the alkali atom is embedded \[20\]. Detection of the atomic excitation is thus a signature of the absorption of the axion. In order that this detection mechanism works efficiently it is necessary that the two sublevels \( a \) and \( b \) can be sharply resolved as much as possible: this requires that the linewidth of the atomic levels involved be smaller than their energy separation. The linewidth of the excited level \( c \) should be minimized too. It is therefore necessary minimizing all possible effects and interactions leading to the broadening of the spectral lines; this is particularly important in our case, due to the very small energy separation of the two Zeeman sublevels, assumed of the order of the meV.

Matrix Isolation Spectroscopy seems to be an appropriate experimental technique for this purpose, because it allows to control efficiently the interactions between the atoms and the environment, to reduce strongly the mutual interaction between the atoms due to their large separation, as well as suppressing the thermal broadening. It consists in trapping the alkali atoms in a solid matrix of inert materials at cryogenic temperatures, such as rare gases (RG) or inert molecules such as, for example, \( \text{p-H}_2 \), \( \text{O}_2 \), \( \text{CH}_4 \).

In order to find out which is the best combination of alkali atoms and solid-matrix atoms or molecules, minimizing the spectral broadening, it is important to obtain reliable spectroscopic data for different combinations of alkali atoms and inert-gas cold matrices. It is also of fundamental importance developing simple theoretical models of the potential energy between the atoms or molecules, to be easily used for the different realistic possibilities that can be experimentally realized for the detecting scheme, and whose predictions can be compared with the experimental data. Comparison of experimental data with theoretical predictions can also give important hints on how the alkali atoms diffuse in the cold matrix in specific experimental setups. In fact, the potential energies between the alkali atoms and the matrix atoms or molecules, as we will show, can give an indication of the inhomogeneous broadening of the alkali spectral lines, due to the interaction between the host alkali atoms and the atoms of the solid matrix, as well as indications on their position distribution inside the cold matrix. The linewidth of the Zeeman-shifted energy levels should be the same for the unperturbed atoms, i.e. in the absence of the magnetic field, since their electronic wavefunction is the same.

In this paper, in section II we first present experimental spectroscopic data of dilute Rubidium atoms in Argon and Neon cold matrices, with a particular attention to the lineshape of the emission spectra. Next, in section III we propose a simple general theoretical model of the interaction potential energy between the alkali atoms and the inert atoms or molecules of the matrix, in terms of few data that can be found in the literature (theoretically calculated or experimental), specifically equilibrium distance, dissociation energy, van der Waals constant, and the curvature of the potential energy at the equilibrium distance. The theoretical results obtained are then used to estimate the order of magnitude of the broadening of the spectral lines of the alkali atom, to be compared with our spectral experimental results; this can be usefully exploited to estimate the position distribution of the Rubidium atoms in the Argon or Neon cold matrix. Finally, we consider theoretically the case of Lithium atoms in a parahydrogen cold matrix, and estimate the relevant interaction energies, and the expected inhomogeneous spectral broadening in such a case. This theoretical analysis leads us to suggest that the combination of dilute Lithium atoms in a parahydrogen cold matrix could be an excellent candidate for minimizing the inhomogeneous line broadening resulting from the host-matrix interaction in the proposed axion detection scheme. Finally, section IV is devoted to our conclusive remarks.

![Fig. 1: The proposed scheme for the axion detection.](image)
II. DILUTE RUBIDIUM ATOMS IN A SOLID ARGON AND NEON MATRIX: EXPERIMENTAL RESULTS

In this section we report about the growth and spectral measurements of dilute Rubidium atoms in Argon and Neon solid matrices at cryogenic temperatures. Dependence of the spectra of solid Argon doped with Rubidium atoms from crystal-growth temperature and annealing history, has been reported in [3]. The core of the experimental apparatus is the cold finger of a pulse tube refrigerator that could reach a minimum temperature of 4 K allowing thus to grow and to maintain rare gas crystals. The cold finger is placed in the middle of a six-hole cross stainless-steel chamber (SSC) and at its center is mounted a 25 mm diameter sapphire window (SW) that holds the crystal and allows optical transmission measurements. The SW temperature is monitored through a silicon diode, and its precise control is ensured using a 15 W heater placed nearby the SW. A quartz and a BK7 windows are placed in the two ports of the SSC along the normal direction to the surface of the SW, while the port in the transverse axis is equipped with a mechanical manipulator where both a gas nozzle and an alkali metal dispenser are installed. The manipulator can be placed in front of the SW or 10 cm backwards depending if the growth or the measurements are ongoing. A sketch and a picture of the apparatus described above are shown in figure 2. Both vacuum and pressure of gas into the SSC are measured using pressure gauges in the range [10⁻⁹ – 10⁻⁵] mbar.

