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a S Dickinson. Quantum-reflection model for Penning ionization rate coefficients in cold collisions of metastable helium and rubidium. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 2010, 43 (21), pp.215302. 10.1088/0953-4075/43/21/215302 . hal-00569861

HAL Id: hal-00569861

<https://hal.science/hal-00569861>

Submitted on 25 Feb 2011

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Quantum-reflection model for Penning ionization rate coefficients in cold collisions of metastable Helium and Rubidium.

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Abstract. A quantum-reflection model is employed to calculate the rate coefficient for the Penning Ionization of Rubidium by cold metastable Helium atoms in unpolarized collisions. Various results for the p -wave transmission coefficient on a $1/R^6$ long-range potential are discussed. The dispersion coefficient for the interaction of these atoms is estimated as 3540 atomic units. The calculated value of the rate coefficient is about four times lower than the recently measured value (Byron et al., Phys. Rev. A **81** 01405 2010) for this process when both atoms are held in magneto-optical traps.

PACS numbers: 34.50.-s, 34.50Fa

30 July 2010

1. Introduction

It was realised by Orzel et al. (1999) that Penning ionization (PI) in cold collisions can be studied using a simple model where every collision reaching the short-range region can be assumed to lead to ionization. Access to the short-range region is limited by quantum reflection on the long-range potential. For collisions of cold metastable Xe atoms, (Xe*) Orzel et al. (1999) obtained good agreement between their calculations using this model and their measurements. This quantum-reflection model was also used successfully by Stas et al. (2006, 2007) and McNamara et al. (2007) for the possible collisions between the stable isotopes of metastable Helium (He 2 3S_1 , He*) at mK temperatures. Here it was assumed that ionization occurred only on collisions following the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ He₂ molecular potentials.

Dickinson (2007) combined this model with the analytic near-threshold results by Friedrich's group (Friedrich and Trost, 2004, 2007) for quantum reflection on long-range inverse-power potentials. This provided a simple, closed-form expression, using only the C_6 dispersion coefficient and the reduced mass, for the ionization rate coefficient and reproduced the work of Stas et al. (2006, 2007) and McNamara et al. (2007) for He*. This model can also be shown to agree with the Xe* calculations of Orzel et al.

(1999). Dickinson (2007) employed a unitarized approximation from Friedrich and Trost (2004) for s -wave collisions. Recent work by Dashevskaya et al. (2009) has shown that this approximation differed from an accurate numerical solution for s -wave quantum reflection by less than 3%.

Stimulated by the recent measurement of Byron, Dall and Truscott (2010) of Penning Ionization of Rb by He^* at a temperature of about 1 mK we have employed the quantum-reflection model for this system. Since the experiment involved both the He^* and the Rb held in Magneto-Optical Traps (MOTs) our calculated values cannot be compared directly with the result of this experiment. We have also investigated some recent results (Dashevskaya et al., 2009; Quéméner and Bohn, 2010) for p -wave quantum reflection. For the He^* -Rb system when this work started we were unaware of any published calculations of the C_6 dispersion coefficient and consequently a simple estimate of the value of this coefficient was made. Fortunately the dominant s -wave contribution to the PI rate coefficient is sensitive primarily to $C_6^{1/4}$ (Dickinson, 2007), reducing the importance of uncertainties in the value of C_6 .

Atomic units are used unless stated otherwise.

2. Theory

2.1. Transmission probability for p -waves on $1/R^6$ potential.

Previously (Dickinson, 2007) we used the low-temperature limit (Friedrich and Trost, 2004) of the p -wave contribution. More recently Dashevskaya et al. (2009) have solved the Schrödinger equation numerically for the p -wave transmission coefficient, $P_p(k)$, k being the wavenumber, and provided an analytic fit to their results. While they don't compare their fit explicitly to their numerical values, the corresponding results for the $1/R^4$ potential suggest the error should be no more than a few percent. We have used this fit to determine the rate coefficient numerically.

