# $\mathrm{He}\left(1^{1} S\right)-\mathrm{He}\left(2^{3} S\right)$ collision and radiative transition at low temperatures 

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#### Abstract

There has been considerable recent interest in low-temperature interrogation of quantum helium nanodroplets. We consider the interaction of helium ground and metastable states, employing the best known molecular dimer potentials. Radiative transitions between different metastable rovibrational levels are compared with the discharge emission transition lines and good agreement is found. Collisional interactions between helium ground and metastable atoms are studied and elastic scattering, metastability excitation transfer and diffusion cross sections and rate coefficients are calculated at ultralow energies. The integral elastic cross section at ultralow energies is about $5000 \AA^{2}$. Effect of shape resonances that form in the potential barriers, on the cross sections is investigated. We find that some shape resonances live for longer than 100 s . Long-range potential wells could support "shelf" levels. We discuss their collisional and spectroscopic properties.


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## I. BACKGROUND DISCUSSION

Helium collisions and spectroscopic interrogation are fundamental to understanding collisional ionization [1], Penning and associative ionization of metastable atoms [2], spectral shift and broadening [3], radiative and nonradiative rovibrational quenching [4], formation of extremely weakly bound helium dimer [5], three-body Effimov states [6], formation of nanodroplets and bubbles in superfluid helium [7], electron production and dissociative recombination in discharge plasma [8], high-precision measurements of fundamental constants [9], and ultracold trapping and Bose-Einstein condensation [10]. The development of experimental techniques for probing and embedding atomic and molecular systems with finite, helium nanodroplets, have sparked a renewed interest in physics and chemistry of helium molecules [11]. Formation of metastable helium dimers in or on the helium nanodroplets offers a sensitive probe of the physics of such finite quantum systems.

Whereas, owing to their tight electron bindings and small polarizabilities, helium atoms in the ground state hardly form a molecular state-dimer binding energy of about 1 mK [5], the excited helium molecules are mostly covalently bound and support a large number of vibrational levels. In the spinpolarized triplet metastable configuration, helium atoms are far removed in energy from the ground state ( $\approx 19.8 \mathrm{eV}$ ) and are prohibited from radiative coupling to the ground state [the lifetime of the $\mathrm{He}\left(2^{3} S\right)$ is more than 1 h [12] and roughly 0.1 ms for $\operatorname{He}\left(2^{3} P\right)$ ]. Hence, in the triplet states, helium atoms act more like alkali metals with one active electron. Collisions between maximally spin-oriented $\mathrm{He}\left(2{ }^{3} S\right)$ atoms have been known to result in greatly reduced rate of Penning ionization and large elastic-scattering cross sections, optimal for condensation in a magneto-optical trap [10]. Recent development of techniques for spectroscopic in-

[^0]vestigation of atomic and molecular species that attach to finite quantum helium droplets at low temperatures has sparked a surge of interest in collisional and spectroscopic properties of helium metastables. The ultralow energy collision of helium atoms in metastable state with atoms in the ground state and the spectroscopy of the dimer molecules that dissociate to these levels are the subjects of the present study.

## II. POTENTIAL CURVES

The nonrelativistic molecular potentials resulting from the interaction of $\mathrm{He}\left(1^{1} S\right)$ and $\mathrm{He}\left(2^{3} S\right)$ atoms have the $a^{3} \Sigma_{u}^{+}$ and $c^{3} \Sigma_{g}^{+}$symmetries [13,14]. Both electronic states have maximum well depth around the internuclear separation of $R_{e} \sim 2$ a.u. (atomic units), while the $a^{3} \Sigma_{u}^{+}$potential well is deeper by roughly $11000 \mathrm{~cm}^{-1}$. The barrier height for the $a^{3} \Sigma_{u}^{+}\left(c^{3} \Sigma_{g}^{+}\right)$states occurs near $R_{b} \sim 5.1$ (3.6) a.u. at a height of $U_{b} \sim 500$ (2450) $\mathrm{cm}^{-1}$. The repulsive barriers are due to exchange interaction between the $1 s$ and $2 s$ electrons on each center. The large barrier for the $c^{3} \Sigma_{g}^{+}$state is due partly to the nonadiabatic interactions with electronic states that dissociate to $\mathrm{He}\left(1^{1} S\right)+\operatorname{He}\left({ }^{3} P\right)$.

We employ the parametric representation of the triplet potentials as given by Jordan, Siddiqui, and Siska [15]. The potentials are broken into three regions: the parameters describing the intermediate- $R$ values, including the potential wells, are determined from Rydberg-Klein-Rees (RKR) fits to experimental vibrational energies [16]. Near the potential barriers, the parametric potentials are directly matched to the intermediate- $R$ region (for the $c^{3} \Sigma_{g}^{+}$symmetry) and to the long-range region (for the $a^{3} \Sigma_{u}^{+}$symmetry) using an exponential spline cubic fit. The long-range potentials, including exchange, were modeled after Tang and Toennies [19]. The van der Waals potentials are determined from the dispersion coefficients, $C_{6}, C_{8}$, and $C_{10}$, due to Victor and Sando [20] and Proctor and Stwalley [21], while the other parameters for the exchange and the long-range potentials are obtained from fitting of the angle-resolved differential scattering data in the