Crystallization occurs through spraying the purified rare gas mixed with alkali atoms onto the cold surface of the SW. Prior to be sprayed, the gas passed within a purification system that allows an impurity contamination below the ppb level especially for high-electronegativity elements. This system is described with more specific details in a previous paper [22]. The Rubidium dispenser is connected through two vacuum-feedthroughs to a power supply that delivers up to 6 A necessary to sublimate the metal. The parameters that have been used to control crystal formation are the partial pressure of the gas and of the dopant during the growing (P<sub>gas</sub>, P<sub>disp</sub>), the SW temperature (T<sub>g</sub>) and the time of growing (t<sub>g</sub>). Initially, we grew a ~ 100 µm slab of pure rare-gas with a flow rate maintained at about 1 mbar·l/s that leads in P<sub>gas</sub> ~ 5 · 10⁻⁵ mbar. Only after ~ 30 min the doping dispenser has been activated with a current set to ~ 3.5 A which gives P<sub>disp</sub> ~ 5 · 10⁻⁷ mbar. In such a way, Rubidium atoms have been embedded into Argon and Neon matrices respectively with a ratio between the two species of about 1%. Finally, also in the last ~ 100 µm we deposited only RG, indeed during this step the dispenser current has been set to zero. Given the total time of growth t<sub>g</sub> ~ 4 h, the thickness of the Rb-Ar and Rb-Ne films are about 1 mm.

During the growth, T<sub>g</sub> has been set to ~ 60 K and ~ 10 K for Argon and Neon respectively, while after crystals formation, an annealing process of ~ 1 h at a temperature T<sub>g</sub>+10 K has been performed. Finally, for the measurements, the temperature was lowered to about 5 K for all the crystals. Three different samples has been grown to check the reproducibility of any matrix.

The optical part of the experimental set-up is mainly composed by a Titanium-sapphire (Ti:Sa) CW laser tunable in the near-infrared (NIR) region, whose output power varies between 150 mW and 800 mW depending on the wavelength. This laser system has been used to cover the broadest range for crystal excitation. Appropriate quartz lenses have been adopted to couple the light coming from the laser source to the crystal and a small fraction (≤ 1%) of the beam has been focused into a silicon photodiode that acts as a laser system monitor. No control of the polarization of the source has been done. An optical fiber connects the output BK7 window to the the light-detection system that can be made of a NIR spectrometer or of a Silicon (Si) photodiode coupled with long-pass filters. Through these kind of sensors we can measure the fluorescence spectra in different visible and NIR regions. To minimize the background noise, the measurements have been carried out in a dark environment. We report here only the measurements relevant for the analysis of the width of the emitted spectrum, and for the comparison with the theoretical calculations that will be presented in the following section.

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1 Sumitomo RP062B
2 Lakeshore DT670
3 Pfeiffer PKR251
4 SAES Getter
5 Ocean Optics NirQuest
Figure 3 shows the fluorescence spectrum in the NIR region of the Rb-Ar crystal excited at $\lambda_{\text{excitation}} = 770$ nm. At this excitation wavelength, the emission spectrum is optimized in amplitude; furthermore this $\lambda$ is very close to the D$_2$ line of the rubidium [23]. The blue line represents the acquired data while purple curves are the Lorentzian fits of the peaks, given by:

$$L(\lambda) = y_0 + \frac{2A\Delta\lambda/\pi}{4(\lambda - \lambda_c)^2 + (\Delta\lambda)^2},$$

(1)

where $\lambda_c$, $A$, $\Delta\lambda$ are respectively the central wavelength, the width and the area of the Lorentzian, and $y_0$ is an offset. The results of the fits are listed in the table I.

![Fluorescence spectrum of the Rb-Ar crystal excited with 770 nm photons.](image)

**FIG. 3:** Fluorescence spectrum of the Rb-Ar crystal excited with 770 nm photons. The blue line represents experimental data, while purple curves are the Lorentzian fits.

| peak | $A$ (a.u.) | $\lambda_c$ (nm) | $\Delta\lambda$ (nm) |
|------|------------|-----------------|---------------------|
| 1    | $(70\pm3)\cdot10^4$ | 927.4±0.3       | 71±10               |
| 2    | $(56\pm5)\cdot10^5$  | 1034.9±0.3      | 92±4                |
| 3    | $(151\pm3)\cdot10^5$ | 1154.8±0.2      | 39±10               |
| 4    | $(79\pm4)\cdot10^2$  | 1624.7±0.4      | 37±2                |

If we consider the three main peaks of the emission spectrum (peak 1, 2 and 3 of Table I), their relative energy widths $\Delta E/E = |\Delta\lambda/\lambda_c|$ are:

$$\frac{(\Delta E/E)}_1 \sim 7\%, \frac{(\Delta E/E)}_2 \sim 9\% \quad \frac{(\Delta E/E)}_3 \sim 4\%$$

(2)

We can identify these peaks as energy-shifted transitions from the ground state of the Rubidium atoms to the first excited-states group [24], with energy levels corrected by the matrix interaction (the unperturbed transition wavelengths from ground to the first upper excited states are in the range $\lambda \sim [770 - 795]$ nm, according to the specific fine and hyperfine transition).

This is very reasonable, because the transitions of the Argon atoms in the solid matrix are at a quite higher energy.

We can meaningfully identify the large broadening of these peaks of the spectrum as the effect of an inhomogeneous broadening of the energy levels, for both the ground and the first electronically-excited levels, consequent (in part, at least) to the interaction of the alkali atoms with the Argon atoms of the solid matrix.

Figure 4 shows the measured fluorescence emission integrated for $\lambda_{\text{emission}} > 850$ nm as a function of the excitation wavelength. Also in this case the experimental data have been fitted with Lorentzian curves and the corresponding parameters are listed in the table II. In this case the relative widths of the three peaks are relatively smaller with respect of the previous case ($\sim 3\%$ for the two peaks at lower wavelength, and $\sim 2\%$ for the third peak), allowing the same physical considerations given above.

