Calculations of liquid helium and neon VUV emission spectra, self-absorption and scattering for a neutrino detector

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To evaluate the feasibility of the recently proposed detection scheme of low energy neutrinos released from the Sun and supernovae called CLEAN, Cryogenic Low Energy Astrophysics with Noble Gases, which relies on the transparency of noble-gas cryogenic liquids to VUV radiation produced by neutrinos, we analyze theoretically VUV emission, self-absorption, and scattering of liquid helium and neon, primary candidates for CLEAN. Owing to strong repulsion of noble-gas atoms in the ground states at the equilibrium distance of the relevant excited state, the emission spectrum is substantially shifted from the absorption spectrum, and in principle the absorption is expected very small, allowing building large detectors. Our analysis, however, shows that the self-absorption and Rayleigh scattering are comparable to the size of the proposed detector.

Our theoretical emission spectra are found in agreement with experimental observations although some deviation exists due to binary-interaction approximation, and our ab initio Rayleigh scattering lengths are found in agreement with other calculations based on the extrapolation of experimental refraction indices. The absorption process can result in either re-emission, which conserves the number of photons but delays their escape from the liquid, or in non-radiative quenching.

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Recently, McKinsey and Doyle [1] has proposed the detection of low energy neutrinos released from the Sun and supernovae with the scheme called CLEAN, Cryogenic Low Energy Astrophysics with Noble Gases. The central element of a CLEAN detector is a 6-meter diameter Dewar filled with liquid neon which is functioning both as a passive shielding medium and an active self-shielding detector. The advantage of liquid neon is high scintillation yield and low radiative background. Other noble-gas liquids can be used as well, of particular interest is liquid helium. The self-absorption and scattering of UV light produced by these liquids are critical for determination of the size of the detector, the interpretation of neutrino events, and exclusion of background events. The emission of liquid helium and neon in UV has already been studied [2, 3, 4] and scattering lengths of noble-gas liquids at scintillation wavelengths has been estimated from extrapolations of refraction indices [5]; the self-absorption is yet to be measured. Because there are many factors such as spectral reshaping and the effects of impurities (for example, 0.2% of N₂ impurities in liquid helium reduces the emission intensity by 20-40% in the region 700-850Å [2]) that influence the interpretation of the experimental results, the theoretical calculations of emission, self-absorption, and scattering, which constitute the subject of this letter, are important. Spectral properties of noble-gas liquids are not well understood mostly due to interdisciplinary nature (atomic, molecular, condensed-matter physics) of the phenomenon as well as the scarcity of the data, so this paper also has the aim of attracting the attention of theorists of diverse expertise and motivating further UV spectroscopic measurements.

The scintillation of liquid helium due to energetic α-particle stopped in the liquid was first studied by Moss and Hereford [6] and by Kane et al. [7]. Moss and Hereford [6] observed significant decrease of the intensity below λ-point, and attributed this to the change of the oscillator strength of 2P-1S He transition due to the differences in spatial distribution of nearest neighbors in the superfluid and the normal fluid. The emission spectrum of liquid helium was also studied experimentally by Stockton et al. [8] who obtained and compared UV spectra of electron-bombarded superfluid helium at 1.4 and 2.1 K with those of high-pressure helium discharge lamp in the range of 1000-600 Å. The spectra were very similar, but the liquid spectrum had an earlier cut-off at about 600 Å due to stronger absorption. Keto et al. [9] and Hill et al. [10] showed that the ionization of the helium results in formation of He²⁺(A²Σ⁺) and He²⁺(a²Σ⁺) dimers in the liquid which decaying produce UV scintillation. A number of publications [10, 11, 12, 13] addressed an unusual phenomenon in liquid helium such as the formation of cavities around free electrons and excited atoms and molecules. The dynamics of the formations of cavities is fast, 5 × 10⁻¹¹ s [10], so that excited molecules do not decay significantly during the time of cavity formation in which case the liquid effects on the spectral properties are greatly reduced.

