PHYSICAL REVIEW A, VOLUME 61, 060703(R)

Close-coupled calculation of field-free collisions of cold metastable helium atoms

V. Venturi and I. B. Whittingham
School of Mathematical and Physical Sciences, James Cook University, Townsville 4811, Australia
(Received 1 February 2000; published 8 May 2000)

A quantum-mechanical close-coupled calculation of field-free collisions of cold metastable helium atoms has been performed. Theoretical predictions of the rate coefficients for elastic processes and losses due to the Penning and associative ionization processes are reported for temperatures ranging from 1 μK to 1 K. The sensitivity of the rate constants to uncertainties in the molecular potentials and autoionization widths has been investigated. The total ionization loss rates were found to be sensitive to the short-range form of the $^1\Sigma_g^+$ molecular potential and the autoionization widths, while the total elastic rate constants exhibit greater sensitivity to the short-range $^5\Sigma_g^+$ molecular potential.

PACS number(s): 34.50.−s, 32.80.Dz, 32.10.Hq

Over the past decade there has been a growing experimental interest in the cooling and trapping of metastable helium [1–12]. There has also been a focus on producing an intense, slow and well-collimated beam of metastable helium atoms [13–15] that can be used in molecular spectroscopy, atom-optics experiments, and to investigate scattering processes that are inaccessible using conventional techniques. This interest has been motivated in part by the possibility of attaining Bose-Einstein condensation in spin-polarized triplet helium $\mathrm{He}^*(2\,^3S)\uparrow$ [2,16–18].

The investigation of cold collisions of metastable helium atoms has been necessitated by their consequences for the performance of cooling and trapping applications. Of particular interest are the ionization reactions that limit the achievable density of atoms within the trap:

$$\mathrm{He}^* + \mathrm{He}^* \rightarrow \begin{cases} \mathrm{He} + \mathrm{He}^+ + e^-, \\ \mathrm{He}_2{}^+ + e^-, \end{cases} \tag{1}$$

where the first of these processes is Penning ionization (PI) and the second is associative ionization (AI). There have been detailed theoretical studies of collisions of spin-polarized metastable triplet helium atoms to investigate the feasibility of Bose-Einstein condensation [17,18], and Julienne and Mies [19] have investigated the threshold behavior of the Penning ionization process to provide a theoretical estimate for the ionization rate coefficient for unpolarized metastable triplet helium. Recently several experimental studies of optical collisions of cold metastable helium atoms have been undertaken [20–24]. As part of some of these investigations [21–23] the ionization rate constant in the absence of the external field has been measured. Mastwijk *et al.* [21] and Kumakura and Morita [22] have also reported theoretical predictions. However, little detail has been provided about these calculations and no consideration has been given to the sensitivity of the calculated rate constants to the input molecular potentials or the representation of the Penning and associative ionization processes.

This present investigation involves a close-coupled calculation for field-free collisions of metastable triplet helium atoms, in which the Penning and associative ionization processes are represented by a complex optical potential. The elastic and loss rate coefficients due to Penning and associative ionization are calculated and the sensitivity of these rate constants to the molecular potentials and autoionization widths are investigated.

The quantum close-coupling theory involves the expansion of the total wave function in terms of a complete set of molecular basis states $|R,J\,M_J\,j\,l\rangle$ and a set of unknown radial functions $F^J_{jl,j'l'}(E,R)$:

$$|\Psi^{J\,M_J}_{j'l'}(E,R)\rangle = \sum_j \sum_l \frac{1}{R} F^J_{jl,j'l'}(E,R)|R,J\,M_J\,j\,l\rangle, \tag{2}$$

where E is the total energy of the system, R is the internuclear separation of the two colliding atoms, and the molecular basis states are given by

$$|R,J\,M_J\,j\,l\rangle = \sum_{M_l M_j} C(j\,l\,J;M_j\,M_l\,M_J)\,Y_{l,M_l}(\hat{\mathbf{R}})|R,j\,M_j\rangle. \tag{3}$$

