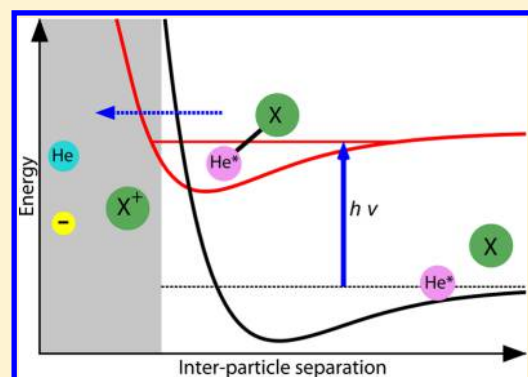


# Photoassociation Spectroscopy in Penning Ionization Reactions at Sub-Kelvin Temperatures

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**ABSTRACT:** Penning ionization reactions in merged beams with precisely controlled collision energies have been shown to accurately probe quantum mechanical effects in reactive collisions. A complete microscopic understanding of the reaction is, however, faced with two major challenges—the highly excited character of the reaction's entrance channel and the limited precision of even the best state-of-the-art *ab initio* potential energy surfaces. Here, we suggest photoassociation spectroscopy as a tool to identify the character of orbiting resonances in the entrance channel and probe the ionization width as a function of interparticle separation. We introduce the basic concept, using the example of metastable helium and argon, and discuss the general conditions under which this type of spectroscopy will be successful.



## INTRODUCTION

Understanding chemical reaction dynamics in a microscopic perspective from first-principles has been a long-standing goal in physical chemistry. Over many decades, molecular beams have been the prime tool to study gas phase reactions. Controlling the beams with electric or magnetic fields has recently rejuvenated this field.<sup>1–5</sup> In particular, merging two beams with a magnetic field<sup>6–11</sup> has allowed for continuously tuning the collision energy from room temperature down to the milli-Kelvin range. This has bridged the gap between the regimes of classical and quantum collisions and brought unprecedented precision to the low energy range. Studying, with that technique, Penning ionization reactions comes with the additional advantage of nearly unit efficiency in detecting the ionic reaction products. Orbiting resonances were thus observed at sub-Kelvin temperatures,<sup>6</sup> including an isotope effect,<sup>7</sup> and the role of internal rotation for the reaction was elucidated.<sup>11</sup> However, a complete microscopic understanding of the reaction dynamics requires high-level *ab initio* theory in addition to precise experimental data. Although the entrance channel of the reaction can be described with reasonable accuracy,<sup>12</sup> a full model of Penning ionization reactions is faced with two major challenges. First, because it necessarily involves metastable states, the entrance channel is a highly excited electronic state, which is embedded in a continuum of ionized states. The corresponding electronic wave function does not belong to the space of square integrable functions and thus cannot be correctly described by standard electronic structure methods, designed for the description of bound states. The difficulty of coupling to a continuum of ionized states can be circumvented by replacement with an imaginary potential, defined within the Fano-Feshbach formalism for an isolated resonance.<sup>13,14</sup> In this approach, a projection operator is

introduced, which allows for partitioning the total Hilbert space into discrete and continuum parts. The imaginary potential is obtained from the coupling matrix elements between wave functions in the two subspaces. However, choice and construction of the Feshbach projection operator are nontrivial, in particular in highly correlated approaches. Second, even for diatomics, the best, currently available potential energy curves are not sufficiently accurate to correctly predict the scattering length and thus exact position and character of orbiting resonances.<sup>15</sup>

Here, we suggest photoassociation spectroscopy of Penning ionization reactions to address these two issues. Photoassociation refers to the formation of a chemical bond upon laser excitation.<sup>16,17</sup> In standard photoassociation spectroscopy, the laser excites two colliding ground-state atoms to an electronically excited state. Detuning the laser frequency from the atomic excitation energy probes molecular levels below the excited-state dissociation threshold.<sup>16,17</sup> Photoassociation rates are limited by the amplitude of collision wave functions at the Condon radius, i.e., the interparticle separation where the laser frequency matches the energy difference between ground and excited potential energy surface.<sup>18</sup> At sub-Kelvin temperatures, only a few partial waves contribute to the collision and, due to the rotational barrier and quantum reflection, their wave functions have little amplitude at short interparticle separations. Photoassociation is thus most efficient at intermediate and large

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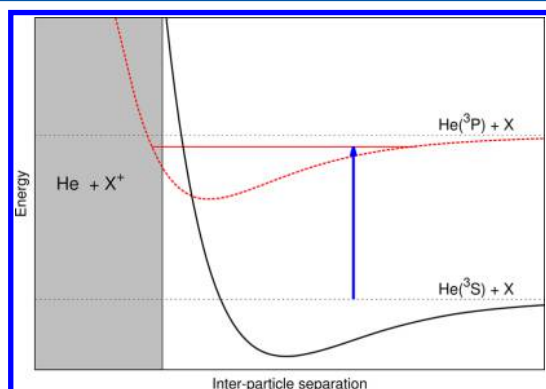
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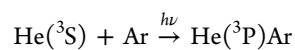
separations.<sup>19</sup> This implies excitation into weakly bound levels just below the dissociation threshold.