FIG. 1. The $a^{3} \Sigma_{u}^{+}$and $c^{3} \Sigma_{g}^{+}$potential energy curves for the interaction of $\mathrm{He}\left(1^{1} S\right)$ and $\mathrm{He}\left(2^{3} S\right)$ atoms, from Ref. [15]. Also shown is the transition dipole matrix element that radiatively connects these potentials, from Ref. [14]. The insets give magnified views of the barrier regions and the long-range van der Waals wells.
low-energy collision of helium ground and metastable atoms [13]. More recent values for the dispersion coefficients calculated by Spelsberg and Meyer [22] are essentially the same as those used in the construction of the above potential curves. Due to coherent interference between scattering amplitudes on the gerade and ungerade potentials, oscillations in the differential scattering cross sections occur-the $a^{3} \Sigma_{u}^{+}$ and $c^{3} \Sigma_{g}^{+}$states are asymptotically degenerate. The smalland intermediate-angle scattering measurements probe largeand intermediate-impact parameters and are used to construct the parametric molecular potentials.

In Fig. 1, we reproduce the potential curves appropriate to the collision of $\mathrm{He}\left(1^{1} S\right)$ and $\mathrm{He}\left(2^{3} S\right)$ atoms. Shallow van der Waals wells (well depth of about $1 \mathrm{~cm}^{-1}$ ) form near $R \sim 6.5 \AA$ and because of the crossing of the $a^{3} \Sigma_{u}^{+}$and $c^{3} \Sigma_{g}^{+}$curves near $R \sim 5.5 \AA$, the long-range well for the $c^{3} \Sigma_{g}{ }_{g}^{+}$state is slightly more attractive (see inset in Fig. 1). These wells could potentially support very long-range bound levels, reminiscent of the "shelf" states in Rydberg alkali dimers [23]. The transition dipole moment $\mu$, between the $c$ and $a$ states, is taken from a calculation by Yarkony [14]. Although, the experimental differential scattering cross sections, used in the construction of the potentials, alone are not sufficient to determine conclusively the depth of the asymptotic wells, the possibility that such fragile states may exist could have ramifications for ultracold collisions of helium ground and metastable states and in superfluid and finite quantum droplets of helium. The insets show the repulsive barriers in both symmetries and the long-range potential wells near $7 \AA$.

## III. SPECTROSCOPY

The rovibrational levels in the $a^{3} \Sigma_{u}^{+}$and $c^{3} \Sigma_{g}^{+}$states are forbidden from radiative transitions to the ground electronic state of helium dimer, due to spin selection rules. Radiative transitions between $a$ and $c$ states are, however, spin allowed and also to the $b^{3} \Pi_{g}\left[\operatorname{He}\left(1^{1} S\right)+\operatorname{He}\left(2^{3} P\right)\right]$ state. Nonadiabatic coupling (spin-orbit and Breit-Pauli) of such states to
the $A^{1} \Sigma_{g}^{+}$, dissociating to $\operatorname{He}\left(1^{1} S\right)+\operatorname{He}\left(2^{1} S\right)$, represents a possible pathway for the quenching of $\operatorname{He}\left(2^{3} S\right)$ atoms [14]. Ginter [16] measured the $P$ and $R$ emission branches of $\mathrm{He}_{2}$ in a helium discharge between different electronic states. Specifically, he measured the rovibrational band transition, $a^{3} \Sigma_{u}^{+}(\nu, N) \rightarrow c^{3} \Sigma_{g}^{+}\left(\nu^{\prime}, N \pm 1\right)$, where $N$ is the rotational quantum number for the molecule.

Table I gives the calculated vibrational transition frequencies in wave numbers for both molecular symmetries and compares them to available spectroscopic data. Altogether, we find 13 bound vibrational levels and one shape resonance in the $a^{3} \Sigma_{u}^{+}$potential and three bound vibrational levels and three shape resonances in the $c^{3} \Sigma_{g}^{+}$potential. The number of bound and shape resonances agrees with the calculation of Ref. [15]. Spin-allowed transition dipole matrix elements in the adiabatic representation has been reported by Yarkony [14], $D(R)=\left\langle a^{3} \Sigma_{u}^{+}\right| \mu\left|c^{3} \Sigma_{g}^{+}\right\rangle$, where $\mu$ is the electronic dipole, and is reproduced in Fig. 1. The $D(R)$ dipole matrix element peaks near $R \sim 2.5$ a.u., and drops to zero as $R$ $\rightarrow \infty$, as expected. Our calculated transition dipoles $d_{N}$ $\left.=\left|\left\langle\chi_{N}^{(a)}(R)\right| D(R)\right| \chi_{N}^{(c)}(R)\right\rangle\left.\right|^{2}$, where $\chi_{N}^{(a, c)}(R)$ are the rovibrational wave functions in the $a^{3} \Sigma_{u}^{+}$and $c^{3} \Sigma_{g}^{+}$potential curves, are given in Table I for the $P(N)$ and $R(N)$ branches, referring, respectively, to $N-1$ and $N+1$ transitions. (0-0) and (1-1) transitions have the largest transition amplitudes and because of the large potential barrier heights, there is little variation of the transition strength across the rotational manifolds.