The set of spherical harmonics $Y_{l,M_l}(\hat{\mathbf{R}})$ represents the relative rotational motion of the nuclei, $|R,j\,M_j\rangle$ is the molecular state that approaches asymptotically the total electronic state of the two free atoms, and $C(j_1\,j_2\,j_3;m_1\,m_2\,m_3)$ is a Clebsch-Gordan coefficient [25]. Here l and M_l are, respectively, the quantum numbers associated with the relative rotational angular momentum $\mathbf{l}$ and its the projection onto the quantization axis Oz in the space-fixed frame $Oxyz$, and the quantum numbers j and M_j are associated with the total electronic angular momentum $\mathbf{j}$ and its projection onto the space-fixed quantization axis, respectively. The Hund's case-(e) molecular basis states $|R,J\,M_J\,j\,l\rangle$ are total angular-momentum states where the total angular momentum of the system is $\mathbf{J}=\mathbf{l}+\mathbf{j}$, and M_J is the projection of $\mathbf{J}$ onto the Oz axis. For field-free collisions J and M_J are conserved and the close-coupled equations for the radial functions $F^J_{jl,j'l'}(E,R)$ are independent of M_J.

The close-coupled scattering equations are generated by using the expansion of the total wave function, Eq. (2), in the time-independent Schrödinger equation and forming the inner product with the individual basis states, Eq. (3). For collisions of two metastable triplet helium atoms the total Hamiltonian is $H=T+H_{\mathrm{rot}}+H_{\mathrm{el}}+H_{\mathrm{sd}}$, where T

$=(-\hbar^2/2\mu R)\,d^2/dR^2\,R$ is the radial kinetic-energy operator of the two atoms, $H_{\rm rot}=\mathbf{l}^2/(2\mu R^2)$ is the kinetic-energy operator of the rotating molecule of reduced mass μ, and the electronic Hamiltonian is $H_{\rm el}=H_1+H_2+H_{12}$, for which H_1 and H_2 are the Hamiltonians for the unperturbed atoms and H_{12} is the Hamiltonian for the electrostatic interaction between the two atoms. $H_{\rm sd}$ is the Hamiltonian for the spin-dipole interaction. Within the Born-Oppenheimer approximation and the pure precession approximation, which assumes l to be a good quantum number for all internuclear separations R, the matrix elements of the Hamiltonian terms can be evaluated explicitly [18] to obtain the N coupled second-order differential scattering equations:

$$\left[\frac{d^2}{dR^2}-\frac{l''(l''+1)}{R^2}-\frac{2\mu}{\hbar^2}\,{}^{2S+1}V_\Sigma(R)+k^2\right]F^J_{j''l'',j'l'}(E,R)$$

$$=\frac{2\mu}{\hbar^2}\sum_j\sum_l V^{\rm sd}_{j''l'';jl}(R)F^J_{jl,j'l'}(E,R), \tag{4}$$

where

$$V^{\rm sd}_{j'l';jl}(R)=\frac{\mu_0}{4\pi}\frac{(g_s\mu_{\rm B})^2}{R^3}C^{\rm sd}(j,j')D^{\rm sd}(J,j,j',l,l'), \tag{5}$$

$$D^{\rm sd}(J,j,j',l,l')=(2l+1)^{1/2}C(l\,2\,l';000)W(J\,j'\,l\,2;l'\,j), \tag{6}$$