Very recently, in the context of cold reactive p -wave collisions of identical fermions, Quéméner and Bohn (2010) have used an alternative model. They assumed that the transmission coefficient behaves as k^3 , its threshold behaviour, until the energy reaches the height of the p -wave centrifugal barrier, V_b where the probability is assumed to be unity and also for all higher energies. We have used this probability to determine the p -wave cross section, σ_p and integrated this p -wave cross section analytically to find the p -wave contribution to the rate coefficient:

$$k_p^{QB}(T) = \frac{\beta \hbar \pi T}{\mu T^*} \left(\frac{3^{17/4}}{2^{19/4}} \right) \left[\text{erf}(\sqrt{x_0}) - 2\sqrt{x_0/\pi} \exp(-x_0) \right], \quad (1)$$

where $\beta = (2\mu C_6/\hbar^2)^{1/4}$, μ is the reduced mass, $x_0 = V_b/(k_B T) = 2(2/3)^{3/2}(T^*/T) \approx 1.089(T^*/T)$, $T^* = \hbar^2/(2\mu\beta^2 k_B)$ and k_B is Boltzmann's constant. Note that the scaled temperature T_0 introduced in Dickinson (2007) is related to T^* by $T_0 = \frac{16}{\pi^2}[\Gamma(5/4)]^4 T^* \approx 1.094 T^*$. The low-temperature limit of (1) agrees with the expression of Quéméner and Bohn (2010).

Guided by this temperature dependence we have attempted to fit our numerical result based on the transmission probability of Dashevskaya et al. (2009):

$$K_p(T) \approx \frac{\beta\hbar 5.73 T}{\mu T^*} \left[\operatorname{erf}(\sqrt{x_1}) - 2\sqrt{x_1/\pi} \exp(-x_1) \right], \quad (2)$$

where $x_1 = 1.826(T^*/T)$. This fit agrees with the low- and high-temperature limits of the Dashevskaya et al. (2009) expressions. Note that the low-temperature limit of their expression differs by about 13% from the analytic result of Friedrich and Trost (2004). As Dashevskaya et al. (2009) note 'tolerating an incorrect behavior of the small probability in the limit $k \rightarrow 0$ allows one to achieve a better approximation in the region where the probability is noticeable.'

However at intermediate temperatures the value of $K_p(T)$ can deviate by up to about 35% from the numerical values, $k_p^{DLNT}(T)$ based on the transmission probability results of Dashevskaya et al. (2009). Accordingly we have introduced a correction, based on the behaviour of the Morse potential function:

$$\begin{aligned} \operatorname{Corr}(x) = & 1 - 0.4 \{ \exp[-2.4 \ln 2(x - 1.1)] \\ & - 2 \exp[-1.2 \ln 2(x - 1.1)] \}, \end{aligned} \quad (3)$$

$$k_p^{DLNT}(T) = K_p(T) / \operatorname{Corr}(x_1). \quad (4)$$

The value of $k_p^{DLNT}/(\beta\hbar/\mu)$ peaks at about 3.8 at $T^* \approx 4$. Deviations from the numerical results for $T^* \leq 3$ range between +5% at $T^* \approx 1$ and -11% at $T^* = 3$.

The transmission probability, the p -wave cross section, $\sigma_p(\kappa)$, where $\kappa = k\beta$ and the p -wave rate coefficient, in units of $(\beta\hbar/\mu)$, are compared in Figure 1. It can be seen that the threshold analytic result of Friedrich and Trost (2004) for the transmission probability is significantly smaller than the approximation of Quéméner and Bohn (2010) below their unitarity limit, which is reached at $\kappa \approx 1$. Above about $\kappa = 1.25$ their cross-section expression is superior to the threshold result, converging to that of Dashevskaya et al. (2009) by about $\kappa = 2.5$. Consistent with this behaviour, their rate-coefficient values lie significantly below those of Quéméner and Bohn (2010). The fit, (4), can be seen to be in satisfactory agreement with the numerical results. However, because the low-energy cross section contributes relatively little to the rate coefficient, the low-temperature limit of the rate coefficient differs from the numerical result by more than 20% for $T^* > 0.25$.