The agreement of the other measured [17] transition frequencies is of the same level of accuracy as the results shown in Table I, where calculation is compared with Ginter's experiments [16].

The only absorption measurement of $P(N)$ and $R(N)$ transition lines in $\mathrm{He}_{2}^{*}$ molecule that we are aware of, is due to Yurgenson et al. [18], in which the $a^{3} \Sigma_{u}^{+} \rightarrow c^{3} \Sigma_{g}^{+}$electronic transitions of the (0-0) rotational band on the surface of helium nanodroplets were observed. At temperatures of the nanodroplet, $T \approx 1 \mathrm{~K}$, nonthermal rovibrational lines, $11 \leqslant N \leqslant 29$ were observed along the $N=1$ lines. The transition frequencies from this measurement correspond nicely to our calculations and to the experiment of Ginter [16]. A theory describing the nonthermal behavior of the metastable helium transition will be provided in a subsequent work.

In Fig. 2, the nuclear wave function for the shape resonance ( $\nu=13, N=0$ ), in the $a^{3} \Sigma_{u}^{+}$potential at an energy of $16184.7 \mathrm{~cm}^{-1}$ is shown, while the dissociation energy for the $a^{3} \Sigma_{u}^{+}$molecular state is $15808 \mathrm{~cm}^{-1}$. The wave function has large amplitude near $R \approx 2.3 \AA$ where the barrier height is maximum. The tunneling width for this resonance is $\Gamma=0.97 \mathrm{~cm}^{-1}$. Previous calculations indicated the existence of two shape resonances in the $a^{3} \Sigma_{u}^{+}$state [13,24].

Rovibrational bound states and resonances are obtained for a total of 50 rotational angular quantum numbers using Fourier Hamiltonian grid method [25] and a complex absorbing potential [26] of the form $V_{c a p}=-i \lambda\left(R-R_{0}\right)^{2} \theta(R$ $-R_{0}$ ), where the unit step function $\theta$ ensures that the Hamiltonian is unaltered for internuclear distances less than some

TABLE I. Calculated and measured [16] rovibrational frequencies in wave numbers for $a^{3} \Sigma_{u}^{+}(\nu, N)$ $\rightarrow c^{3} \Sigma_{g}^{+}\left(\nu^{\prime}, N \pm 1\right)$ transitions. Both $P(N)$ and $R(N)$ branches are shown. Also shown are the radiative transition squared dipole matrix elements, $d_{N}$ in $\AA^{2}$.