$C^{\rm sd}(0,0)=0, C^{\rm sd}(1,1)=\sqrt{30}, C^{\rm sd}(0,2)=C^{\rm sd}(2,0)=\sqrt{10}$ and $C^{\rm sd}(2,2)=-\sqrt{70}$. $W(abcd;ef)$ is a Racah coefficient [25], and $k^2=2\mu/\hbar^2\,[E-E^\infty]$, where E^∞ is the total internal energy of the asymptotically free atoms. For collisions of metastable triplet helium atoms, Penning and associative ionization occur at small radial separations from the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ quasimolecule states. For these states the molecular potential in Eq. (4) is replaced by the complex potential ${}^{2S+1}V_\Sigma(R)-i\,{}^{2S+1}\Gamma(R)/2$, where ${}^{2S+1}V_\Sigma(R)$ is the usual adiabatic molecular potential and ${}^{2S+1}\Gamma(R)$ is the corresponding total autoionization width representing the loss of flux due to the ionization processes [26]. In Eq. (4) the N linearly independent solutions are labeled by the singly primed quantities, and due to parity considerations there is no coupling between the gerade states ${}^1\Sigma_g^+$ and ${}^5\Sigma_g^+$ and the ungerade state ${}^3\Sigma_u^+$.

The collisions under investigation involve identical atoms, and therefore symmetrization requirements must be considered. Following Mies [27], symmetrized channel states were used in these calculations and hence properly symmetrized scattering matrices and cross sections were calculated. This particular collision system involves identical nuclei of zero spin and the symmetrization of the channel states has the consequences that for the gerade states ${}^1\Sigma_g^+$ and ${}^5\Sigma_g^+$ of the molecule only even partial-wave values contribute to the scattering process, while for the ungerade state ${}^3\Sigma_u^+$ only odd partial-wave values contribute.

The scattering cross section for transitions from states with electronic angular momenta j_i to states with electronic angular momenta j_f is given by

$$\sigma(E;j_i\to j_f)=\frac{\pi}{k_i^2}\sum_{l_il_fJ}\left(\frac{2J+1}{2j_i+1}\right)$$

$$\times|\,\delta_{j_i,j_f}\delta_{l_i,l_f}-S^J(E;j_il_i\to j_fl_f)|^2, \tag{7}$$

where $S^J(E;j_il_i\to j_fl_f)$ are the scattering matrix elements extracted from the asymptotic solutions of Eq. (4), and the total scattering cross section is defined as

$$\sigma^{\rm tot}(E)=\sum_{j_i}(2j_i+1)\sigma(E;j_i\to j_f)\Big/\sum_{j_i}(2j_i+1). \tag{8}$$

The scattering matrix element for Penning ionization from the initial state Γ_i can be obtained from the calculated, nonunitary $N\times N$ scattering matrix [18]:

$$|S_{\Gamma_i\to\Gamma_{\rm PI}}|^2=1-\sum_{\Gamma'=1,N}|S_{\Gamma_i\Gamma'}|^2. \tag{9}$$

The rate coefficient is given by $K(T)=\langle\sigma(E)\,v_i\rangle$, where $v_i=\hbar\,k_i/\mu=(2E/\mu)^{1/2}$ and the angle brackets denote an average over the distribution of the relative velocities of the colliding atoms. For identical atoms the loss rate constants involve a factor of 2 times the transition rate constants since two atoms are lost per collision event. Loss-rate constants are reported in the present study, with the exception of the total ionization rate constant K_{SS}, which is most commonly reported by experimentalists.

The ${}^5\Sigma_g^+$ adiabatic molecular potential calculated by Stärck and Meyer [28] was used in this close-coupled scattering calculation. The potentials for the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ molecular states, and the corresponding autoionization widths ${}^1\Gamma(R)$ and ${}^3\Gamma(R)$, were obtained from Müller *et al.* [26]. Since the ${}^5\Sigma_g^+$ potential is claimed to be the more accurate potential, the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ potentials were modified to have the same long-range form as the ${}^5\Sigma_g^+$ potential. The short-range form given by Müller *et al.* [26] was maintained for $R<12\,a_0$, and for $R\geqslant 12\,a_0$ the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ potentials differ from the ${}^5\Sigma_g^+$ potential by an exchange energy term. The sensitivity of the calculations to the uncertainty in these molecular potentials and the autoionization widths has been numerically investigated. To study the dependence of the results on the form of the autoionization widths, an alternative form, $\Gamma_{\rm GMS}(R)=0.3\exp(-R/1.086)$, suggested by Garrison *et al.* [29], has also been used. This exhibits a steeper exponential behavior and does not dampen at small internuclear separations like that of Müller *et al.* [26]. The present close-coupled calculation has been performed using the numerical techniques employed in Ref. [18] and the results reported in this investigation are accurate to better than 1% for all temperatures considered.