![Spectrum of Rb-Ar obtained integrating the fluorescence for $\lambda_{\text{emission}} > 850$ nm.](image)

**FIG. 4:** Spectrum of Rb-Ar obtained integrating the fluorescence for $\lambda_{\text{emission}} > 850$ nm, and changing the excitation of the laser pump in the NIR range. Blue dots are experimental data, while the gray line is the three Lorentzian fits obtained.

| peak | $A$ (a.u.) | $\lambda_c$ (nm) | $\Delta\lambda$ (nm) |
|------|------------|-----------------|---------------------|
| 1    | 10028±60   | 748.01±0.01     | 21.34±0.08          |
| 2    | 14288±70   | 772.63±0.02     | 28.05±0.09          |
| 3    | 86233±50   | 798.02±0.008    | 15.28±0.06          |

We also report some measurements of the spectra of Rubidium atoms embedded into the Neon matrix. Figure 5 shows the spectrum of the Rb-Ne crystal, observing the emitted light at $\lambda_{\text{emission}} = 1270$ nm as a function of the excitation wavelength from 755 nm to 775 nm. The relative width of the line, which is about 1 % (smaller
than in the Argon case), should imply that the interaction energy of the Rubidium atoms with Ne matrix is smaller, or that the inhomogeneity of the atoms distribution in this crystal is smaller than in Argon. Possible theoretical interpretations of these results in terms of host-matrix interaction energies will be discussed in the next section.

III. DILUTE ALKALI ATOMS IN A SOLID INERT-GAS MATRIX: THEORETICAL RESULTS

A. The theoretical model

We now consider the effect of a solid matrix of inert atoms or molecules at cryogenic temperatures on embedded dilute alkali atoms. In this section we estimate the potential energy of a host alkali atom in the solid matrix, starting from tabulated values of the relevant parameters, obtained experimentally or theoretically calculated. We base our analysis on two models for the potential energy between the alkali atom and one atom or molecule of the matrix. Argon, Neon or parahydrogen for example, specifically the Buckingham-Hill potential [25–27], and the Morse potential [25,28]. Evaluating these potentials through simple analytical expressions is essential as a first step for estimating the inhomogeneous linewidth of the energy levels of the dilute host atoms in the matrix. In fact, the actual potential energy depends on the position of the atoms in the solid crystal, which can be (slightly) different from atom to atom, yielding different contribution to the resulting inhomogeneous width of the spectral lines.

In the case of our interest, the Buckingham-Hill and the Morse potentials can give a reliable prediction only in different distance ranges: large distances for the Buckingham-Hill potential, and short distances for the Morse potential. As we will now discuss in detail, both of them are in general necessary in order to evaluate the potential felt by the alkali atom in the solid matrix using known and tabulated values of the relevant parameters for the potential. Thus, it can be helpful to use an appropriate combination of both models in order to obtain an approximated analytical expression of the actual potential, assuming that the alkali atom substitutes one of the atoms or molecules of the solid matrix. This potential, together with our experimental spectroscopical data of section II, will be then exploited in subsection IIIB to discuss the consequent inhomogeneous broadening of the alkali-atom spectral lines.

We first consider the case of the doped crystal experimentally analyzed in the previous section, that is dilute Rubidium atoms in an Argon or Neon solid matrix, comparing the theoretical results with our experimental data reported in section II. Secondly, we will consider the case of dilute Lithium atoms in a parahydrogen (p-H$_2$) solid matrix, obtaining insights that this alkali-matrix system yields quite smaller interaction energies, and thus sharper spectral linewidths are expected. We finally suggest that this could be an excellent host-matrix combination for the proposed axion detection scheme.

Both the inert-gas atoms of the cold matrix and the alkali atoms have a spherical electronic structure, without permanent dipole moments, and thus the only potential outside the region of wavefunction overlap is the van der Waals potential, scaling with the distance as $r^{-6}$ (dipolar two-body dispersion interaction energy) [29–31]. We can thus write the total two-body potential between a ground-state alkali atom (spherically symmetric) and one atoms of the solid matrix in the following form (the same is valid in the case of of Li-(p-H$_2$) we will consider successively)

$$V(r) = V_{vdw}(r) + V_{rep}(r),$$  \hspace{1cm} (3)

where $V_{vdw}(r)$ is the attractive two-body van der Waals potential, and $V_{rep}(r)$ is a repulsive exchange or Coulomb potential, acting at short distances when a significant wavefunction’s overlap occurs. Taking the usual $r^{-6}$ dipolar attractive van der Waals potential energy, and a simple exponential for the repulsive short-distance component, we have the Buckingham-Hill potential [25–27]

$$V_{BH}(r) = -\frac{C_6}{r^6} + Ae^{-r/R_{rep}},$$  \hspace{1cm} (4)

where the three parameters $C_6, A, R_{rep}$, i.e. van der Waals constant, strength and distance scale of the repulsive potential, respectively, appear.

We assume that the total potential felt by the alkali atom inside the solid matrix is just the sum of the two-body potentials due to the first neighbors molecules of the matrix, thus neglecting many-body effects. We also

![FIG. 5: Blue dots are the spectrum of the Rb-Ne crystal, observing the light output at $\lambda_{emission}=1270\text{nm}$ as a function of the excitation wavelength. The orange curve is the Lorentzian $L(\lambda)$ fit of the data.](image)
neglect higher multipolar dispersion (long-range) interactions \[30\], scaling with the distance as \(r^{-8}\) and higher inverse powers of the distance \[32, 33\]. These approximations are justified by the relatively large reticular distance, \(a_{Ar} = 5.26\ \text{Å}\) for Ar and \(a_{Ne} = 4.43\ \text{Å}\) for Ne \[21, 34, 36\].