| N | $R(N)$ |  |  | $P(N)$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Present | Ref. [16] | $d_{N}$ | Present | Ref. [16] | $d_{N}$ |
| (0-0) |  |  |  |  |  |  |
| 1 | 10915.73 | 10915.43 | 7.78 | 10874.64 | 10874.31 | 7.80 |
| 3 | 10935.65 | 10935.34 | 7.76 | 10839.94 | 10839.61 | 7.82 |
| 5 | 10949.48 | 10949.18 | 7.74 | 10799.52 | 10799.17 | 7.82 |
| 7 | 10957.11 | 10956.84 | 7.72 | 10753.48 | 10753.14 | 7.83 |
| 9 | 10958.45 | 10958.17 | 7.70 | 10701.94 | 10701.61 | 7.84 |
| 11 | 10953.39 | 10953.13 | 7.67 | 10645.00 | 10644.64 | 7.84 |
| 13 | 10941.84 | 10941.58 | 7.64 | 10582.76 | 10582.40 | 7.84 |
| 15 | 10923.68 | 10923.40 | 7.60 | 10515.31 | 10514.92 | 7.84 |
| 17 | 10898.79 | 10898.47 | 7.55 | 10442.73 | 10442.28 | 7.82 |
| 19 | 10867.03 | 10866.66 | 7.50 | 10365.06 | 10364.54 | 7.81 |
| 21 | 10828.23 | 10827.75 | 7.44 | 10282.34 | 10281.76 | 7.79 |
| 23 | 10782.19 | 10781.58 | 7.38 | 10194.55 | 10193.89 | 7.76 |
| 25 | 10728.64 | 10727.90 | 7.29 | 10101.64 | 10100.86 | 7.72 |
| 27 | 10667.23 | 10666.37 | 7.20 | 10003.49 |  | 7.68 |
| 29 | 10597.52 | 10596.52 | 7.08 | 9899.89 |  | 7.61 |
| 31 | 10518.91 | 10517.86 | 6.94 | 9790.51 |  | 7.53 |
| (1-0) |  |  |  |  |  |  |
| 1 | 12398.01 | 12393.64 | 1.09 | 12358.70 | 12354.34 | 1.08 |
| 3 | 12413.80 | 12409.41 | 1.11 | 12322.23 | 12317.85 | 1.07 |
| 5 | 12421.11 | 12416.69 | 1.12 | 12277.67 | 12273.28 | 1.06 |
| 7 | 12419.78 | 12415.36 | 1.14 | 12225.11 | 12220.64 | 1.06 |
| 9 | 12409.67 | 12405.24 | 1.16 | 12164.61 | 12160.10 | 1.05 |
| 11 | 12390.60 | 12386.20 | 1.18 | 12096.22 | 12091.68 | 1.06 |
| 13 | 12362.37 | 12358.06 | 1.21 | 12019.97 | 12015.46 | 1.06 |
| 15 | 12324.75 | 12320.60 | 1.24 | 11935.84 | 11931.40 | 1.07 |
| 17 | 12277.46 | 12273.59 | 1.27 | 11843.80 | 11839.49 | 1.08 |
| 19 | 12220.18 | 12216.68 | 1.31 | 11743.73 | 11739.68 | 1.09 |
| 21 | 12152.51 | 12149.98 | 1.35 | 11635.49 | 11631.80 | 1.11 |
| 23 | 12073.94 | 12071.82 | 1.40 | 11518.83 | 11516.12 | 1.13 |
| 25 | 11983.83 | 11982.70 | 1.45 | 11393.40 | 11391.10 | 1.16 |
| 27 | 11881.36 | 11881.48 | 1.51 | 11258.69 | 11257.40 | 1.19 |
| 29 | 11765.39 | 11767.05 | 1.57 | 11114.01 | 11113.99 | 1.23 |
| 31 | 11634.37 | 11638.51 | 1.64 | 10958.37 |  | 1.28 |
| (1-1) |  |  |  |  |  |  |
| 1 | 10665.85 | 10662.00 | 5.32 | 10626.53 | 10622.67 | 5.37 |
| 3 | 10684.02 | 10680.19 | 5.27 | 10592.45 | 10588.58 | 5.40 |
| 5 | 10695.62 | 10691.79 | 5.22 | 10552.19 | 10548.31 | 5.42 |
| 7 | 10700.51 | 10696.71 | 5.15 | 10505.84 | 10501.97 | 5.43 |
| 9 | 10698.54 | 10694.78 | 5.07 | 10453.48 | 10449.61 | 5.43 |
| 11 | 10689.55 | 10685.88 | 4.99 | 10395.17 | 10391.31 | 5.41 |
| 13 | 10673.35 | 10669.83 | 4.91 | 10330.95 | 10327.18 | 5.41 |
| 15 | 10649.72 | 10646.42 | 4.79 | 10260.81 | 10257.18 | 5.37 |
| 17 | 10618.41 | 10615.42 | 4.67 | 10184.75 | 10181.35 | 5.34 |
| 19 | 10579.12 |  | 4.53 | 10102.67 | 10099.57 | 5.27 |
| (2-0) |  |  |  |  |  |  |
| 1 | 13764.65 | 13763.47 | 0.14 | 13727.33 |  | 0.13 |
| 3 | 13775.76 | 13774.52 | 0.14 | 13688.86 | 13687.62 | 0.13 |
| 5 | 13775.66 | 13774.52 | 0.15 | 13639.63 | 13638.33 | 0.13 |
| 7 | 13764.17 | 13763.47 | 0.15 | 13579.67 | 13578.49 | 0.13 |
| 9 | 13741.04 |  | 0.16 | 13509.00 | 13507.78 | 0.13 |
| 11 | 13705.99 | 13705.19 | 0.16 | 13427.59 | 13426.49 | 0.13 |
| 13 | 13658.67 | 13658.17 | 0.17 | 13335.35 | 13334.41 | 0.13 |
| 15 | 13598.70 | 13598.60 | 0.18 | 13232.15 | 13231.48 | 0.13 |
| 17 | 13525.56 | 13525.98 | 0.19 | 13117.75 | 13117.47 | 0.14 |
| 19 | 13438.63 | 13439.72 | 0.21 | 12991.83 | 12992.08 | 0.14 |
| 21 | 13337.14 | 13338.82 | 0.22 | 12853.94 | 12854.81 | 0.15 |
| 23 | 13220.04 | 13221.71 | 0.24 | 12703.46 | 12704.96 | 0.15 |
| 25 | 13085.91 |  | 0.26 | 12539.50 | 12540.99 | 0.16 |

TABLE I. (Continued).