2.2. Estimation of the C_6 coefficient

We employ the expression for the C_6 coefficient between species 1 and 2 in terms of dipole oscillator strengths (Hirschfelder et al., 1964):

$$C_6^{(1,2)} = \frac{3}{2} \mathbf{S}'_s \mathbf{S}'_t \frac{f_s^{(1)} f_t^{(2)}}{\omega_s^{(1)} \omega_t^{(2)} (\omega_s^{(1)} + \omega_t^{(2)})}, \quad (5)$$

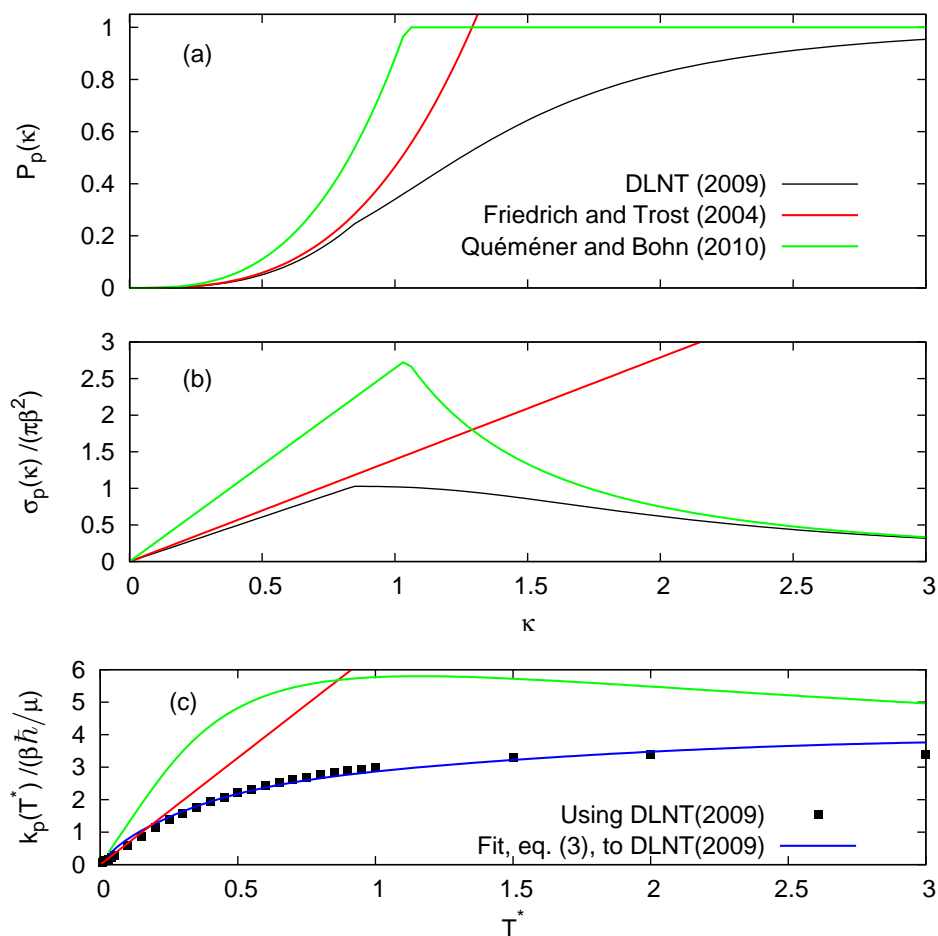


Figure 1. (a): The p -wave transmission coefficient, $P_p(\kappa)$; (b): cross section, $\sigma_p(\kappa)$; (c): rate coefficient $k_p(T^*)$ using the results of Dashevskaya et al. (2009), denoted DLNT(2009); Friedrich and Trost (2004) and Quéméner and Bohn (2010).

where \mathbf{S}' denotes a sum over discrete states, omitting the initial state, and an integral over the continuum states, $f_n^{(i)}$ and $\hbar\omega_n^{(i)}$ are the dipole oscillator strength and the transition energy, respectively, between state n and the initial state of species i .

