Electronic radiative transition in He($2^{1,3}S$)-Ne weakly bound molecules. Temperature dependence

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Abstract. The metastable states $He(1s2s2^{1,3}S)$ are the champions in terms of radiative lifetime of neutral atomic states, $\sim 20\cdot10^{-3}\text{s}$ and $\sim 7\cdot10^{3}\text{s}$ for the single and triplet states respectively. However in numerous applications one deals with a metastable atom surrounded by buffer gas atoms. In the case of low temperatures the processes of recombination lead to the formation of clusters and dimers containing exited $He^*$ atoms. The present calculations reveal that lifetimes of quasi-bound molecules $He(2^{1,3}S)Ne$ are lowered by a factor equal to $\sim10^{-9}-10^{-7}$ in comparison with free metastable atoms. Temperature dependences of lifetimes are presented as well as averaged spectral line shapes. It is shown that radiative transitions mainly lead to the formation of free $He$ and $Ne$ atoms in their ground-state with the kinetic energy of relative motion in the range of 0-0.03 eV.

1. Introduction
Knowledge of the $He(2^{1,3}S)$ state lifetimes is important owing to the role that metastable atoms play in numerous applications. The extremely long lifetimes in atomic scale, $\tau_1^{0} = 20\cdot10^{-3}\text{s}$ for the singlets [1] and $\tau_3^{0} = 7\cdot10^{3}\text{s}$ for the triplets [2], arise from the fact that direct photon decay of the $2^{1,3}S$ states to the $1^{1}S$ ground state is forbidden by selection rules $\Delta S = 0, \Delta L = \pm 1$. However, in numerous applications, e.g., in ionosphere and discharge plasmas, one deals with a metastable atom surrounded by buffer gas atoms. Thus, one needs to account for the influence of the interaction between atoms on radiative properties of metastable atoms including lifetimes and spectral profiles. The issue is of topical in the case of low temperatures when the processes of recombination lead to the formation of clusters and dimers containing excited atoms. The present work focuses on the radiative transitions in

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the weakly bound dimers. In the case of $\text{He}(2^{1,3}S) - \text{Ne}$ the transitions can lead either to the formation of free $\text{He}(1^1S)$ and $\text{Ne}(1^1S)$ atoms:

$$\text{He}(2^{1,3}S) - \text{Ne}(1^1S) \Rightarrow \text{He}(1^1S) + \text{Ne}(1^1S) + \hbar \omega$$  \hspace{1cm} (1)$$

or to the formation of bound molecules in ro-vibrational states of the ground molecular state:

$$\text{He}(2^{1,3}S) - \text{Ne}(1^1S) \Rightarrow \text{HeNe}(v, j) + \hbar \omega$$  \hspace{1cm} (2)$$

with $\hbar \omega \sim 166300 \text{ cm}^{-1}$. The physical reason of the reactions (1)-(2) is related to the optical transition dipole moment of the $\text{He}(2^{1,3}S) - \text{Ne}$ dimers. An atomic interaction destroys the spherical symmetry of the helium atom in the metastable state via admixture of p-atomic states of helium with the zero projection of the electric moment on the molecular axis and takes off the selection rules [3].

The present paper accounts for both reactions (1,2) in performing the calculations of the averaged lifetimes and spectral profiles produced by optical transitions from four vibrational states of the weakly bound molecule $\text{He}(2^{1,3}S) - \text{Ne}$. The calculations performed are based on an improved version of the recent $ab\ initio$ quantum chemical data [4].

2. Quantum chemical input

The starting point of the present calculations of lifetimes and spectral profiles is a quantum chemical input that includes potential energy curves and electronic dipole transition moment. As the previous calculations [5] for the singlet case, the present calculations are mainly based on the $ab\ initio$ results [4] for the potential energy curves of the initial excited molecular states $0^+$ and $1$ that correlate at large interatomic distances with the atomic states $\text{He}(2^{1,3}S)$ correspondingly and for the potential energy curve of the ground molecular state $0^+$. Thus obtained potentials allowed us to calculate both the positions of vibrational levels and the nuclear wave functions by numerical solution of the time-independent Schrödinger equation by means of the expansion of nuclear wave functions in the Discrete Variable Representation (DVR) basis functions sinc(R). The results for the adiabatic potential energies together with positions of vibrational levels and wave functions are shown in figure 1 for the ground and excited $0^+$ states in the case of $\text{He}(1^1S), \text{He}(2^1S) - \text{Ne}$ dimers. The dipole moment for the parallel radiative transition [4] is shown in figure 1c. As discussed above, this information was used afterwards for the calculation of the lifetime.

2.1. Excited state

The excited molecular state produced by the interaction of the metastable atom $\text{He}(2^1S)$ with the $\text{Ne}(1^1S)$ atom gives rise to the adiabatic potential energy curve with two wells at $R_m^e = 5.1a_0$ and $R_m^c = 10.6a_0$ separated by a hump at the interatomic distance $R_h = 7.4a_0$; see figure 1a. As discussed in [4], the asymptotic value of the calculated potential should be lowered in order to match the experimental data for the separated atoms. The new fitting of the $\text{He}(2^1S) - \text{Ne}(1^1S)$ potential performed in the present study leads to the correction of 469 cm-1. The ambiguity in the asymptotic value for the potential energy curve with two potential wells implies an ambiguity in the number of vibrational states. The ground vibrational state, whose wave function is shown by the thin solid line in figure 1a, is entirely localized in the interior well. This well is about 150 cm-1 in depth with respect to the atomic asymptote (260 cm-1 to the top of the barrier), but rather narrow, so that the ground vibrational level is located roughly 86 cm-1 below the dissociation limit. The external well can be regarded as a van der Waals one, although its depth is about 38 cm-1. The calculations in [4] mainly
concentrated on the relatively short distances in the 3–8 \( \text{a}_0 \) range. Therefore the present value 38 cm\(^{-1} \) should be treated as an estimate only, due to the problems with the multireference CI approach. This problem is not crucial for the present lifetime calculation of the ground vibrational state (the vibrational quantum number \( \nu = 0 \)), as the corresponding vibrational wave function is localized entirely at short internuclear distances, \( R < 7\text{a}_0 \), see figure 1a. It is important for the vibrational states with \( \nu = 1, 2, 3 \), whose levels lie above the minimum of the external well and whose vibrational wave functions are localized completely in this well; so that their vibrational level values should be considered as the first-order estimates only.