When applied to a collision complex undergoing a Penning ionization reaction, the electronic ground state as entrance channel is replaced by a metastable one, Figure 1. Such a



**Figure 1.** Photoassociation spectroscopy in Penning ionization. The laser, indicated by the blue arrow, excites a scattering pair colliding with collision energy  $E$  in the  $\text{He}(^3\text{S}) + \text{X}$  state into a bound rovibrational level in the potential energy curve dissociating into  $\text{He}(^3\text{P}) + \text{X}$ . The gray shaded area at short interparticle separations indicates the region where the probability for Penning ionization is almost unity. It can be estimated by assuming that Penning ionization reactions obey first-order kinetics and treating their dynamics classically.<sup>20</sup> When the bound level extends toward this region, ionization will happen faster than in the entrance channel; i.e., photoassociation will be observed in terms of an increased ionization rate.

configuration of electronic states can also be used to produce diatomic metastable helium molecules via photoassociation.<sup>21,22</sup> Though, in that case, the giant bond length of the helium dimer and symmetry constraints preclude Penning ionization, here we consider interactions where the particles approach each other close enough to Penning ionize. As a specific example, we consider photoassociation in the Penning ionization of metastable helium and argon. However, our considerations hold also when argon is replaced by a different ground-state scattering partner  $X$ . Penning ionization in collisions between  $\text{He}(^3\text{S})$  and Ar was extensively studied in the past (see ref 20 and references therein); the most recent state-of-the-art experimental investigation used velocity controlled merged beams.<sup>6</sup> As indicated by the blue arrow in Figure 1, the laser is taken to be red-detuned with respect to the  $^3\text{P} \leftarrow ^3\text{S}$  line of helium,<sup>a</sup> which is a dipole-allowed transition,



Excitation then happens into bound levels below the  $\text{He}(^3\text{P}) + \text{Ar}$  threshold. Because the excited-state potential energy curve extends to shorter interparticle separation, where the probability for Penning ionization is significantly increased, the reaction rate is larger than in the entrance channel. Such a configuration of potential energy curves, together with the orders of magnitude increase in reaction rates, has recently been reported for Penning ionization of helium and  $\text{H}_2$ .<sup>11</sup> Photoassociation should thus be measurable by an enhancement of the Penning ionization rate. However, observation of the bound levels is possible only if the Penning ionization reaction is not too fast. More quantitatively, the inverse lifetime of the bound levels due to Penning ionization needs to be

smaller than the level spacing. We will discuss the prospects for photoassociation spectroscopy for the example of the Penning ionization of metastable helium and argon, on the basis of a first-principles model.

The remainder of the paper is organized as follows: We first introduce our model and the computational details and then present our results. In particular, we discuss prospects to use photoassociation spectroscopy as a means to unequivocally identify the rotational quantum number of orbiting resonances and as a tool to map out the imaginary potential governing the ionization probability. Finally, we conclude with an assessment of the experimental viability of our proposal.

## MODEL AND COMPUTATIONAL DETAILS

The interaction between two particles undergoing a Penning ionization reaction can be modeled by means of a complex potential,<sup>20</sup>

$$W(R) = V(R) - \frac{i}{2}\Gamma(R) \quad (1)$$

where  $R$  denotes interparticle separation.  $V(R)$  is the real part of the potential, and  $\Gamma(R)$  its width, also called imaginary or optical potential. In a semiclassical picture,  $V(R)$  governs the collisional dynamics of the interacting species whereas  $\Gamma(R)$  reflects the probability for Penning ionization as a function of interparticle distance. Both  $V(R)$  and  $\Gamma(R)$  depend on the electronic state, on which the interaction takes place.