For our purposes, it is important to relate the constants in the Buckingham-Hill potential \[4\] to tabulated experimentally measured or theoretically computed quantities, such as the equilibrium distance and the dimer dissociation energy (that is the potential energy at the equilibrium position). The van der Waals constant \(C_6\) is tabulated for many atoms and molecules in their ground or excited states \[33, 37\].

In order to evaluate the constant \(A\) in \[4\] in terms of known parameters, we can impose that \(\partial V_{BH}(r)/\partial r = 0\) for \(r = R_{eq}\), \(R_{eq}\) being the equilibrium distance of the alkali-inert-atom dimer. We immediately find

\[
A = \frac{6C_6R_{rep}}{R_{eq}^7}e^{R_{eq}/R_{rep}}, \quad (5)
\]

yielding

\[
V_{BH}(r) = \frac{6C_6R_{rep}}{R_{eq}^7}e^{(R_{eq}-r)/R_{rep}} - \frac{C_6}{r^6}. \quad (6)
\]

By taking into account that the quantities experimentally measured are the van der Waals constant \(C_6\), the equilibrium distance \(R_{eq}\), and the dissociation energy \(V(R_{eq})\) (that is the potential energy at the equilibrium distance), from \[6\] we can obtain the following expression for \(R_{rep}\)

\[
R_{rep} = \frac{R_{eq}^7}{6C_6} \left( V_{BH}(R_{eq}) + \frac{C_6}{R_{eq}} \right). \quad (7)
\]

The complete expression of the potential is then

\[
V_{BH}(r) = -\frac{C_6}{r^6} + \left( V_{BH}(R_{eq}) + \frac{C_6}{R_{eq}} \right) \times \exp \left[ \frac{6C_6}{R_{eq}^7}(V_{BH}(R_{eq}) + \frac{C_6}{R_{eq}})(R_{eq} - r) \right]. \quad (8)
\]

Thus, using Eq. \[8\], the Buckingham-Hill potential is entirely expressed in terms of hopefully known and tabulated parameters (for example, the various parameters for several alkali and RG atoms can be found in \[33, 37, 38\]).

The Buckingham-Hill potential is a good approximation for distances around \(R_{eq}\), yielding a good approximation to the equilibrium distance, and for larger distances, where it correctly reduces to the van der Waals potential, but not for shorter distances: in fact, for distances smaller than \(R_{eq}\) the Buckingham-Hill potential decreases to negative values, while it should grow and give the short-distance repulsion. In other words, the equilibrium position of the potential \[3\] is an unstable point.

We thus need an appropriate approximation to the potential energy valid for distances smaller than the equilibrium distance. As it will be evident in the next subsection, the short-distance case is the one we are mainly interested in. We can then use the Morse potential, given by \[25, 28\]

\[
V_M(r) = D \left( 1 - e^{-\alpha(r-R_{eq})} \right)^2 - D, \quad (9)
\]

\(D = |V_M(R_{eq})|\) being the dissociation energy of the dimer, that is the energy at the equilibrium distance \(R_{eq}\), \(\alpha = \sqrt{\kappa/(2D)}\), with \(\kappa = \partial^2 V(r)/\partial r^2|_{r=R_{eq}}\) the curvature of the potential at the equilibrium distance; \(\kappa\) is a second parameter characterizing the interatomic potential energy.

Although the Morse potential \[9\] is a good approximation to the short-range exchange/Coulomb potential, it fails at large distances. Both the Buckingham-Hill and the Morse potential are expected to give a reasonably good approximation around the equilibrium distance.

The Morse potential \[9\] contains three free parameters, but its mathematical expression does not allow to obtain a relation between them exploiting the fact that its derivative must vanish at the equilibrium distance \(R_{eq}\). For this reason, in order to obtain the constant \(\kappa\) defined above, not always available in the literature, we can resort to tabulated data when available, or use the Buckingham-Hill potential to evaluate it. In the second case, this can be done by calculating the modulus of its second derivative at the equilibrium position, and then the parameter \(\alpha\) appearing in the Morse potential \[9\]. In this case, we are however assuming that, around the equilibrium distance, the modulus of the curvature of both potentials are similar; this is indeed a tricky point, because the Morse potential has a minimum at the equilibrium distance, while the Buckingham-Hill potential has a maximum. Thus, from \[8\] we get

\[
\kappa = \left. \frac{\partial^2 V_{BH}(r)}{\partial r^2} \right|_{r=R_{eq}} = \frac{6C_6}{R_{eq}^8} \left( \frac{R_{eq}}{C_6} V_{BH}(R_{eq}) + 1 \right). \quad (10)
\]

Because in our case the distance between the alkali atom and any inert-gas atom molecule of the solid matrix is smaller than the equilibrium distance (3.72 Å, to be compared to 5.49 AS, for the Rb-Ar dimer, for example), we expect that the Morse potential gives a better approximation to the true potential than the Buckingham-Hill potential. How good is this procedure for obtaining the parameter \(\kappa\) could be checked in specific cases where \(\kappa\) is known, experimentally or theoretically, from independent considerations, as we will explicitly discuss later on in the case of Rubidium in a solid Argon or Neon matrix.