The rate constants for the various elastic and ionization loss processes involved in field-free collisions of metastable helium atoms are shown, as a function of temperature, in Fig. 1. The rate constants were calculated for temperatures ranging from 1 nK to 1 K, but in Fig. 1 are only shown down to $T=1\,\mu$K, where the threshold temperature dependence for all transitions is already evident.

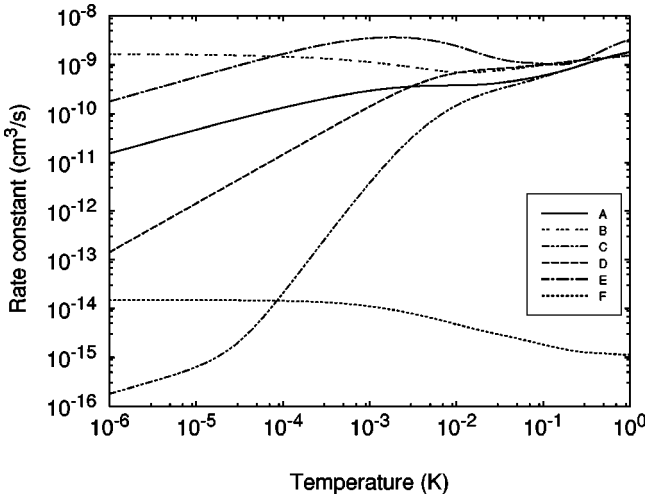

FIG. 1. Elastic and ionization loss rate constants as a function of temperature for various transitions: (A) $j=0\rightarrow j=0$, (B) $j=0\rightarrow PI$, (C) $j=1\rightarrow j=1$, (D) $j=1\rightarrow PI$, (E) $j=2\rightarrow j=2$, and (F) $j=2\rightarrow PI$.

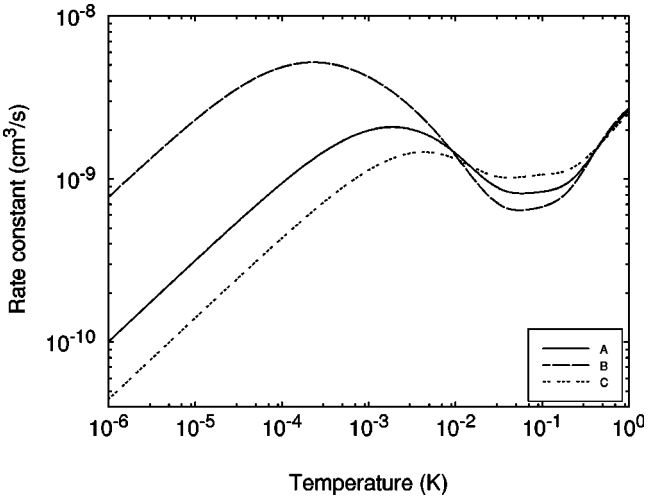

FIG. 2. Total elastic rate constant as a function of temperature for (A) no variation, (B) $+1\%$, and (C) -1% variation of the short-range $^5V_\Sigma(R)$ potential.