| N | $R(N)$ |  |  |  | $P(N)$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Present | Ref. [16] | $d_{N}$ |  | Present | Ref. [16] | $d_{N}$ |
|  | (2-1) |  |  |  |  |  |  |
| 1 | 12032.48 | 12031.73 | 1.88 |  | 11995.16 | 11994.38 | 1.86 |
| 3 | 12045.98 | 12045.22 | 1.89 |  | 11959.08 | 11958.29 | 1.85 |
| 5 | 12050.18 | 12049.40 | 1.91 |  | 11914.14 | 11913.39 | 1.84 |
| 7 | 12044.90 | 12044.40 | 1.93 |  | 11860.40 | 11859.70 | 1.84 |
| 9 | 12029.91 | 12029.51 | 1.96 |  | 11797.87 | 11797.26 | 1.85 |
| 11 | 12004.94 | 12004.79 | 2.00 |  | 11726.54 | 11726.08 | 1.86 |
| 13 | 11969.65 | 11969.86 | 2.02 |  | 11646.33 | 11646.14 | 1.85 |
| 15 | 11923.67 | 11924.37 | 2.06 |  | 11557.12 | 11557.23 | 1.88 |
| 17 | 11866.51 | 11867.79 | 2.09 |  | 11458.69 | 11459.31 | 1.89 |
| 19 | 11797.57 | 11799.55 | 2.13 |  | 11350.77 | 11351.94 | 1.92 |
| 21 | 11716.10 | 11718.76 | 2.17 |  | 11232.91 | 11234.76 | 1.95 |
| 23 | 11621.10 | 11623.76 | 2.21 |  | 11104.52 | 11107.06 | 1.99 |
|  |  |  |  |  |  |  |  |
| 1 | 10378.94 | 10377.85 | 3.05 |  | 10341.63 | 10340.58 | 3.12 |
| 3 | 10394.90 | 10393.85 | 2.99 |  | 10308.00 | 10306.96 | 3.15 |
| 5 | 10403.53 | 10402.55 | 2.91 |  | 10267.49 | 10266.50 | 3.16 |
| 7 | 10404.66 | 10403.88 | 2.82 |  | 10220.16 | 10219.22 | 3.16 |
| 9 | 10398.06 | 10397.46 | 2.71 |  | 10166.02 | 10165.27 | 3.14 |
| 11 | 10383.47 | 10383.20 | 2.59 |  | 10105.08 | 10104.50 | 3.11 |
|  | (3-1) |  |  |  |  |  |  |
| 1 | 13271.23 | 13276.95 | 0.40 |  | 13236.20 | 13241.95 | 0.39 |
| 3 | 13279.36 | 13285.02 | 0.41 |  | 13197.83 | 13203.53 | 0.38 |
| 5 | 13275.09 | 13280.64 | 0.42 |  | 13147.53 | 13153.17 | 0.38 |
| 7 | 13258.12 | 13263.56 | 0.43 |  | 13085.31 | 13090.83 | 0.38 |
| 9 | 13228.10 | 13233.38 | 0.45 |  | 13011.09 | 13016.46 | 0.38 |
| 11 | 13184.58 | 13189.65 | 0.47 |  | 12924.73 | 12929.95 | 0.39 |
| 13 | 13126.97 | 13131.79 | 0.49 |  | 12825.97 | 12830.96 | 0.39 |
| 15 | 13054.54 | 13058.97 | 0.52 |  | 12714.44 | 12719.13 | 0.40 |
| 17 | 12966.27 | 12970.19 | 0.54 |  | 12589.57 | 12593.86 | 0.41 |
| 19 | 12860.74 | 12863.82 | 0.58 |  | 12450.53 | 12454.32 | 0.43 |
| 21 | 12735.84 | 12737.67 | 0.61 |  | 12296.08 | 12299.03 | 0.44 |
| 23 | 12588.04 |  | 0.65 |  | 12124.26 | 12125.94 | 0.47 |
|  | (3-2) |  |  |  |  |  |  |
| 1 | 11617.69 | 11623.06 | 2.29 |  | 11582.66 | 11588.20 | 2.28 |
| 3 | 11628.29 | 11633.67 | 2.30 |  | 11546.75 | 11552.14 | 2.28 |
| 5 | 11628.44 | 11633.67 | 2.30 |  | 11500.88 | 11506.25 | 2.28 |
| 7 | 11617.87 | 11623.06 | 2.31 |  | 11445.06 | 11450.31 | 2.28 |
| 9 | 11596.24 | 11601.29 | 2.31 |  | 11379.23 | 11384.42 | 2.29 |
| 11 | 11563.11 | 11568.03 | 2.31 |  | 11303.26 | 11308.36 | 2.29 |
| 13 | 11517.92 | 11522.64 | 2.31 |  | 11216.91 | 11221.83 | 2.29 |
| 15 | 11459.92 | 11464.39 | 2.29 |  | 11119.82 | 11124.53 | 2.29 |
| 17 | 11388.15 | 11392.40 | 2.27 |  | 11011.45 | 11016.13 | 2.30 |
|  | (4-2) |  |  |  |  |  |  |
| 1 | 12710.67 | 12715.94 | 0.76 |  | 12678.48 | 12683.93 | 0.75 |
| 3 | 12714.58 | 12719.44 | 0.77 |  | 12639.73 | 12645.00 | 0.74 |
| 5 | 12704.06 | 12708.40 | 0.79 |  | 12587.18 | 12592.10 | 0.74 |
| 7 | 12678.58 | 12682.12 | 0.81 |  | 12520.68 | 12525.02 | 0.74 |
| 9 | 12637.42 | 12639.98 | 0.83 |  | 12439.95 | 12443.52 | 0.74 |
| 11 | 12579.51 | 12580.82 | 0.86 |  | 12344.43 | 12347.01 | 0.75 |
| 13 | 12503.36 | 12503.04 | 0.88 |  | 12233.31 | 12234.62 | 0.76 |
| 15 | 12406.61 |  | 0.89 |  | 12105.26 | 12104.98 | 0.77 |

exterior critical radius $R_{0}$. Parameter $\lambda$ is variationally chosen such that the desired eigenvalues remain stationary. The widths of resonances are determined from the imaginary part of the eigenvalues, $E_{\text {res }}=E_{0}+i \Gamma / 2$.