2.2. Ground state
The calculated potential for the ground state, the thick solid line in figure 1b, is in good agreement with the previous results [6]. The key parameters of the potential are the well depth \( D_m = 20 \text{cm}^{-1} \) and the equilibrium distance \( R_m = 5.7\text{a}_0 \). The present calculation shows that the ground-state potential well supports one vibrational level with the dissociation energy \( D_m = 3.6 \text{cm}^{-1} \), see figure 1b, the thick long-dashed line.
2.3. Electric transition dipole moment

The electric transition dipole moment for transitions $\text{He}(2^1S) - \text{Ne}(1^1S) \Rightarrow \text{He}(1^1S) - \text{Ne}(1^1S)$ as a function of internuclear distance is shown in figure 1c. Dipole moment has two important features: a sharp maximum in the region of strong configuration interaction at $R \approx 0.5a_0$ and a node at $R \approx 1.3a_0$. In general, the existence of a node is important in calculations of radiative properties, especially of spectral profiles, as it leads to the formation of a minimum in the radiative width and the spectral profiles.

3. Results and conclusions

The present calculation of the $\text{He}(2^{1,3}S) - \text{Ne}$ radiative lifetime is based on the following formula (in atomic units) [7,8]:

$$\tau^{-1} = \frac{4}{3} \sum_j (\alpha \omega_g)^3 \left[ \frac{j+1}{2j+1} \langle j|d(R)|f\rangle (j+1)^2 + \frac{j}{2j+1} \langle ij|d(R)|f\rangle (j-1)^2 \right]$$  \hspace{1cm} (3)

where $\alpha$ is the fine structure constant; $\omega_g$ is the angular frequency of the emitted photon, which means that $\hbar \omega_g = E_i - E_f$ in the case of a bound-bound transition or $\hbar \omega_g = E_i - T_f$ in the case of a bound-free transition, whereby the energies of the bound states $E_i$ and the kinetic energy $T_f$ are taken with respect to the ground-state asymptotic value; $d(R)$ is the electric transition dipole moment calculated between the initial and the final electronic adiabatic states at fixed nuclei; $|ij\rangle$ and $|fj\rangle$ are the nuclear radial wave functions for the initial (excited) and the final (ground) molecular states, respectively, with the orbital quantum number $j$. In the present case, the initial states are the electronically excited molecular states $\text{He}(2^{1,3}S) - \text{Ne}$ in allowed vibrational levels $v$. Table 1 shows the lifetime values calculated by equation (3) for four vibrational states of the excited adiabatic term $\text{He}(2^1S) - \text{Ne}$. The results for the average lifetime under the Boltzmann distribution are shown in figure 2. The thick solid curve referred to the case when four allowed vibrational levels are populated, dashed line and dotted line refer to the cases of three and two vibrational levels respectively, and finally, thin line depicts the case when only the ground vibrational level is populated.

| $v$ | $\tau (s)$ |
|-----|-------------|
| 0   | $1.35 \times 10^{-8}$ |
| 1   | $2.11 \times 10^{-8}$ |
| 2   | $1.00 \times 10^{-8}$ |
| 3   | $1.30 \times 10^{-8}$ |
Figure 2. Temperature dependence of averaged lifetimes for the $\text{He}(2^1S)$ – $\text{Ne}$ molecules.

The square of the calculated averaged dipole moment matrix elements $\langle i | d | f \rangle^2$ is shown as a function of the emitted photon energy in figure 3. It is worth mentioning that the bound-bound transition contributes 16% to the inverse lifetime in equation (3), the rest is coming from the bound-free transitions. Figure 3 clearly shows that the radiative transitions mainly lead to the formation of the ground-state He and Ne atoms with the kinetic energy of relative motion in the range of $T_e = 0 - 0.03eV$. The spectral profiles of the bound-free transitions averaged over the Boltzmann distribution are shown in figure 4.

Figure 3. The square of the transition dipole moment averaged over the initial and the final wave functions in the case of the $\text{He}(2^1S)$ – $\text{Ne}$ molecules as a function of photon energy, which determines the kinetic energy of relative motion of free He and Ne atoms. Vertical solid line at 166194 cm$^{-1}$ shows the position of the bound–bound transitions.
Thus, the interaction of atoms lead to the pronounced decreasing of lifetimes of the metastable atomic states, namely $\tau_1 \approx 6.7 \cdot 10^{-7} \tau_1^0$ for the singlet state and $\tau_3 \approx 1.3 \cdot 10^{-9} \tau_3^0$ for the triplet one. Although $He-Ne$ gas mixtures and, in particular, radiative emission of the excited $He$ atoms have been intensively studied since the advent of the first gas laser it would be interesting to study such transitions in the $He-Ne$ gas mixtures under temperatures below 100 K, when the process of the excitation transfer is negligible [9] but recombination processes should produce a large number of the $He(2^1S)-Ne$ molecules. It is expected that the increase of surrounding buffer gas atoms will decrease the lifetimes. The same is true for experiments in cold matrices.

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