Elastic scattering in the $^5\Sigma_g^+$ molecular state dominates the elastic-scattering processes and contributes to at least 70% of the total elastic rate constant, for all temperatures considered. For $T\lesssim 10$ mK, elastic scattering in the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states contributes less than 10% to the total elastic rate constant. The total loss rate due to Penning and associative ionization is dominated by loss from the $^1\Sigma_g^+$ molecular state for $T\lesssim 1$ mK, but for higher temperatures where higher partial waves contribute, loss from the $^3\Sigma_u^+$ state becomes important. Penning and associative ionization from the $^5\Sigma_g^+$ molecular state is spin forbidden, and loss due to these processes is only possible through spin-relaxation-induced Penning ionization, which is mediated by the spin-dipole interaction. The loss rate constants for spin-relaxation-induced Penning ionization from the $^5\Sigma_g^+$ molecular state, shown in Fig. 1, are at least five orders of magnitude smaller than for loss from the $^1\Sigma_g^+$ state, across the temperature range considered. This is in agreement with previous predictions from detailed studies of spin-polarized metastable triplet helium [17,18] and from an estimate of the threshold loss rate from the $^1\Sigma_g^+$ state [19].

The rate constants for the $^1\Sigma_g^+$ and $^5\Sigma_g^+$ molecular states exhibit the expected low-temperature threshold behavior [30,31] for *s*-wave scattering, with the elastic-scattering rate constants varying as k and the ionization rate constants tending to a constant. For low temperatures the contribution from *p* waves is small and therefore the low-temperature rate constants for the $^3\Sigma_u^+$ state are small. The elastic scattering rate constants for the $^3\Sigma_u^+$ molecular state, for temperatures $T\lesssim 10^{-5}$ K, display the appropriate k^1 dependence for *p*-wave scattering and the R^{-3} spin-dipole interaction. For $5\times 10^{-5}\lesssim T\lesssim 5\times 10^{-3}$ K, the elastic-scattering rate constants for $^3\Sigma_u^+$ switch to a k^5 dependence that is due to *p*-wave scattering and the long-range R^{-6} potential. The ionization rate constants for the triplet state display a k^2 dependence, consistent with inelastic *p*-wave scattering.

The sensitivity of the rate constants to the potentials and the autoionization widths was investigated by considering a 1% variation of the short-range molecular potentials, which is within the claimed accuracy of the potentials [28], and by considering various forms of the autoionization width. It was shown in previous studies [18,32] that the rate constants display little sensitivity to the long-range form of the potential and that the number of bound states does not change with the 1% variation of the short-range potential.

The total elastic rate constant was found to be most sensitive to the $^5\Sigma_g^+$ molecular potential. As displayed in Fig. 2, for temperatures less than 1 mK, a $+1\%$ variation of the $^5\Sigma_g^+$ molecular potential resulted in a factor of 7.5 increase, whereas a -1% variation produced a factor of 2.3 decrease. For higher temperatures the variation was greater than 5%. The total loss rate due to Penning and associative ionization displays a sensitivity to the form of the autoionization width, as shown in Fig. 3, with variations in the rate constant values as large as 10% for temperatures less than 1 mK. For $T\lesssim 1$ mK, the total ionization loss-rate constant exhibits a greater sensitivity to the short-range $^1\Sigma_g^+$ molecular potential with variations as large as 20% in the rate constant values. For higher temperatures, where loss from the $^3\Sigma_u^+$ state contributes, the total ionization rate constant is also sensitive to the short-range $^3\Sigma_u^+$ potential with changes of up to 15% observed.

Table I gives the rate constant for Penning and associative ionization for temperatures of 0.5 mK and 1 mK. The possible range of rate constant values, arising from variation of the molecular potentials within the claimed accuracy and various forms of the autoionization widths, is also shown.