The computed vibrational levels, $(\nu, N=0)$ are given in Table II. The $(\nu, 0)$ levels do not exist in the $a^{3} \Sigma_{u}^{+}$state, but are given here for comparison with other calculations [13,14,24]. The widths for the shape resonances are also
tabulated. The ( $\nu=3, N=0$ ) shape resonance, attached to the $c^{3} \Sigma_{g}^{+}$state lives for longer than 100 s and lies $\approx 70 \mathrm{~cm}^{-1}$ above the dissociation limit.

The rotational levels, attached to each vibrational level, are shown in Fig. 3, including quasibound levels (shape resonances). All rovibrational levels, irrespective of symmetry, are shown. The last bound vibrational level in the $a^{3} \Sigma_{u}^{+}$ $\left(c^{3} \Sigma_{g}^{+}\right)$potentials becomes unbound (shape resonance) with


FIG. 2. The nuclear wave function for the lone shape resonance in the $a^{3} \Sigma_{u}^{+}$potential barrier.
$N=5$ (14) units of rotational angular momentum. Figure 3 includes all the rovibrational levels above the dissociation limit, including top-of-the-barrier orbiting resonances.

## IV. COLLISIONS

## A. Low-energy collisions

Low-temperature physics and chemistry in helium gases and droplets require precise knowledge of scattering properties of $\mathrm{He}-\mathrm{He}$ collision. In this work, we calculate the collisional cross sections between helium ground and metastable atoms, which result from elastic scattering, excitation transfer, and diffusion in the gas at low temperatures. Figure 4(a) gives our calculated elastic-scattering cross section as a function of collisional energy (in a.u.),

$$
\begin{equation*}
\sigma_{e l}=\frac{4 \pi}{k^{2}} \sum_{N}(2 N+1) \sin ^{2}\left(\delta_{N}\right) \tag{1}
\end{equation*}
$$

TABLE II. Calculated vibrational levels in wave numbers of $\mathrm{He}_{2}^{*}$. Numbers in parentheses denote the width $\Gamma\left(\mathrm{cm}^{-1}\right)$ of corresponding resonance. The dissociation energies are, respectively, at $15808 \mathrm{~cm}^{-1}$ and $4803 \mathrm{~cm}^{-1}$.

| $\nu$ | $a^{3} \Sigma_{u}^{+}(\nu, 0)$ | $c^{3} \Sigma_{g}^{+}(\nu, 0)$ |
| ---: | :---: | :---: |
| 0 | 894.94 | 779.72 |
| 1 | 2627.59 | 2263.77 |
| 2 | 4281.62 | 3632.40 |
| 3 | 5855.53 | $4873.44\left(5.05 \times 10^{-14}\right)$ |
| 4 | 7347.36 | $5969.26\left(2.82 \times 10^{-7}\right)$ |
| 5 | 8753.57 | $6862.64(0.48)$ |
| 6 | 10067.98 |  |
| 7 | 11285.63 |  |
| 8 | 12404.49 |  |
| 9 | 13419.22 |  |
| 10 | 14321.42 |  |
| 11 | 15094.71 |  |
| 12 | 15720.69 |  |
| 13 | $16184.62(0.97)$ |  |



FIG. 3. Rotational energy-level diagrams for the $a^{3} \Sigma_{u}^{+}$and $c^{3} \Sigma_{g}^{+}$symmetries. The shaded horizontal lines denote the positions of shape (tunneling) and orbiting (top-of-the-barrier) resonances (lighter shade).
where $k^{2}=2 \mu E$, is the asymptotic wave vector at infinite separation, and $\delta_{N}$ is the elastic phase shift at an energy $E$ and rotational angular momentum $N$, calculated for each $a^{3} \Sigma_{u}^{+}$and $c^{3} \Sigma_{g}^{+}$potential separately, as

$$
\begin{equation*}
\left[\frac{d^{2}}{d R^{2}}-\frac{N(N+1)}{R^{2}}+2 \mu[E-U(R)]\right] \chi_{N}(R)=0 \tag{2}
\end{equation*}
$$

where $\mu$ is the reduced mass for the molecule and $U(R)$ represents the potential energies. The nuclear wave functions $\chi_{N}(R)$ are regular at origin and are box normalized $\left[\chi_{N}(R)\right.$ $\rightarrow \exp (-\kappa R)]$ as $R \rightarrow \infty$ and $\kappa=\sqrt{2 \mu|E-U(R)|}$ at $E<0$ for bound rovibrational levels, and energy normalized ( $\chi_{N}(R)$ $\rightarrow(2 \pi / k)^{1 / 2} \sin \left(k R-N \pi / 2+\delta_{N}\right) \quad$ as $\quad R \rightarrow \infty \quad$ and $k$ $=\sqrt{2 \mu[E-U(R)]})$ at $E>0$.