An appropriate use of the Buckingham-Hill and Morse potentials can thus allow us to obtain an estimate of the
potential energy between the alkali atom and a single atom or molecule of the solid matrix at all distances, in terms of known and tabulated parameters.

B. Numerical estimates of the host-matrix interaction energies

We can now use the potentials of subsection III.A to obtain approximated estimates of the value of the interaction energy between an alkali atom (Lithium, Sodium, Potassium, Rubidium) and an atom or molecule of the solid matrix (in this section we will consider Rubidium in Argon and Neon, and then Lithium in parahydrogen), assuming that the alkali atom replaces one atom or molecule of the solid crystal. From that, the interaction energy between a host alkali atom and the solid RG or parahydrogen matrix can be easily obtained, assuming only pairwise interactions between the nearest neighbours. As mentioned before, this should be a fairly good approximation due to the large reticular distance of the solid matrix.

Possible trapping sites of alkali atoms in RG crystals, and their stability, have been recently studied in the literature [39, 41]. We first consider the Rb-Ar case and then the Rb-Ne case, comparing our theoretical estimates with the measured spectra reported in the previous section. At the end, we will also analyze the Li-(p-H2) case. Throughout this subsection, the units used are eV for the energy and Å for the distance.

Solid Argon and solid Neon have both a face-centered cubic (fcc) crystal structure; the reticular distance is equal to $a_{\text{Ar}} = 5.26$ Å for Ar and to $a_{\text{Ne}} = 4.43$ Å for Ne [21, 34–36]. The host alkali atom considered is the Rubidium (Rb) atom. We assume that the Rubidium atom substitutes one of the atoms of the matrix. Assuming only pairwise interactions between the nearest neighbours, this should be a fairly good approximation due to the large reticular distance of the solid matrix.

In order to evaluate the potential energy, we need the numerical values of the equilibrium distance $R_{\text{eq}}$, the dissociation energy $D = |V(R_{\text{eq}})|$, and the curvature $\kappa$ of the potential energy at the equilibrium distance. The van der Waals coefficient $C_6$ is also important for a check. Theoretical estimates of the equilibrium distance $R_{\text{eq}}$ and the dissociation energy $D$ can be found in several works [32–34, 41]. The curvature of the potential energy at the equilibrium distance can be found in [42–44]. The $C_6$ coefficients for several alkali atoms and RG atoms, both in the ground state and in excited levels, can be found in [33, 37, 38, 39]. Although there is a good agreement in the literature on the values of $R_{\text{eq}}$ and $C_6$, the tabulated values of $D$ and $\kappa$ can significantly differ in different papers, and even in the same paper when different methods of calculation are used, in particular for Rb-Ne, while for Rb-Ar they are more uniform. For this reason we will consider mainly the case of Rb-Ar. We have chosen to use the data reported in [43], where the three necessary parameters $R_{\text{eq}}$, $D$, $\kappa$ are calculated. We will also compare these data with those reported in [44]. However, the small variability of the tabulated data for Rb-Ar is not much relevant for our purposes, because we only need an order-of-magnitude estimate of the interaction energy, and not its exact value.

\( \left(i\right) \) Rb-Ar (ground and excited)

We first consider the ground-state configuration $X^2\Sigma^+_{1/2}$ of the Rb-Ar dimer; it corresponds to the electronic configuration of both the Rubidium and Argon atoms in the ground state. The relevant data are [43]

$$
R_{\text{eq}}^{\text{Rb-Ar}} = 5.498 \text{ Å},
D^{\text{Rb-Ar}} = 4.45 \cdot 10^{-3} \text{ eV},
\kappa^{\text{Rb-Ar}} = 5.96 \cdot 10^{-3} \text{ eVÅ}^{-2}.
$$

For the same configuration, the data in [44] for the equilibrium distance and the dissociation energy (the curvature of the potential is not explicitly given) are not very dissimilar: $R_{\text{eq}}^{\text{Rb-Ar}} = 5.482$ Å, $D^{\text{Rb-Ar}} = 6.07 \cdot 10^{-3}$ eV.

As mentioned above, we need to evaluate the potential energy at the distance $a_{\text{Rb-Ar}} = a_{\text{Ar}}/\sqrt{2} = 3.72$ Å, because we are assuming that the Rubidium atom replaces an Argon atom of the matrix. Since $a_{\text{Rb-Ar}} < R_{\text{eq}}^{\text{Rb-Ar}}$, we use the Morse potential [9]. The $\alpha = \sqrt{\kappa/(2D)}$ parameter in Eq. [9] in the present case is therefore $0.818 \text{ Å}^{-1}$. Using all these data in [9], we immediately find

$$V_M^{\text{Rb-Ar}}(r = a_{\text{Rb-Ar}}/\sqrt{2}) \approx 4.35 \cdot 10^{-2} \text{ eV}. \quad (12)$$

In this case we have been able to estimate the potential energy using the Morse potential only, because the potential curvature $\kappa$ is known. In subsection III.A we proposed that $\kappa$ could be obtained using the Buckingham-Hill potential through Eq. [10]. The van der Waals constant $C_6$ can be found in [32–34, 41], for example, as $C_6^{\text{Rb-Ar}} = 201 \text{ eVÅ}^6$. From Eq. [10] we thus obtain $\kappa_M = \kappa^{\text{Rb-Ar}} = 4.73 \cdot 10^{-3} \text{ eVÅ}^{-2}$, that is relatively close to the tabulated value shown in [11]. This is an important consistency check for the analytical method presented in this section.