The luminescent spectrum of liquid and solid neon was observed by Packard et al. [4] in the range 700-900 Å. It is interesting to note that the solid has a narrow peak at 743 Å, but the liquid does not; similar peaks in solid and liquid exist at 774 Å with widths about 30 Å. The luminescence of neon gas was also briefly investigated: at low pressure $P < 40$ Torr, a single narrow line was detected near 743 Å. At higher pressures, the intensity of the 743 Å line decreased but the second line at 800 Å appeared. At low temperature, 25 K, the 800 Å line does not persist.
Absorption and emission spectra of liquids can be obtained approximately from the spectra of molecules. For example, in Ref. [3] it was found that lines in the 600 Å band of He₂ appear in the liquid emission spectrum and can be well predicted from potential curves of the pair interaction using Franck-Condon principle. We would like to apply this principle to obtain theoretical UV emission in helium and neon liquids (molecules) near 16 eV. The main peak of helium scintillation according to Ref. [3] appears around 15.5 eV (800 Å), and neon liquid scintillation was observed at 16 eV [4]. For calculations of the wavelength of the maximum of emission it is enough to know the equilibrium interatomic distance (Rₑ) of the lowest singlet excited molecular state, the energy of this state, and the interatomic energy of two ground state atoms at the distance Rₑ. Detailed spectral distribution can be obtained from the overlap of wave functions of nuclear motion, according to the classical work by Condon [14]. Absorption transitions start from ground state atoms which are separated by a relatively large distance. Thus the small energy shift due to environment can be neglected and it is a reasonable approximation to consider only the strongest allowed atomic transitions which have transition energies close to the emission energy of about 16 eV.

The helium interatomic or molecular potentials are well-known [15, 16, 17, 18]. The potential curves of the lowest excited states of Ne₂ are given in Ref. [19]. The ground state of neon diatomic molecule is investigated in [20, 21, 22, 23]. Analytical expansions of the ground-state interatomic potentials of noble-gas atoms that reproduce well the available vibrational spectra are given in [24]. Most studies do not consider small interatomic distances in detail which are important for our application, so we supplement them with our own calculations described below.

Our ab initio ground-state interatomic potentials at small distances are calculated using Pauli’s principle. When two closed-shell atoms have wavefunctions overlapping, electrons are promoted to excited atomic states increasing the energy of each atom. In helium, the repulsion increases the energy by 22 eV times overlap and in neon 16 eV times overlap. Wavefunction overlaps are obtained using Dirac-Hartree-Fock potentials, 1s² in the case of helium and 1s²2s²2p⁶ in the case of neon. Overlaps of all electrons of one atom with those of the other are taken into account. In the range of interatomic energies of interest for self-absorption other effects such as electrostatic direct and exchange interactions are weaker because of screening. We have checked the magnitude of electrostatic effects in case of helium, and found that the dominant contribution comes from the Pauli principle.

In Fig. 1 we show the comparison of the ground-state helium interatomic potentials obtained from the overlap theory, the extrapolation using the expansion of Ref. [24], and ab initio calculations with exponentially correlated Gaussian (ECG) functions [18]. The expansion of [24] agrees well with calculations of [18] up to 10 eV indicating good precision of both methods. The overlap calculations agree with the expansion results over a larger range, with some deviation in the middle of the curve due to approximations of our theory. We can conclude that our method describes well the repulsive interaction in helium and the expansion method is suitable for calculations below 10 eV. In the case of neon (Fig. 2), we find close agreement between different methods: the overlap theory, the extrapolation from experiment [24], configuration-interaction (CI) method [22], and self-consistent field (SCF) calculations [23] below 8 eV. We also found agreement between our method and that of Ref. [24] in argon, although not as close as in neon. Therefore, the expansion of Ref. [24] gives the energies of ground state noble-gas dimers with sufficient precision for calculations of emission spectra and the analysis of self-absorption.