Since the resonance transition of Rb (species 2) provides almost all the contributions to the the Thomas-Reiche-Kuhn dipole oscillator strength sum rule, it is convenient to approximate the sum over t in (5) by its leading term yielding

$$C_6^{(1,2)} \approx \frac{3 f_1^{(2)}}{2 \omega_1^{(2)}} \mathbf{S}'_s \frac{f_s^{(1)}}{\omega_s^{(1)} (\omega_s^{(1)} + \omega_1^{(2)})}. \quad (6)$$

Taking the Rb oscillator strength as 1.029 (Zhang and Mitroy, 2007) and using this single-term approximation for the Rb–Rb C_6 coefficient yields a value about 15% below that obtained in the full calculation of Derevianko et al. (2001).

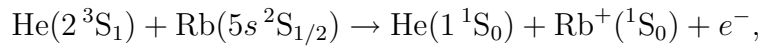
Employing all the available He^* oscillator strengths and transition energies from

Wiese and Fuhr (2009*a,b*) we obtain, summing over He levels up to 10^3P , $C_6^{(1,2)} = 3540$. To estimate the uncertainty in this value of C_6 we assumed that He* could be treated as a one-electron system and that the oscillator strength for the transition to 11^3P provided the remainder (0.342) of the oscillator-strength sum rule. This gave an additional contribution of 230, an approximately 7% correction. We note that this value lies between that for He*–He*, 3277 (Yan and Babb, 1998) and Rb–Rb, 4691 (Derevianko et al., 2001) and about 10% below the geometric mean of the two pure-species C_6 coefficients, a general approximation suggested by Hirschfelder et al. (1964).

Peach (2010) has recently calculated a value of 3685 a.u. for the He*–Rb C_6 coefficient, using a method based on atomic model-potentials. This value differs by less than 5% from that obtained here and is consistent with the additional estimated contribution from the 11^3P He* level giving an upper bound. Given the low sensitivity of the rate coefficient to the value of the C_6 coefficient, we assumed simply 3540.

2.3. Penning Ionization Rate Coefficient

In the reaction of interest



the reactants can collide at short range along the $^4\Sigma^+$ and $^2\Sigma^+$ molecular potentials. Neglecting the spin-orbit interaction, by spin conservation only the $^2\Sigma^+$ interaction can lead to Penning Ionization. We need to examine the possible effect of the Rb hyperfine structure since in the experiment of Byron, Dall and Truscott (2010) the ^{87}Rb atoms were prepared in the $f = 2$ level, f denoting the total angular momentum of the system, including the nuclear contribution. This is the upper of the two ^{87}Rb electronic ground state levels. At long range, for collisions between atoms in their S -states where one atom, denoted 1, has no nuclear spin, the colliding states are best described by a representation $|s_1(s_2i_2)f_2FM_F\rangle$. Here $s_1(= 1)$ and $s_2(= 1/2)$ are the electron spins of the He* and of the Rb, respectively, $i_2(= 3/2)$ is the nuclear spin of the ^{87}Rb , $\mathbf{f}_2 = \mathbf{s}_2 + \mathbf{i}_2$ is the Rb total angular momentum, $\mathbf{F} = \mathbf{f}_2 + \mathbf{s}_1$ is the total angular momentum of the system, apart from the angular momentum of relative motion and M_F is the z-component of \mathbf{F} . At short range the system is best described in a representation $|(s_1s_2)Si_2FM_F\rangle$, where $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$ is the total electron spin and now $\mathbf{F} = \mathbf{S} + \mathbf{i}_2$.

Following McNamara et al. (2007) in their discussion of $^4\text{He}^* - ^3\text{He}^*$ collisions, we neglect the coupling of the relative motion and the internal motion and assume that the transition between the states at long-range, best described as products of atomic states, and the short-range molecular states ($^2\Sigma^+$ and $^4\Sigma^+$), is well described as diabatic. Hence we simply expand the long-range atomic product states on to the short-range molecular states and add their contributions.