In our model of Penning ionization of metastable helium and argon, three nonrelativistic electronic states are relevant: (1)  $^3\Sigma^+$ , asymptotically dissociating into  $\text{He}(^3\text{S}) + \text{Ar}$  atoms, and (2)  $^3\Sigma^+$  and  $^3\Pi$ , dissociating into  $\text{He}(^3\text{P}) + \text{Ar}$  atoms. For each electronic state,  $V(R)$  is obtained from *ab initio* calculations. The potential of the (1)  $^3\Sigma^+$  state is taken from ref 12. For the states resulting from the interaction of argon with  $\text{He}(^3\text{P})$ , we have calculated the relevant potential energy curves by using the spin-restricted open-shell coupled cluster method restricted to single, double, and noniterative triple excitations [RCCSD(T)]. In the initial restricted open-shell Hartree–Fock (ROHF) calculations, we have alternated the occupied orbitals to force convergence of the ROHF wave function to the desired excited electronic state. A similar approach was successfully used to describe the interaction between  $\text{He}(^3\text{S}, ^3\text{P})$  and  $\text{H}_2$ .<sup>11,12</sup> Here, we have employed a doubly augmented d-aug-cc-pVQZ basis set for the helium atom and a singly augmented aug-cc-pVQZ basis set for the argon atom.<sup>23</sup> The electronic structure calculations were performed with the MOLPRO suite of codes.<sup>24</sup> The long-range part of  $V(R)$ , for  $R > 20$  bohr was taken in its asymptotic form,  $C_6/R^6$  accounting only for the leading order term, and fixing the van der Waals  $C_6$  coefficients to 214.1 au for the (1)  $^3\Sigma^+$  state,<sup>12</sup> 369.2 au for the (2)  $^3\Sigma^+$  state, and 201.9 for the  $^3\Pi$  state. To calculate the last two  $C_6$  coefficients, the polarizability for  $\text{He}(^3\text{P})$  was constructed from the sum-overstates expression as described in ref. 11

For the imaginary part, we have employed the functional form of  $\Gamma(R)$  from ref.,<sup>25</sup>

$$\Gamma(R) = Ae^{-\alpha R} + Be^{-\beta R} \quad (2)$$

where the original values of the parameters,  $A = 896$  eV,  $B = 0.0043$  meV,  $\alpha = 4.08 \text{ \AA}^{-1}$ , and  $\beta = 0.28 \text{ \AA}^{-1}$ , were obtained by a fitting procedure to reproduce the Penning ionization cross sections for collisions between  $\text{He}(^3\text{S})$  and Ar at thermal

energies.<sup>25</sup> We have assumed  $\Gamma(R)$  to be identical for all relevant electronic states. This assumption can be justified on the grounds of recent results for  $\text{He}(^3\text{S},^3\text{P}) + \text{H}_2$ ,<sup>11</sup> where calculations have shown  $\Gamma(R)$  to be almost the same for  $\text{He}(^3\text{S}) + \text{H}_2$  and  $\text{He}(^3\text{P}) + \text{H}_2$ .

The Hamiltonian for the nuclear motion in each electronic state  $n$  takes the following form:

$$\hat{H}_n = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2 l(l+1)}{2\mu R^2} + V_n(R) - \frac{i}{2} \Gamma(R) \quad (3)$$

with  $\mu$  denoting the reduced mass, and  $l$  the rotational quantum number. In the rotational kinetic energy, we have neglected the spin-rotational coupling and nonadiabatic coupling between  $^3\Sigma$  and  $^3\Pi$  states. These simplifications are justified because we are mostly interested in collision energies of the order of 1 K and relatively high partial waves,  $l \sim 7$ , where the rotational Hamiltonian is dominated by the  $l(l+1)$  term, so  $l$  is a good quantum number. Diagonalization of this Hamiltonian for each  $n$  and  $l$  gives the bound vibrational levels and continuum states. The presence of the optical potential implies complex eigenvalues,  $W_{v,l} = E_{v,l} - (i/2)\Gamma_{v,l}^p$  where  $E_{v,l}$  denotes the position of the resonance and  $\Gamma_{v,l}^p$  is the corresponding width due to Penning ionization process.

Photoassociation rate coefficients  $K_{\text{PA}}$  for collision energies  $E$  and a laser frequency  $\omega$  are obtained from the standard expression,<sup>26,27</sup>

$$K_{\text{PA}}(E, \omega) = \frac{\pi \hbar}{\mu k} \sum_l (2l+1) \sum_{v',l'} |S_{v',l'}(E, \omega, l)|^2 \quad (4)$$

where  $k = \sqrt{2\mu E/\hbar^2}$ , adapted to Penning ionization. The transition probability  $|S_{v',l'}(E, \omega, l)|^2$  for photoassociation from a continuum state with energy  $E$  just above the  $\text{He}(^3\text{S}) + \text{Ar}$  asymptote into a bound level with quantum numbers  $v', l'$  just below the dissociation limit  $\text{He}(^3\text{P}) + \text{Ar}$  reads