Existing theoretical and experimental values for K_{SS} are tabulated in Table I. The results of the present investigation at $T=1$ mK are in close agreement with the theoretical value reported by Mastwijk *et al.* [21], which was obtained from a quantum-mechanical scattering calculation using the potentials of Müller *et al.* [26]. The theoretical prediction for K_{SS} provided by Kumakura and Morita [22] is much larger than

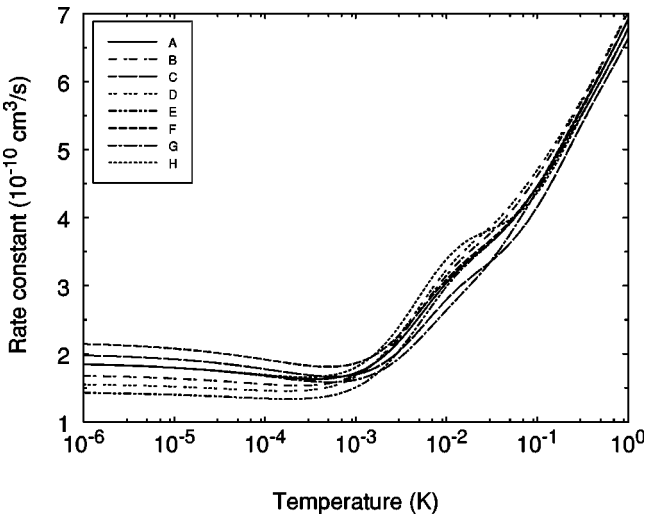

FIG. 3. Total ionization loss rate constant as a function of temperature for (A) no variation; the autoionization widths (B) $\Gamma_{GMS}(R)$, (C) $0.5\Gamma_{GMS}(R)$, and (D) $2\Gamma_{GMS}(R)$; (E) $+1\%$ and (F) -1% variation of the short-range $^1V_\Sigma(R)$ potential, and (G) $+1\%$ and (H) -1% variation of the short-range $^3V_\Sigma(R)$ potential.

the other theoretical estimates. It was calculated using a simple model assuming unit ionization probability for partial waves able to cross the centrifugal barrier. Julienne and Mies [19] have also theoretically estimated the bounds for the threshold rate constant for Penning ionization from the $^1\Sigma_g^+$ molecular state. The lower bound of $5\times10^{-10}\,\mathrm{cm^3\,s^{-1}}$ was obtained in the limit $T\rightarrow0$, while the upper bound was calculated from the unitarity limit for $T=100\,\mu$K to be $1\times10^{-9}\,\mathrm{cm^3\,s^{-1}}$. In the present investigation, the rate constant for Penning and associative ionization from the $^1\Sigma_g^+$ molecular state, for $T=100\,\mu$K, was calculated to be $7.4\times10^{-10}\,\mathrm{cm^3\,s^{-1}}$, and variation of the potential and autoionization width for the $^1\Sigma_g^+$ molecular state produced values ranging from 5.8×10^{-10} to $8.4\times10^{-10}\,\mathrm{cm^3\,s^{-1}}$.

TABLE I. Total ionization rate constant K_{SS} for various temperatures. For the present calculations the possible range of values of K_{SS} arising from variation of the potentials is also given.

Temperature	K_{SS} ($10^{-10}\,\mathrm{cm^3\,s^{-1}}$)	
	Theoretical	Experimental
0.5 mK	0.82	
	($0.69\leqslant K_{SS}\leqslant0.91$)	
	2.2 [a]	3.8 ± 1.1 [a]
1 mK	0.86	
	($0.75\leqslant K_{SS}\leqslant0.93$)	
	0.73 [b]	2.7 ± 1.2 [b]
		1.3 ± 0.2 [c]

[a]Reference [22]. [c]Reference [23].
[b]Reference [21].

The theoretical values obtained in this investigation, and that of Mastwijk *et al.* [21], are significantly lower than the reported experimental values. Although the present study has shown that the theoretical predictions are sensitive to uncertainties in the molecular potentials and autoionization widths used in the calculations, the variation in the results is not sufficient to produce agreement with experiment.

We thank P.J. Leo for useful comments about particular aspects of this work.

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