Summing the potential [12] over the 12 nearest-neighbors of the Rubidium atom (pairwise summation), we get

$$V_{\text{tot}}^{\text{Rb-Ar}} \approx 0.52 \text{ eV}. \quad (13)$$

Using the very recent data for the equilibrium distance and the dissociation energy in [47], $R_{\text{eq}}^{\text{Rb-Ar}} = 5.541$ Å, $D^{\text{Rb-Ar}} = 4.716 \cdot 10^{-3} \text{ eV}$, and the data for the curvature of the potential at the equilibrium distance communicated to us by the authors of that paper [35], $\kappa^{\text{Rb-Ar}} = 5.617 \cdot 10^{-3} \text{ eVÅ}^{-2}$, we get

$$V_M^{\text{Rb-Ar}}(r = a_{\text{Rb-Ar}}/\sqrt{2}) =$$
3.72 Å $\simeq$ 3.99 - 10^{-2} eV, that is very close to (12). Interpolation of recent numerical data for the potential energy (38) (see also (17), yields a somehow lower value, $\simeq$ 3.1 - 10^{-2} eV, not far from our analytical estimate. We can thus say that, even using numerical data from different sources, we obtain essentially the same value of $V_M^{Rb-Ar}$.

We can use the same procedure to estimate the potential energy of an excited state of the Rubidium atom in the solid Argon matrix. Specifically, we consider the first excited state in the Rb-Ar molecular configuration $A^2P_{1/2}$ (corresponding to a $^2P_{1/2}$ configuration of Rubidium, and the Argon in its ground state). We use the following tabulated data: $R^{Rb-Ar}_{eq(exc)}$ = 3.60 Å, $D^{Rb-Ar}_{(exc)}$ = 3.162 · 10^{-3} eV (43); $C^{Rb-Ar}_{6(exc)}$ = 325.7 eVÅ^{6} (33). Because in this case the distance at which we should evaluate the potential, $r = a^{Rb-Ar}/\sqrt{2}$ = 3.72 Å, is very close (slightly larger, to be precise) to the equilibrium distance $R^{Rb-Ar}_{eq(exc)}$, we can use the Buckingham-Hill potential (3), and we obtain

$$V^{Rb-Ar}_{BH(exc)} \simeq -3.07 \cdot 10^{-2} \text{ eV}. \quad (14)$$

As mentioned, the interatomic distance now considered is close to the equilibrium distance, and we thus expect that the Morse potential should yield the same result too. An explicit evaluation by using Eq. (9), with the potential curvature obtained from (10), gives indeed practically the same result.

After pairwise sum over the 12 nearest neighbors Argon atoms, we have

$$V^{Rb-Ar}_{tot(exc)} \simeq -0.37 \text{ eV}. \quad (15)$$

These host-matrix potential energies can yield two effects in the spectrum of the Rubidium atoms in the solid matrix: an energy shift (in fact, from Eqs. (13) and (15), it follows that the transition frequency is reduced, because the lower level is shifted upwards and the upper level downwards), and an inhomogeneous line broadening. In this paper we are mainly concerned with this second effect, that is the line broadening. The transition wavelength from the $5^2P_{1/2}$ to the $5^2P_{1/2}$ level of the isolated Rubidium atom is 795 nm, corresponding to an energy of $\sim 1.56$ eV.

We now assume that the inhomogeneous broadening of the lines due to the interactions between the dilute alkali atoms and the RG solid matrix is some small fraction of the energy given in (13) and (15). Which value has this fraction is very difficult to evaluate from a theoretical point of view only, because it depends on specific details of the position distribution of the alkali atoms inside the solid matrix, for example the inhomogeneity of their position, imperfections of the crystal structures, etc. Thus, it can significantly depend on how the solid matrix is growth, and, importantly, how the dilute alkali atoms are embedded inside the matrix.

We are assuming that the main effect is due to a (slight) inhomogeneous distribution of the position of the host alkali atoms in the RG solid matrix. Comparing our experimental results for the spectral linewidth, reported in section III with our present theoretical prediction of the host-matrix interaction energy, we now show that we can predict a semi-quantitative estimate of the atoms’ position distribution in the matrix.

Quantitatively, a spreading of the alkali positions inside the crystal determines an inhomogeneous contribution to the linewidth of the spectrum, which strongly depends on how steep the potential energy is at their average position, of course. Assuming, as before, that the alkali atoms replace one of the atoms of the matrix, being $r^{Rb-Ar} < R_{eq}$, we can expand the Morse potential (9) around $r^{Rb-Ar}$ (taking into account the measured relative energy widths given in (2), we expect a relatively sharp distribution of the positions). We indicate with $\Delta r$ a small displacement from the average distance $r_0$, which is equal to $r^{Rb-Ar}$ in the present Rb-Ar case, we can obtain the consequent change of the potential energy as

$$\Delta V_M(\Delta r) = V_M(r_0 + \Delta r) - V_M(r_0) \approx 2\alpha D e^{\alpha(R_{eq} - 2r_0)} \left( e^{\alpha r_0} - e^{\alpha R_{eq}} \right) \Delta r \quad (16)$$

and thus the relative absolute value of the change of the potential energy is

$$\left| \frac{\Delta V_M(\Delta r)}{V_M(r_0)} \right| \approx \frac{2\alpha}{e^{\alpha R_{eq}} - 2e^{\alpha r_0}} \Delta r. \quad (17)$$