Using standard angular momentum theory we have

$$|f_2 F M_F\rangle = (-1)^{s_1+s_2+F+i_2} (2f_2+1)^{1/2} \times \sum_S (2S+1)^{1/2} \left\{ \begin{array}{ccc} s_1 & s_2 & S \\ i_2 & F & f_2 \end{array} \right\} |S F M_F\rangle, \quad (7)$$

where the fixed angular momenta s_1 , s_2 and i_2 have been omitted from the state vectors for brevity and $\left\{ \begin{array}{ccc} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{array} \right\}$ denotes a 6-j coefficient. Recognising that rate coefficients will be independent of M_F we have

$$\bar{K}(f_2) = (2f_2+1)^{-1} (2s_1+1)^{-1} \sum_F (2F+1) K(f_2 F),$$

where $\bar{K}(f_2)$ is the rate coefficient from Rb level f_2 and $K(f_2 F)$ is the rate coefficient from level f_2 when the composite system has angular momentum F . Then, using the weights from (7),

$$\bar{K}(f_2) = (2f_2+1)^{-1} (2s_1+1)^{-1} \sum_F (2F+1) \sum_S (2f_2+1)(2S+1) \left\{ \begin{array}{ccc} s_1 & s_2 & S \\ i_2 & F & f_2 \end{array} \right\}^2 \kappa(S), \quad (8)$$

where $\kappa(S)$ is the rate coefficient for atoms colliding on the short-range $(^{2S+1}\Sigma^+$ potential, since at short range the hyperfine structure can be ignored. Performing the sum over F in (8) we obtain

$$\bar{K}(f_2) = (2s_1+1)^{-1} (2s_2+1)^{-1} \sum_S (2S+1) \kappa(S). \quad (9)$$

We note that $\bar{K}(f_2)$ is independent of the value of f_2 so, in effect, consideration of the hyperfine structure was unnecessary. This result, (9) is consistent with the weightings employed by McNamara et al. (2007) in their study of collisions between $^3\text{He}^*$ and $^4\text{He}^*$. Hence the maximum probability of ionization in a close He^* -Rb collision is $1/3$.

Using the s -wave model described fully in Dickinson (2007) and the p -wave model based on the fit of Dashevskaya et al. (2009) to the p -wave quantum-reflection probability described in Section 2.1 the results obtained are shown in Figure 2. Here the s -, p - and d -wave contributions have been included, although the d -wave contribution is negligible in the temperature range shown.

In the experiment of Byron, Dall and Truscott (2010) the temperatures of the He^* and Rb atoms were 1 mK and 100 μK , respectively. Assuming that the MOTs maintained the gas clouds at these temperatures and no significant temperature equilibration occurred the temperature, T_{rel} of the relative motion is given by (Viehland and Mason, 1975, eq.(A26))

$$\frac{T_{\text{rel}}}{\mu} = \frac{T_{\text{He}}}{m_{\text{He}}} + \frac{T_{\text{Rb}}}{m_{\text{Rb}}}, \quad (10)$$