The emission spectra of helium and neon molecules...
are shown in Fig.3. The initial He excited state has equilibrium distance $R_e = 1$ Å, energy 18.2 eV and the harmonic-oscillator frequency $\omega_e = 1861$ cm$^{-1}$ [17]. Corresponding values for the Ne $3\pi^2\Sigma_u^+$ initial state are: 1.75 Å, 16.11 eV, and 540 cm$^{-1}$ [14, 22]. Neglecting anharmonic corrections, we can write the nuclear wavefunction of the lowest vibrational state as

$$\Psi(R) = \frac{\alpha}{\pi^{1/2}} \exp\left[-\frac{\alpha^2 (R - R_e)^2}{2}\right] \quad (1)$$

where $\alpha = (2\pi\mu\omega_e/\hbar)^{1/2}$, $\mu$ is the reduced mass, $c$ is the speed of light. Although excited vibrational states are always populated in the process of any non-radiative excitation, very fast collisions and quenching will transfer much of their population into lowest vibrational states. Since only direct transitions are the most probable, the absorption spectrum will have the weighting factor $|\Psi(R)|^2$. The helium theoretical molecular spectrum is in better agreement with the emission spectrum observed in condensed helium discharge [23] than with that observed in liquid [24]. High-pressure discharge emission has maximum located at 15.3 eV [23, 25], while theoretical prediction is 15 eV, and the maximum of the emission of liquid is located at 15.5 eV [22] and 15.8 eV [24]. The width at half maximum of discharge spectrum is 2 eV [25], the same as our prediction, while the liquid spectrum has the width about 3 eV [22, 24]. From this comparison, we can conclude that the liquid effects shift the energy by 0.5-0.8 eV and broaden the spectrum by 1 eV. A similar situation occurs in neon. High-pressure neon discharge gives the maximum of emission at 15.5 eV, while the liquid has the maximum at 16 eV [24]; the theoretical prediction is 15.2 eV. The theoretical width is about 1 eV, and the width of the liquid spectrum obtained with 1 eV resolution is about 2 eV. The liquid effects result in shift of at least 0.5 eV and broadening less than 1 eV. The shift is not easy to explain; we can suggest that the interactions of more than two atoms can be responsible and the distance between an excited atom and closest ground state atoms can be different than that in the diatomic molecule.

Apart from calculations of emission spectra, we also investigated various absorption mechanisms and calculated self-absorption coefficients. In liquids as well as in dense gases in the vicinity of an atomic or molecular resonance collisional broadening is very important, and the absorption due to collisionally broadened Lorentzian wings is expected to be very strong; however, the impact approximation from which the Lorentzian shape-factor can be derived is not valid for far-off-resonance transitions, which is the case in our system, and instead more appropriate is to use quasi-static approximation (see for example [26], pp. 241-245) in which the absorption profile is determined from probabilities $W(R)dR$ of nearest particles within the range of distances $(R, R+dR)$ from a given atom. Either the classical distribution or quantum-mechanical wavefunctions can be used to obtain these probabilities. In the classical case, the Boltzman distribution for low temperatures of the liquids gives very strong exponential suppression for the detuning of order 1 eV and the absorption can be neglected. On the other hand, the consideration of wavefunctions of nuclear motion (the tunnelling into classically-forbidden region) gives negligible increase in absorption because the tunnelling probability is small and the energy deficit will remain whether the tunnelling occurs in the ground state, excited state, or both. Finally, we conclude that the dominant absorption is likely due to wings of the radiatively-broadened profile.

For large detuning and radiative broadening, the absorption coefficient $\alpha_a$ is (see for example Ref. [27])

$$\alpha_a = \frac{Ne^2\omega_0}{cm\epsilon_0} \left(\frac{\gamma \omega_f}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}\right) \quad (2)$$

where $\gamma$ is the width of the resonance, $\omega_0$ is the resonance frequency, $\omega$ is the frequency of the light, $N$ is the number density, $c$ is the speed of light, $\epsilon_0$ is permittivity constant, $f$ is the oscillator strength of the dominant atomic transition. The equation assumes CI units. Note that the frequency dependence approaches Lorentzian for detuning much smaller than the resonance frequency. The self-absorption coefficients for liquid helium and neon calculated using the above equation are given in Table 4.