This relation allows us to estimate the position dispersion $\Delta r$ of the alkali atoms in the solid matrix, once the relative dispersion of the potential energy is known. The latter can be obtained from the spectral experimental results of the previous section, specifically from the relative energy widths (2). In the case of Rb-Ar here considered, for the peak 3 of table I (see also Fig. 3) with an energy width of 4%, and using the numerical data in (11), Eq. (17) yields the Argon-atoms position dispersion

$$\left| \Delta r \right| \approx 1.7 \cdot 10^{-2} \text{Å}. \quad (18)$$

that means a relative dispersion of $\sim 0.5\%$.

Our experimental measurements, combined with our theoretical model, has thus allowed us to obtain relevant hints on how the host atoms in our Rb-Ar experimental setup diffuse in the cold matrix, and relate the measured spectral widths to the alkali-matrix interactions. This method can be also applied to the case of other host-atoms-matrix, for example Rubidium atoms in a cold Neon matrix.

ii) Rb-Ne (ground state)

We now consider the Rb-Ne case, whose spectral measurements have been reported at the end of section III. The relevant numerical values for equilibrium distance, dissociation energy and van der Waals constant can be
potential energy. The parameters can yield a consistent variation of the estimated energy. This can yield different estimates of the interaction energy in the solid matrix, according to the numerical data used.

Solid Neon has a fcc crystal structure as solid Argon, with a reticular distance $a_{Ne} = 4.43\,\text{Å}$. We first use the very recent data of the equilibrium distance and dissociation energy for the Rb-Ne dimer reported in [47], $R_{eq}^{Rb-Ne} = 6.188\,\text{Å}$ and $D^{Rb-Ne} = 7.28 \cdot 10^{-4}\,\text{eV}$ respectively, supplemented with the value of the potential curvature at the potential minimum [18], $\kappa^{Rb-Ne} = 1.107 \cdot 10^{-3}\,\text{eVÅ}^{-2}$. In this case we obtain

$$V_M^{Rb-Ne}(r = 3.13\,\text{Å}) \simeq 0.13\,\text{eV},$$

which is larger than in the previous Rb-Ar case. A similar result is obtained using the data in [12], $R_{eq}^{Rb-Ne} = 6.212\,\text{Å}$, $D^{Rb-Ne} = 6.07 \cdot 10^{-4}\,\text{eV}$, $\kappa = 1.061 \cdot 10^{-3}\,\text{eVÅ}^{-2}$, where the value of the curvature $\kappa$ of the potential at the equilibrium position has been inferred from their data of the harmonic wavenumbers, obtaining in this case $V_M^{Rb-Ne}(r = 3.13\,\text{Å}) \simeq 0.17\,\text{eV}$. These interaction energies are lower compared to the case of Argon. This is also confirmed by other recent numerical data [18] (see also [47]), yielding $V(r = 3.13\,\text{Å}) = 0.061\,\text{eV}$: this value is quite lower than our theoretical estimate based on the Morse potential, showing again a larger variability of the energies in the Rb-Ne case according to the analytical or numerical method used.

These values for the theoretical prediction of the interaction energy for the Rb-Ne are quite larger than those for the Rb-Ar dimer, as a comparison with [12] immediately shows, while our spectra of section II show sharper linewidths in the Rb-Ne case. A possible interpretation of this fact is that the position distribution of the host atoms in the solid matrix is smaller for Neon compared with Argon. Indeed, the two solid matrices have different physical properties, related to the interactions between the matrix atoms, for example the condensation temperature, $T_{cond} = 82\,\text{K}$ for Ar and $T_{cond} = 20\,\text{K}$ for Ne, and the reticular distance: thus, nontrivial differences in the way the host atoms arrange themselves in the matrix are not unexpected. We plan to discuss this point in a future work. In any case, we believe that the case of Neon deserves a more precise analysis from the theoretical side, also because the alkali-RG atoms distance in the Neon matrix is smaller than in the Argon matrix, in particular when considered relative to the corresponding equilibrium distance ($R_{eq}^{Rb-Ar} = 5.498\,\text{Å}$, $r = 3.72\,\text{Å}$ for Rb-Ar; $R_{eq}^{Rb-Ne} = 6.19\,\text{Å}$, $r = 3.13\,\text{Å}$ for Rb-Ne). At shorter distances, the potential energy is very steep, as, consistently, the plots of the potential energies in [47] clearly show. All this makes the details of the model more critical: even a small variation of the relevant parameters can yield a consistent variation of the estimated potential energy.

A reliable estimate of the Rubidium position distribution in the solid Neon matrix from the experimental spectra reported in the previous section, as we did for the Argon case, therefore still requires a more precise theoretical analysis of the potential energy at the small Rb-Ne distances relevant for our system.

iii) Li-(p-H$_2$) (ground state)

Finally, we consider theoretically the Li-(p-H$_2$) case, that is dilute Lithium atoms diffused in a solid parahydrogen matrix. We will obtain a strong indication that this system shows a quite smaller host-matrix interaction energy.