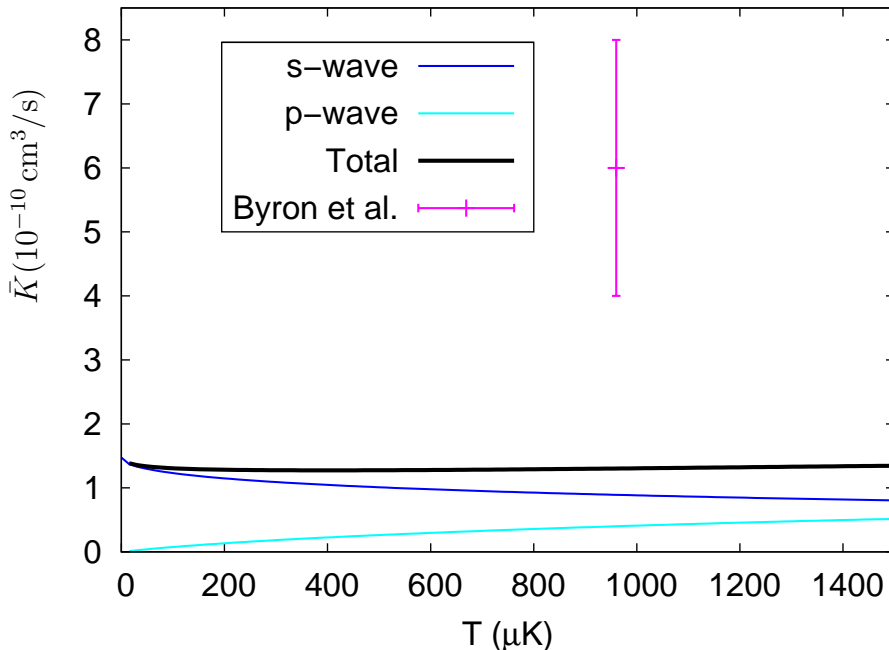


Figure 2. Penning Ionization rate coefficients for cold He^* -Rb collisions. The measured value (Byron, Dall and Truscott, 2010) is not directly comparable - see text.

where μ is the reduced mass, T_{He} and T_{Rb} are temperatures of the He and Rb atoms, respectively, and m_{He} and m_{Rb} are the corresponding masses. Using (10), $T_{\text{rel}} = 0.96$ mK. The value of the reduced temperature, T^* is about 3.2 mK.

The measured value, also shown in Figure 2, involves collisions in MOTs of both He 2^3S and He 2^3P with Rb($5s$) and Rb($5p$), where none of the sub-level populations are known so direct comparison cannot be made with this calculated value for equilibrium sub-level populations of He^* and Rb($5s$).

3. Conclusion

Given the insensitivity of the the PI rate coefficient to the value of the C_6 coefficient, the calculated value of the rate coefficient appears rather low compared to experiment. However, the upper levels of the optical transitions in the MOTs will almost certainly have stronger long-range interactions, enhancing the rate coefficient. Also the leading long-range interaction between He 2^3P and Rb $5p^2\text{P}$ will behave as $1/R^5$.

The assumption of 100% ionization probability on transmission to the inner $^2\Sigma^+$ potential curve clearly gives an upper bound to its contribution but a three-fold enhancement of the PI rate coefficient could arise if ionization occurs from the $^4\Sigma^+$ entrance channel. While the spin-orbit interaction is undoubtedly larger in Rb than in He^* , it appears unlikely to be important in the ground S level and the electron spin-spin He^* -Rb interaction looks too weak to cause significant $^4\Sigma^+ - ^2\Sigma^+$ mixing. In

addition, the measurements of Byron, Dall, Wu Rugway and Truscott (2010), using spin-polarization of both atoms, show a suppression of the ionization rate coefficient by at least a factor of ≈ 100 , confirming that the ionization probability on the $^4\Sigma^+$ channel is indeed small.

The weak He* electron-spin – ^{87}Rb nuclear-spin ($\mathbf{s}_1 \cdot \mathbf{i}_2$) interaction could in principle lead at long range to a transition to the lower $f = 1$ level of Rb with an energy release equivalent to 0.32 K. If the atoms, particularly the He*, which gains almost all the energy released, remained bound in the trap, from (9) the $f = 1$ level has the same probability as the $f = 2$ level of following the doublet and quartet molecular potentials at short range. However the value of the rate coefficient would be somewhat larger for the higher-energy collision.

Clearly it would be of interest to have a direct measurement of the ground-state PI rate coefficient.

Acknowledgments

I thank Dr G Peach, Professor I Whittingham and Dr A Truscott for helpful discussions and in addition Dr Peach for providing her value of the C_6 coefficient in advance of publication.

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