$$|S_{v',l'}(E, \omega, l)|^2 = \frac{\Gamma_{v',l'}^s(E, l) \cdot \Gamma_{v',l'}^d}{(E - \Delta_{v',l'})^2 + 1/4[\Gamma_{v',l'}^s(E, l) + \Gamma_{v',l'}^d]^2} \quad (5)$$

where  $\Gamma_{v',l'}^s(E, l)$  is the stimulated emission rate,  $\Gamma_{v',l'}^d$  is the total decay rate, and  $\Delta_{v',l'} = E_{v',l'} - \hbar\omega$  is the detuning of the laser frequency from the vibrational level. The total decay rate  $\Gamma_{v',l'}^d$  is the sum of the natural radiative width  $\Gamma_{v',l'}^n$  and the Penning ionization width  $\Gamma_{v',l'}^p$ . At low laser intensity  $I$ , the stimulated emission rate  $\Gamma_{v',l'}^s(E, l)$  is given by Fermi's golden rule,

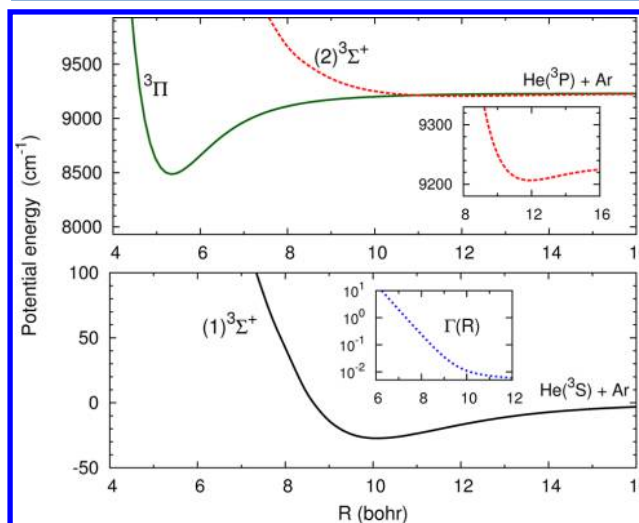
$$\Gamma_{v',l'}^s(E, l) = \frac{4\pi^2 I}{4\pi \epsilon_0 c} (2l'+1) H_l |\langle \psi_{E,l}(R) | d(R) | \psi_{v',l'} \rangle|^2 \quad (6)$$

where  $H_l$  is the Höln–London factor equal to  $(l'+1)/(2l'+1)$  for  $l' = l-1$ , to  $1/(2l'+1)$  for  $l' = l$ , and to  $l/(2l'+1)$  for  $l' = l+1$ .  $\psi_{E,l}(R)$  denotes the continuum wave function for energy  $E$  and partial wave  $l$ , obtained from diagonalization of the Hamiltonian for the  $(1)^3\Sigma^+$  state with a very large grid, whereas  $\psi_{v',l'}(R)$  is the bound-state wave function of either the  $(2)^3\Sigma^+$  or  $^3\Pi$  electronic state. The molecular transition dipole moments  $d(R)$  from  $(1)^3\Sigma^+$  to  $(2)^3\Sigma^+$  and from  $(1)^3\Sigma^+$  to  $^3\Pi$  electronic states were assumed to be constant and equal to the atomic transition dipole moment  $^3\text{S} \leftarrow ^3\text{P}$  in He, which is 2.53 au. Similarly, a constant transition dipole moment  $d$  was assumed in the calculations of the natural radiative widths  $\Gamma_{v',l'}^n$ . We do not perform any thermal averaging to calculate  $K_{\text{PA}}(E)$

because the experimental conditions with merged beams allow for probing a particular collision energy with essentially no thermal broadening. The accuracy of this approximation will be estimated below. In all photoassociation calculations we have assumed a laser intensity of 1 W/cm<sup>2</sup>.

## RESULTS

Figure 2 presents the three potential energy curves  $V(R)$  of the helium–argon collision complex relevant for photoassociation



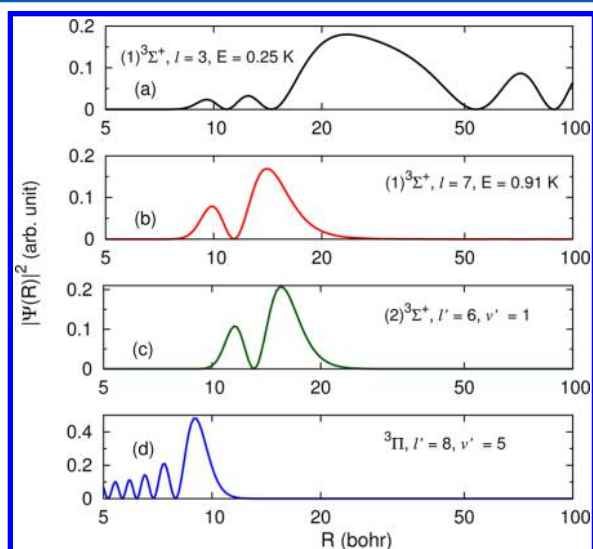
**Figure 2.** Potential energy curves for the  $(1)^3\Sigma^+$ ,  $(2)^3\Sigma^+$ , and  $^3\Pi$  electronic states. Zero interaction energy is fixed at the  $\text{He}(^3\text{S}) + \text{Ar}$  atomic asymptote. Inset in the bottom panel shows also the imaginary potential  $\Gamma(R)$  from ref 25.