The scattering lengths can be found from the theory of Rayleigh scattering given by Landau and Lifshitz [28]:

$$\alpha_s = \frac{\omega^4}{6\pi c^2} kT \rho^2 \kappa_T \left(\frac{\partial \rho}{\partial \rho}\right)_T^2 \quad (3)$$

We neglected the temperature derivative term which was estimated to be small in Ref. [22]. The compressibility $\kappa_T$ of He and Ne are $208 \times 10^{-10}$ and $4.95 \times 10^{-10}$ cm$^2$/dyne; $\rho$ is the density. The dielectric constant is related to the refractive index: $\epsilon = n^2$. The refractive index can be calculated using the equation (see for example Ref. [24])

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\alpha^2 N\alpha_0^2}{3\pi} \sum_i \frac{\lambda_i^2 f_i}{\lambda_i^2 - \lambda_i^2} \quad (4)$$
where $\alpha$ is the fine-structure constant, $N$ is the number-density of atoms, and $a_0$ is the Bohr radius. The summation is extended over continuum. For neon, we included 9 values from Ref. [30] and estimated remaining contribution from the Thomas-Reiche-Kuhn rule. For helium we calculated 40 oscillator strengths with CI method using B-spline basis sets obtained in a cavity 30 a.u. The continuum contribution in helium is larger than that in neon because of larger detuning from the dominant transition for the wavelengths of interest. To check our continuum contributions in helium, we calculated the refraction index at wavelengths in the range from 168 to 288 nm to compare with available the precise measurement by Smith et al. [28]. We found that our ab initio values agree well with the experimental values. The largest uncertainty in our helium calculations at 78 nm comes from the replacement of continuum states with quasicontinuum states, and in neon calculations from the estimation of continuum contributions using the sum rule. The results of calculations of scattering coefficients are given in Table I.

We found that our results for scattering lengths and dielectric constants, $\epsilon_H = 1.086 \pm 0.006$ and $\epsilon_N = 1.5 \pm 0.2$, are in agreement with those obtained by Seidel et al. [29] using extrapolation of experimental refraction indices: $\epsilon_H = 1.077, \epsilon_N = 1.52, R_H = 600 \text{ cm}$, and $R_N = 60 \text{ cm}$. Our calculations has been done to check the previous results and to evaluate the uncertainty.

In our calculations we found that absorption lengths are smaller than the size of the neutrino detector, so that it is important to know whether the excited atom re-emits an absorbed photon or it is quenched non-radiatively. Because for non-radiative decay triplet and singlet states are similar and in Ref. [31] it has been found that lifetime of the helium triplet state in solid exceeds 15 s, we can conclude that quenching is a slow process and the total emission power will not be reduced much. The absorption-re-emission process is equivalent to the scattering in this case.

In this paper we have analyzed UV emission, self-absorption, and scattering of liquid helium and neon. For emission spectra we have found reliable data for helium and neon molecules and developed our own model of repulsive interaction to check and understand the existing calculations. Using potential curves we obtained emission spectra which agree well with experimentally observed condensed discharge spectra, although liquid emission is shifted due to liquid effects. We have considered various mechanisms of self-absorption and found that the radiative broadening is the dominant mechanism if the emission absorption offset exceeds 1 eV. The self-absorption is significant at the scale of the proposed neutrino detector and can impose restrictions on the experiment; fortunately, non-radiative relaxation seems to be slow and the absorption results mostly in re-emission so that it is similar to scattering in terms of conservation of the number of photons, but dissimilar to it in terms of photons' propagation dynamics. We have also calculated dielectric constants and Rayleigh scattering parameters. Results are in agreement with previous calculations. We understand now dominant effects of the emission, self-absorption, and scattering, but some questions remain and further investigation is necessary: the study of the liquid shifts and other possible liquid effects, the study of quenching mechanisms, the measurement of scattering and absorption lengths. The author is grateful to Dr. McKinsey for valuable discussions and comments on the manuscript.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Liquid & $n, \text{cm}^{-3}$ & $\lambda, \text{nm}$ & $\lambda_0, \text{nm}$ & $\alpha_a, \text{m}^{-1}$ & $\alpha_0, \text{m}^{-1}$ \\
\hline
He & $1.88 \times 10^{22}$ & 78 & 58.43 & 0.36 & 0.028(2) & 0.21(4) \\
Ne & $3.60 \times 10^{22}$ & 80 & 73.59 & 2.02 & 0.15(4) & 1.5(8) \\
\hline
\end{tabular}
\caption{Liquid helium and neon absorption and scattering coefficients. Parenthesis denote of the uncertainty of calculations in the last digit.}
\end{table}

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