A six-step fifth-order symplectic integrator [27] is used to propagate the log-derivative $(d \chi / d R) \chi^{-1}$. The scattering phase shifts are extracted by matching numerical values of the log derivative with the analytical asymptotic log derivative at some large distance $R_{0}$, where the magnitude of the potential energy is much smaller than the collision energy. Owing to the robustness and efficiency of the log-derivative symplectic propagator, accurate results are obtained even


FIG. 4. Elastic, metastability excitation transfer, and diffusion cross sections for the collision of $\mathrm{He}\left(1^{1} S\right)$ and $\mathrm{He}\left(2^{3} S\right)$ atoms.
when a relatively small number of radial mesh points (1000-2000) are used for broad range of energies.

At energies relevant to collisions near room temperature, the elastic cross sections in the $c^{3} \Sigma_{g}^{+}$and $a^{3} \Sigma_{u}^{+}$symmetries are nearly the same and the elastic cross section is about $\sigma_{\text {tot }} \sim 1.5 \times 10^{-14} \mathrm{~cm}^{2}$ at a temperature of 350 K . A classical hard-sphere model of elastic scattering at an impact parameter $b \sim 5$ a.u. (peak of the $a^{3} \Sigma_{u}^{+}$barrier near $500 \mathrm{~cm}^{-1}$ ) yields a value for the cross section, $\sigma_{\text {class }} \sim \pi b^{2}=2.4$ $\times 10^{-14} \mathrm{~cm}^{2}$, in reasonable agreement with the precise quantum-mechanical calculation. A measurement of the elas-
tic cross section at energies about $100 \mathrm{~cm}^{-1}$ [28] obtained a roughly constant cross section $\sigma_{e l} \approx 140-145 \AA^{2}$, in reasonable agreement with our calculation. The oscillations in the low-energy range $1<E<500 \mathrm{~cm}^{-1}$ are due to glory scattering [29].

At very low energies, relevant for ultracold traps, the characteristic Wigner behavior becomes evident [30]; the elastic cross section in the $c^{3} \Sigma_{g}^{+}$potential curve tends to a constant, where $s$-wave scattering dominates, and the cross section in the $a^{3} \Sigma_{u}^{+}$potential curve tends monotonically to zero as $E^{2}$, where $p$-wave scattering dominates. The threshold behavior of the cross sections for scattering in the $a^{3} \Sigma_{u}^{+}$ or $c^{3} \Sigma_{g}^{+}$potential is dictated by symmetry rules that allow for scattering of only odd or even partial waves, respectively. The inset compares our calculated energies for the shape resonances with the sharp features in the elastic cross section. Only resonances whose widths are larger than $1 \mathrm{~cm}^{-1}$ are shown as lines.

In Figs. 4(b) and 4(c), we present our excitation transfer and diffusion cross sections, calculated according to [31]

$$
\begin{equation*}
\sigma_{t r}=\frac{\pi}{k^{2}} \sum_{N}(2 N+1) \sin ^{2}\left(\delta_{N}^{g}-\delta_{N}^{u}\right) \tag{3}
\end{equation*}
$$

and

$$
\begin{equation*}
\sigma_{d}=\frac{4 \pi}{k^{2}} \sum_{N}(N+1) \sin ^{2}\left(\eta_{N}-\eta_{N+1}\right), \tag{4}
\end{equation*}
$$

where $\delta_{N}^{g, u}$ refer, respectively, to the elastic phase shift in the $c^{3} \Sigma_{g}^{+}$and $a^{3} \Sigma_{u}^{+}$symmetries. The phase shifts $\eta_{N}$ and $\eta_{N+1}$ are, respectively, equal to $\delta_{N}^{g}$ and $\delta_{N}^{u}$ for the even $N$ partial waves and $\delta_{N}^{u}$ and $\delta_{N}^{g}$ for the odd $N$ partial waves.

The transfer cross section drops monotonically with energy until $E \sim 20 \mathrm{~cm}^{-1}$, where it has a minimum and rises to reach a constant value at ultralow energies. Since $s$-wave scattering contributes in both channels to the metastability excitation transfer cross section, the behavior at ultralow energies is expected. The minimum in the cross section occurs because of a near cancellation of the background $s$-wave phase shifts, $\delta_{0}^{g}$ and $\delta_{0}^{u}$, resembling a Ramsauer-Townsend minimum. We point out that there is a very sharp shape resonance near $E \approx 70 \mathrm{~cm}^{-1}$ in the $c^{3} \Sigma_{g}^{+}$channel.

The diffusion cross section rises at low energies and tends also to a constant as $E \rightarrow 0$. As expected, the $s$-wave phase shift in the $c^{3} \Sigma_{g}^{+}$channel dominates at low energies.

The rate coefficients for elastic, excitation transfer, and diffusion scattering are shown in Fig. 5. In obtaining the diffusion rate coefficient, the diffusion cross section is thermally averaged according to

$$
\begin{equation*}
\sigma_{d}(T)=\frac{1}{2\left(k_{B} T\right)^{3}} \int_{0}^{\infty} \sigma_{d}(E) E^{2} e^{-E / k_{B} T} d E, \tag{5}
\end{equation*}
$$

where $k_{B}$ is the Boltzman constant. Our diffusion rate coefficients are compared with the experiment of Fitzsimmons, Lane, and Walters [32], where the comparison is satisfactory.