The p-H$_2$ molecule has nuclear spin $I = 0$ and, at low temperatures, an even total angular momentum $J$, with a spherical symmetry yielding vanishing permanent multipolar momenta [50]. Due to the spherical symmetry of the parahydrogen molecule, the same considerations on the potentials discussed above can be applied. Solid parahydrogen has a Hcp (Hexagonal closed packed) structure, with a quite large intermolecular distance compared to the relevant atomic or molecular dimensions. We assume that the alkali atom is placed at the hexagon center, substituting one of the H$_2$ molecules, as shown in Fig. 6 due to the large intermolecular distance of the molecules in the p-H$_2$ matrix, its presence does not change significantly the structure of the crystal. Also, the known large compressibility of parahydrogen solids allows to easily accommodate the alkali atom impurity [51]. The reticular distance for the parahydrogen crystal is $a \simeq 3.78\,\text{Å}$ [32, 33].

![FIG. 6: The alkali atom at the center of the hexagonal structure of the solid p-H$_2$ matrix. The alkali atom (orange circle) is assumed to substitute one of the molecules of the solid matrix of p-H$_2$ molecules (blue circles).](image)

The relevant tabulated data for the dissociation energy $D$ and the equilibrium distance $R_{eq}$ can be found in [38], while the van der Waals constant $C_6$ can be found in [37]: the tabulated values are $D = 3.90 \cdot 10^{-3}\,\text{eV}$, $R_{eq} = 4.76\,\text{Å}$, $C_6 = 49.4\,\text{eVÅ}^6$. From (1) we then get $R_{REP} \simeq 1.52\,\text{Å}$. Since the radius of the Lithium atom, $\simeq 1.45\,\text{Å}$, is quite smaller than the alkali-parahydrogen distance in the solid matrix, $a^{Li-(p(H_2))} = 3.78\,\text{Å}$, our
pairwise-summation of the potentials between nearest-neighbors pairs, as well as neglecting higher multipolar dispersion interactions, should be reasonably good approximations. Because in our case the distance between the alkali atom and any parahydrogen molecule of the solid matrix is smaller than the equilibrium distance, 4.76 Å, we expect that the Morse potential should give a better approximation to the true potential than the Buckingham-Hill potential.

With the numerical values above, taking the second derivative of the Buckingham-Hill potential \( V_{B} \) (Eq. [10]), and evaluating it for the distance \( r = 3.78 \) Å between the alkali atom and any of the nearest neighbors parahydrogen molecules (see Fig. 1), we obtain \( \kappa \approx 4.34 \cdot 10^{-3} \) eVÅ\(^{-2} \), and then \( \alpha = \sqrt{\kappa/(2D)} \approx 0.747 \) Å\(^{-1} \), to be used in the Morse potential \( V_{M} \).

We thus obtain
\[
V_{M}^{Li-\text{H}_{2}}(r = 3.78 \text{ Å}) \approx 0.644 \cdot 10^{-3} \text{ eV}.
\] (20)

Taking into account that each Lithium atom has 6 nearest neighbors parahydrogen molecules of the solid matrix, and assuming a pairwise summation, we obtain the total interaction energy of each Lithium atom in the parahydrogen solid matrix
\[
V_{tot}^{Li-\text{H}_{2}} \approx 3.8 \cdot 10^{-3} \text{ eV}.
\] (21)

Comparing (20) with (12) and (19), we see that the interaction energy in the present case is much smaller than in the Rb-Ar and Rb-Ne cases. On the basis of our previous considerations, this should give a quite smaller energy width of the spectral lines, assuming a similar dispersion of the position of the alkali atoms in the cold solid matrix. Some experimental spectroscopic data on the Li-(p-H\(_2\)) system can be found in [54], while theoretical aspects relevant for the absorption spectra are given in [55]. Finally, taking into account the theoretical results for Li-(p-H\(_2\)) of this section, we can also conclude that the Lithium-parahydrogen system is expected to give quite smaller spectral linewidths, and that, at least in principle, it could be a very promising physical system for the proposed axion detecting scheme.

IV. CONCLUSION

We have considered the spectroscopy of a solid crystal of inert elements, specifically Argon, Neon, and parahydrogen, at cryogenic temperatures, doped with dilute alkali atoms. We have reported experimental spectra of dilute Rubidium atoms in a solid matrix of Argon and Neon, and analyzed the observed line widths. Then, using a simple theoretical model and known tabulated data, we have estimated the interaction energy of a single Rubidium atom with the solid Argon or Neon matrix, and, after comparison with the measured widths of the spectral lines, estimated the inhomogenous spreading of the host-atoms position inside the solid matrix. We have finally theoretically analyzed the case of Lithium atoms in a solid parahydrogen matrix, finding that in such a case the interaction energy is quite smaller than in the Rb-Ar and Rb-Ne cases: this indicates that sharper spectral lines are expected. As discussed in the paper, this work is mainly aimed to a feasibility study of the recently proposed detection scheme for cosmological axions in the meV range (and also other searches for physics beyond the Standard Model), exploiting the Matrix Isolation Spectroscopy technique of magnetic-type transitions between Zeeman sublevels of alkali atoms in a cold solid matrix, induced by the axion absorption. For this proposed detection scheme, the linewidth of the alkali atoms should be reduced as much as possible. We have concluded that Lithium in a parahydrogen matrix systems could be an excellent candidate for the detection scheme analyzed in this paper.

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