in Penning ionization. Both the  $(1)^3\Sigma^+$  and  $(2)^3\Sigma^+$  states are rather shallow with their minima found at relatively large interatomic distances. More precisely, the  $(1)^3\Sigma^+$  state has a well depth of 27.3 cm<sup>-1</sup> with its equilibrium distance equal to 10.09 bohr, whereas the  $(2)^3\Sigma^+$  state has its minimum of 24.3 cm<sup>-1</sup> at 11.92 bohr. A qualitative difference is found for the potential energy curve of the  $^3\Pi$  state, which has a predicted minimum of 745 cm<sup>-1</sup> at 5.34 bohr. This pattern of the electronic states, with weakly bound  $\Sigma$  states and a strongly interacting  $\Pi$  state is fully analogous with the previously reported interaction potentials for  $\text{He}(^3\text{S},^3\text{P})$  colliding with  $\text{H}_2$  molecules<sup>11</sup> or other similar systems where a single-valence atom interacts with closed-shell species, such as  $\text{Li}(^2\text{S},^2\text{P}) + \text{H}_2$ .<sup>28</sup>

The entrance channel for photoassociation spectroscopy of the Penning ionization reaction is the  $(1)^3\Sigma^+$  state, resulting from the interaction between metastable  $\text{He}(^3\text{S})$  and ground-state Ar atoms. We consider a detuning of the photoassociation laser with respect to the  $^3\text{P} \leftarrow ^3\text{S}$  helium atomic line, so the targeted bound levels belong to either the  $(2)^3\Sigma^+$  or the  $^3\Pi$  electronic states. In our model, we neglect any nonadiabatic (spin–rotation or spin–orbit) couplings between the  $(2)^3\Sigma^+$  and  $^3\Pi$  states. These couplings should be important only for ultralow collisional energies and for the most weakly bound levels, where the  $(2)^3\Sigma^+$  and  $^3\Pi$  states are nearly degenerate. For more deeply bound levels and for sub-Kelvin or higher collision energies, the contributions from any nonadiabatic coupling would be of the order or smaller than the accuracy of the electronic potentials. Thus, we can safely neglect them without compromising the essential features of our model.



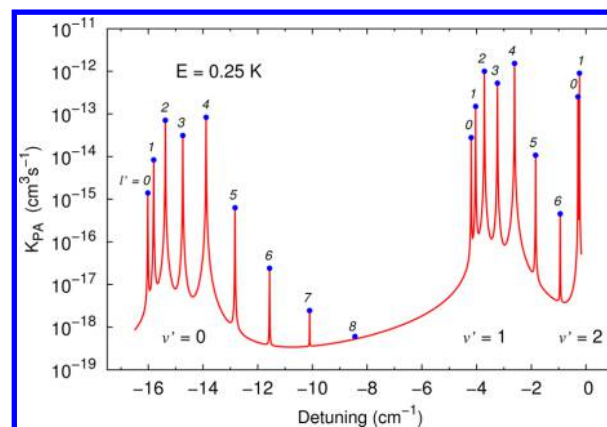
Low-energy collisions between He( $^3S$ ) and Ar are characterized by several shape resonances, as recently demonstrated in an experiment with merged beams.<sup>6</sup> The lowest two resonances are located at approximately 0.23 and 1.10 K. The positions of these shape resonances are comparatively well reproduced by our model—they occur at collisional energies of 0.25 K (partial wave  $l = 3$ ) and 0.91 K (partial wave  $l = 7$ ). Photoassociation at energies corresponding to a shape resonance is highly efficient.<sup>29</sup> The enhanced probability for transitions from a scattering state to a bound level is due to a largely increased amplitude of resonance wave functions. In other words, for an orbiting resonance, amplitude becomes trapped at short interparticle separations, inside the rotational barrier, leading to larger transition matrix elements in photoassociation. To take advantage of this enhancement, we focus on photoassociation at collisional energies matching the theoretical positions of the lowest shape resonances, i.e., 0.25 and 0.91 K. Somewhat unexpectedly, the nature of these two shape resonances is quite different. This is illustrated by the two upper panels of Figure 3, showing the wave functions of these