FIG. 5. Elastic, metastability excitation transfer, and diffusion rate coefficients for the collision of $\mathrm{He}\left(1^{1} S\right)$ and $\mathrm{He}\left(2^{3} S\right)$ atoms. The experimental diffusion rate coefficients (points) are from Ref. [33].

The low-temperature rates are determined by the behavior of long-range potentials. We should mention that our calculated rates are for the bosonic ${ }^{4} \mathrm{He}$ case. We have computed the excitation transfer rates for the Fermionic system ${ }^{3} \mathrm{He}$, and although the calculated values are not given here, the comparison with available experiment [33] is good.

## B. Ultra low-energy collisions

At extremely low energies, collisions between atoms are driven by long-range interactions. The presence of shallow minima in both $a$ and $c$ potentials offers the intriguing possibility that they may support long-range "shelf" states near 6-7 Å. Long-range shelf states have been observed in optical double-resonance measurements of Stwalley and coworkers [23] in alkali dimers. Such states exist in the longrange potential wells produced by curve crossing of Rydberg potential curves with the ion-pair formation curve. Interestingly, bubbles in electron bombardment of superfluid helium and helium droplets with linear dimension about $10 \AA$ form, and have been suggested to contain metastable helium dimers [34]. The long-range wells in our calculations have well depth of about $1 \mathrm{~cm}^{-1}$ and do not support bound states. However, a slight modification of a potential parameter [13] that alters the van der Waals well depth for the $c^{3} \Sigma_{g}^{+}$state-this is the only state that allows for ultra lowenergy $s$-wave scattering-but leaves the short-range potential unchanged, results in a long-range bound vibrational


FIG. 6. The formation of a long-range shelf state in the $c^{3} \Sigma_{g}^{+}$ potential. The $s$-wave scattering length changes rapidly through infinity when a near zero-energy bound state in the van der Waals well appears. The wave function for this bound state peaks near $10 \AA$. In the example presented in the upper plot $\rho=3.3 \AA$.
level. We adjust the depth of the potential wells by tweaking the parameter $\rho$ in the expression for the long-range form of the potential curves [15]

$$
\begin{equation*}
\frac{1}{2}\left[U_{g}(R)+U_{u}(R)\right]=\exp [-i \alpha(R-\rho)]-\sum_{n=3}^{5} f_{2 n}(R) \frac{C_{2 n}}{R^{2 n}} \tag{6}
\end{equation*}
$$

where the parameter $\alpha$ is determined from a fit to the differential scattering cross section at low energies, the coefficients $f_{2 n}(R)$ depend on $\alpha$, and $C_{2 n}$ are the van der Waals coefficients $[20,21]$. Such shelf states are isolated in space from the more-complicated short-range interactions and if exist, can be spectroscopically interrogated. The behavior of the $s$-swave scattering length with the well depth of the van der Waals potential in the $c^{3} \Sigma_{g}^{+}$potential is given in Fig. 6, where the $s$-wave scattering length $a_{0}$ is obtained from the effective-range expansion $\lim _{k \rightarrow 0} \tan \delta_{0} \rightarrow-k a_{0}$. The scattering length passes through infinity as a single vibrational level crosses the dissociation threshold from above, as $a_{0}$ $=1 / 2 \mu\left|E_{b}\right|$. With slight deepening of the long-range well depth, the scattering length becomes large and positive. The wave function for this near-threshold bound vibrational level
has most of its amplitude in the van der Waals well and has negligible overlap with the intermediate- $R$ region. Such states, if formed, can be spectroscopically interrogated with synchrotron photons.

## V. SUMMARY

We revisit the helium ground $\left[\mathrm{He}\left(1^{1} S\right)\right]$ and metastable $\left[\mathrm{He}\left(2^{3} S\right)\right]$ interaction in the $a^{3} \Sigma_{u}^{+}$and $c^{3} \Sigma_{g}^{+}$symmetries and calculate the spectrum of dipole transitions between them using the known transition dipole matrix element. The transition frequencies compare well with the experimental data. We study the collision of helium ground and metastable atoms at low and ultra low energies and calculate the elastic, metastability excitation transfer, and diffusion cross sections rate coefficients and compare them with experiments where available. The elastic cross section at ultra low energies is large, $\sigma_{e l} \approx 5000 \AA^{2}$ and the partial elastic cross sections in the $a^{3} \Sigma_{u}^{+}$and $c^{3} \Sigma_{g}^{+}$potentials exhibit the characteristic

Wigner behavior with energy. The cross sections show sharp features that are due to shape resonances forming under the potential and centrifugal barriers. We calculate the tunneling width for these resonances and find that for some shape resonances, the lifetimes are longer than 100 s . The van der Waals interactions at large internuclear separations influence the collisions at ultra low energies. We study the effect of binding a molecular level in the shallow van der Waals wells in $\mathrm{He}_{2}^{*}$ and calculate the wave function for such a shelf state. Such a state is far removed from the inner region where exchange and core interactions dominate, and may be spectroscopically studied with synchrotron radiation.

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