**Figure 3.** (a), (b) Wave functions for two considered shape resonances in  $(1)^3\Sigma^+$  state. (c), (d) Wave functions for bound levels in  $(2)^3\Sigma^+$  and  $^3\Pi$  electronic states particularly suited for photoassociation starting from the  $l = 7$  shape resonance.

resonances. The energy of the  $l = 3$  resonance is slightly above the maximum of the centrifugal barrier which is equal to 0.22 K. As a result, the wave function is fairly diffuse with only little enhancement of pair density at short interparticle distances. In contrast, the nature of the  $l = 7$  shape resonance (Figure 3b) is very different. It is energetically located deeply inside the well created by the centrifugal barrier. Thus, the amplitude of its wave function is enhanced at short interparticle separations, resembling at these distances the wave function of a typical bound level.

Photoassociation rates for levels in the  $(2)^3\Sigma^+$  and  $^3\Pi$  electronic states are obtained separately from single-channel calculations because we neglect nonadiabatic couplings. Figure 4 presents the spectrum for photoassociation into the  $(2)^3\Sigma^+$  state at a collision energy of 0.25 K. A rotational progression for three vibrational levels is clearly visible. Note that our potential energy curves are not sufficiently accurate to predict the exact detunings of these peaks. Refinement of the potentials based on



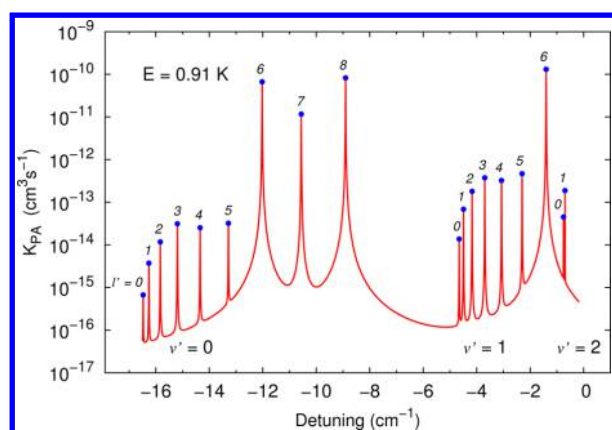
**Figure 4.** Photoassociation rates as a function of laser detuning from the He  $^3S \rightarrow ^3P$  atomic line for rovibrational levels of the  $(2)^3\Sigma^+$  state at a collision energy of 0.25 K and a laser intensity of  $1 \text{ W/cm}^2$ . The vibrational and rotational quantum numbers are indicated for each peak. The peaks for  $l' = 2, 3, 4$  are enhanced due to the  $l = 3$  shape resonance as initial state at 0.25 K, whereas for all other peaks photoassociation starts from regular scattering states.

spectroscopic information would be required to this end. However, the spacing between rotational and vibrational levels can be predicted correctly.

The highest rates in Figure 4 occur for  $2 \leq l' \leq 4$ , i.e., for bound levels that are directly accessible from the  $l = 3$  shape resonance. However, the observed enhancement of the rates compared to that of the other levels is 1 order of magnitude at most. This relatively minor resonance effect is easily explained by the above-the-barrier character of this shape resonance, and the corresponding diffuse nature of its wave function, cf. Figure 3a. The widths of the photoassociation lines range from 30 MHz (for  $v' = 2$ ) up to 160 MHz (for  $v' = 0$ ) and are almost purely determined by the Penning ionization contributions  $\Gamma_{v',l'}^p$ , because the width due to spontaneous radiative emission  $\Gamma_{v',l'}^r$  is only of the order of 1 MHz. Increase of the peak width with binding energy is readily explained by the stronger localization of the bound level amplitude at shorter interparticle separation together with the exponential increase of the ionization probability with decreasing interparticle separation, cf. eq 2. More generally, this also explains why the bound levels ionize faster than scattering states, leading to an observable signature of photoassociation in the Penning ionization reaction.

The photoassociation spectrum for bound levels in the  $(2)^3\Sigma^+$  state at a collision energy of 0.91 K is presented in Figure 5. Here, strongly enhanced peaks are observed at detunings matching the rovibrational levels with  $6 \leq l' \leq 8$ . These levels can be directly accessed from the  $l = 7$  shape resonance at 0.91 K. The enhancement due to the shape resonance is nearly 3 orders of magnitude, reaching a peak rate of  $10^{-10} \text{ cm}^3/\text{s}$  for the assumed laser intensity of  $I = 1 \text{ W/cm}^2$ , much more than in the previous case of the  $l = 3$  resonance. This strong enhancement is easily rationalized by comparing the wave functions for the  $l = 7$  shape resonance and the  $l' = 6$ ,  $(2)^3\Sigma^+$  bound level, shown in panels b and c of Figure 3: The very good overlap between these wave functions leads to the predicted large photoassociation rate.

Overall, Figures 4 and 5 predict, for levels in the  $(2)^3\Sigma^+$  electronic state, photoassociation spectra with a well-resolved rotational–vibrational structure. Penning ionization broadens the peaks compared to the natural line width. However, this

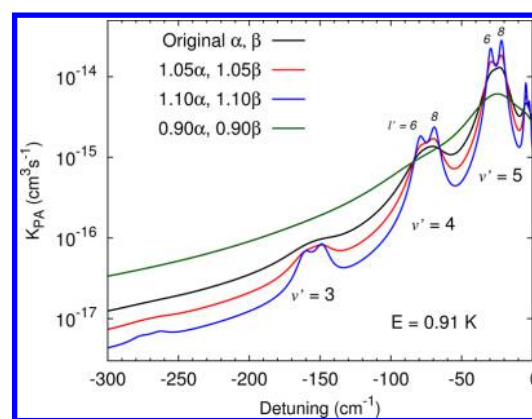


**Figure 5.** Photoassociation rates as a function of laser detuning from the He  $^3\text{S} \rightarrow ^3\text{P}$  atomic line for rovibrational levels of the  $(2)^3\Sigma^+$  state at a collision energy of 0.91 K and a laser intensity of  $1 \text{ W/cm}^2$ . The vibrational and rotational quantum numbers are indicated for each peak. The peaks for  $l' = 6, 7, 8$  are enhanced due to the  $l = 7$  shape resonance as initial state at 0.91 K, whereas for all other peaks photoassociation starts from regular scattering states.

broadening is significantly smaller than the spacing between the lines. Thus, photoassociation spectroscopy is expected to be feasible with high resolution and can be used, for example, to determine the rotational quantum number of the shape resonance that serves as starting point. The basic feature of the potential energy curve which allows for this prediction of well-resolved photoassociation lines is a potential well at comparatively large interparticle separation where the probability for Penning ionization is only moderate.

We have not performed thermal averaging, because the technique of merged beams allows for studying collisions at a well-defined energy.<sup>6,7,11</sup> Typical velocity spreads in the beams result in a broadening of the collision energies of the order of 50–500 mK in the sub-Kelvin regime. However, the actual energy resolution is better by an order of magnitude due to development of correlations in velocity–position space during free propagation of pulsed supersonic beams.<sup>30</sup> Given the widths of the orbiting resonances that we have employed, such a broadening does not change the photoassociation spectrum significantly. We have verified this argument quantitatively by calculating the spectra at energies 0.915 and 0.905 K, obtaining results almost identical to those shown in Figure 5.

Finally, we consider photoassociation into the  $^3\Pi$  state. We focus only on a collision energy of 0.91 K, where the sharpest resonance effect and thus the clearest signal is expected. The photoassociation spectrum, obtained with the original parameters of the imaginary potential,  $\alpha$  and  $\beta$  in eq 2, taken from ref 25 is presented by the black curve in Figure 6. In contrast to the  $(2)^3\Sigma^+$  state, the rovibrational structure of the spectrum has almost disappeared. For bound levels in the  $^3\Pi$  state, the Penning ionization widths are in the range from  $1 \text{ cm}^{-1}$  or 30 GHz (for the weakly bound  $v' = 7$  level) up to  $60 \text{ cm}^{-1}$  (for the most deeply bound  $v' = 0$  level). These large widths, comparable to the spacings between the rovibrational levels, do not allow us to resolve individual lines in the spectrum, in particular for larger detunings, i.e., larger binding energies. This raises the question how the strength of the imaginary potential, or more precisely whether and how the parameters  $\alpha$  and  $\beta$  in eq 2, influence the photoassociation spectrum. To answer this question, we scale the exponents in eq 2 by  $\pm 10\%$ . The resulting photoassociation spectra are also depicted in Figure 6.



**Figure 6.** Photoassociation rates as a function of laser detuning from the He  $^3\text{S} \rightarrow ^3\text{P}$  atomic line for rovibrational levels of the  $^3\Pi$  state at a collision energy of 0.91 K and a laser intensity of  $1 \text{ W/cm}^2$ . The vibrational and rotational quantum numbers are indicated for each peak.  $\alpha$  and  $\beta$  are the parameters of the optical potential, eq 2, with the original values taken from ref 25.

If  $\Gamma(R)$  is being weakened (larger  $\alpha$  and  $\beta$ , red and blue lines in Figure 6), individual rovibrational lines emerge. On the contrary, the spectrum becomes almost flat for stronger  $\Gamma(R)$  (green line in Figure 6), as expected: If the ionization probability is very high, a wave packet cannot oscillate back and forth in the potential even once; i.e., the discrete nature of the bound levels cannot be established. Thus, for a potential energy curve located at shorter interparticle separations, the prospects for photoassociation spectroscopy depend highly on the actual strength of  $\Gamma(R)$ . In turn, photoassociation spectroscopy can be used to determine this strength. If the ionization probability is not too high, such that single rovibrational peaks can be resolved, the increase of peak widths with binding energy should moreover allow us to determine the functional form of  $\Gamma(R)$ . In other words, photoassociation spectra as those represented by the blue line in Figure 6 can be used to fully map out  $\Gamma(R)$ , a quantity that still poses a rather large challenge to *ab initio* calculations.

## CONCLUSIONS

We have studied the prospects for photoassociation as a spectroscopic tool to study Penning ionization reactions. Introducing an *ab initio* model for the simplest example, Penning ionization of metastable helium with argon, we find usability of this tool to be determined by the position of the excited-state well. For a potential with a comparatively large equilibrium distance, about 10 bohr in our case, the probability of Penning ionization is larger than in the entrance channel, yet sufficiently small to allow for resolving single rovibrational levels. Photoassociation can then be observed by peaks in the ionization rate as a function of laser detuning.

Laser light driving the photoassociation process close to the  $^3\text{S} \rightarrow ^3\text{P}$  transition in helium is readily available.<sup>21,22</sup> Standard diodes and fiber amplifiers can be used to realize small detunings from the atomic line and laser intensities much larger than those assumed here. Larger detunings can be achieved by employing several fiber amplifiers or an external cavity diode. To date, photoassociation has been carried out with trapped cold atoms. One might therefore ask whether the different conditions encountered for particles moving in merged beams can indeed be combined with photoassociation. Assuming a velocity of 900 m/s for the merged beams, the interaction time

of a single pair of particles is about 10  $\mu\text{s}$  or longer. This is clearly sufficient for observing the predicted photoassociation spectra. We thus find our proposal to be experimentally feasible with currently available technology.

Metastable helium is particularly well suited for the kind of experiments we are suggesting here due to its simple electronic structure and low mass. These lead to well-isolated rovibrational levels, which can be probed by photoassociation. In contrast, other metastable noble gas atoms with strong spin-orbit coupling might have denser patterns of bound levels which may preclude observation of isolated photoassociation resonances. Use of heavier noble gas atoms for probing Penning ionization reactions with photoassociation spectroscopy will thus require a more detailed examination.

In merged beams, the collision energy in the entrance channel can precisely be controlled. Choosing in this way to photoassociate out of a shape resonance allows for unequivocally determining the rotational quantum number of the resonance because, compared to regular scattering states, a shape resonance leads to clearly enhanced photoassociation peaks in the rotational progression. Although the enhancement amounts to about 1 order of magnitude for diffuse, above-the-barrier shape resonances, enhancements up to 3 orders of magnitude are expected for shape resonances whose energy is well below the top of the rotational barrier.

For a potential with a comparatively small equilibrium distance, about 5 bohr in our case, the probability of Penning ionization becomes very large. Whether photoassociation peaks as a function of laser detuning can be observed or not, then depends very sensitively on the value of the exponents in the imaginary potential. We have started our calculations with values from the literature, obtained by fitting experimental data obtained for thermal collision energies.<sup>25</sup> Changing these values by only  $-10\%$  completely washes out any remnants of a peak structure, whereas a change in  $+10\%$  leads to clearly observable photoassociation peaks. Photoassociation spectroscopy can thus be used to accurately gauge the exponents of the imaginary potential. Moreover, if the Penning ionization probability is sufficiently small to allow for peak widths to be determined, an increase of the peak width with binding energy, respectively laser detuning, can be used to fully map out the functional form of the imaginary potential.

In summary, we find photoassociation spectroscopy to be an extremely useful tool to obtain in-depth information on Penning ionization reactions, provided the ionization proceeds not too fast. Our conclusions should hold also for collision partners other than argon, in particular if these are closed-shell.

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### Notes

The authors declare no competing financial interest.

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## ADDITIONAL NOTE

<sup>a</sup>This transition was also utilized for photoassociation spectroscopy with trapped ultracold metastable helium atoms.<sup>21,22</sup>

The  $J$ -sublevel of the  $^3P$  state is not specified because we neglect spin-orbit coupling in our calculations.

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