Progress toward ultracold chemistry: ultracold atomic and photonic collisions

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Abstract. The dynamics of ultracold quantum gases composed of atoms or molecules with extremely low translational energy $E_t/k_B \ll 1$ millikelvin is dominated by the long-range mutual interactions between particles. Such studies require a detailed modelling of the atom-molecule or molecule-molecule long-range interactions inside the quantum gas with or without the presence of external fields. This paper focuses on two particular aspects relevant to ultracold chemistry: (i) The calculation of rates for photoassociation of a cold atom and a cold molecule to create ultracold excited trimers, based on the knowledge of the long-range interaction between the two species, showing that such rates are encouraging under the density and temperature conditions of a nearly degenerate quantum gas; (ii) The determination of the long-range interactions between two identical polar bialkali molecules in their rovibronic ground level in the presence of an electric field, showing the possibility for the formation of ultracold polar tetramers by stimulated emission.

1. Introduction

The dynamics of ultracold quantum gases composed of atoms or molecules with extremely low translational energy $E_t/k_B \ll 1$ millikelvin is dominated by the long-range mutual interactions between particles. Ultracold molecules are nowadays routinely produced in various laboratories worldwide. Due to their internal structure which is more complex than the one of atoms, they offer new opportunities for creative applications [1, 2, 3] like fundamental studies of few-body dynamics in atomic and molecular physics [4], quantum simulation of Hamiltonians describing many-body phenomena like low-temperature Fermi fluids or artificial gauge fields [5, 6], or ultracold chemistry governed by quantum properties of the particles [7]. When the particles possess an intrinsic magnetic or electric dipole moment their interactions depend on their mutual orientation, which strongly modifies the dynamics of the quantum gas [8, 9, 10].

Laser cooling of translational motion is not as efficient for molecules [11] as for atoms, due to their more complex level structure which prevents finding an optically closed level scheme. It is worth...
noting however that laser-cooling of a specific class of molecules like SrF has been demonstrated [12] following a suggestion made back in 2004 [13]. Several non-optical techniques to slow down, to cool down, or to trap preexisting molecules in a well-defined quantum state, have already been demonstrated like Stark deceleration [14], Zeeman deceleration [15] buffer gas cooling [16], phase space filtering [17], or formation of dimers on helium nanodroplets [18]. An obvious method consists in associating pairs of ultracold atoms into ultracold molecules through a process which does not significantly affect the centre-of-mass motion of the atoms. This is what happens for photoassociation (PA) [19] followed by spontaneous or stimulated emission down to the molecular ground state, as illustrated in Figure 1. This approach [20] initiated the field of ultracold molecules when the first observation of translationally cold molecules has been reported in a gas of ultracold Cs atoms [21]. Alternatively the possibility to associate ultracold atoms using external magnetic fields (magnetoassociation) has been first pointed out in [22, 23], based on the important concept of magnetic tunability of Feshbach resonances to control interatomic interactions [24]. This technique revolutionized the research field as it offers a control of the internal quantum states of the created molecules to an unprecedented accuracy [25].

In this paper we focus on two particular topics induced by the developments above which exemplify the emergence of the field of ultracold chemistry through elementary atomic and photonic processes. First in Section 2 we discuss the possibility to photoassociate an ultracold atom and an ultracold molecule aiming at creating ultracold triatomic molecules, based on the hypothesis that the process is controlled by the long-range interaction between the two particles. In Section 3 we examine the long-range interaction between two polar molecules, i.e. possessing a permanent electric dipole moment in their own frame, which are shown to be strongly anisotropic and thus influencing further association of ultracold molecules into ultracold tetramers.

2. Photoassociation of an ultracold pair of atom and molecule

![Figure 1.](image)

Figure 1. The photoassociation (PA) process for an ultracold cesium pair with translational energy $k_B T$ such that $T<<1\text{mK}$. The pair absorbs a photon with frequency $\nu_1$ close to an atomic resonance frequency $\nu_a$ (the $6s\rightarrow6p$ transition in the figure). An excited short-lived molecule in a high lying rovibrational level ($v, J$) is created, which rapidly emits a photon $\nu_{sp}$ by spontaneous emission to create a pair of free atoms (green arrow) or a stable ultracold molecule (blue arrow). As $k_B T$ is much smaller than any other characteristic energy of the system, this free-bound transition can be considered as a resonant one. Typical radial wave functions are represented for both electronic states.

The principle of the photoassociation process is illustrated in Figure 1 for a pair of ultracold atoms trapped for instance in a magnetooptical trap (MOT). As suggested by the radial wave functions in the figure, the photon absorption preferentially occurs at large distance between the colliding partners, so that their mutual interaction at large distances plays a dominant role in the dynamics. Based on this statement, models for calculating PA rates have been elaborated [26, 27, 28, 29] and probed to be
successful to interpret experimental results [30, 31]. Among other developments this feature allowed for the development of a new high-resolution spectroscopic technique, namely the PA spectroscopy [32]. Assuming favorable conditions at short distances between the radial wave functions, the photoassociated molecules can be stabilized by spontaneous emission (blue downward arrow in Figure 1) to create stable ultracold molecules in a large distribution of rovibrational levels [21, 33, 34, 35]. Using stimulated emission, ultracold molecules can be created in selected ground state levels including the lowest one, so that all their internal energy has been dissipated [36, 37].

Recent experimental developments have probed that it is now possible to observe signatures of ultracold collisions between atoms and ground-state molecules created in trapping setups. For instance, collisions between Cs and Cs₂ have been detected in a MOT as additional losses of molecules detected by photoionization [38, 39]. Similar results have been obtained as well with heteronuclear molecular species like RbCs colliding with Rb and Cs [40] or LiCs colliding with Cs [41]. More recently the JILA group at Boulder reported the observation of collisional losses between ultracold K or Rb atoms with magnetoassociated ground state KRb molecules further transferred into the lowest level with respect to the vibrational, rotational, and hyperfine degrees of freedom [42]. Collisions between KRb molecules have been detected as well [43], and even reactive collisions leading to the destruction of the KRb molecules [42].

The currently reachable densities of atomic and molecular ultracold gases make the prospects for photoassociation of an atom and a molecule to create an ultracold triatomic molecule – i.e. an atom-molecule collision assisted by a photon- quite promising. It is thus desirable to extend the PA models above to the atom-molecule case [44], that we illustrate here with the example of Cs in its 6s ground level, and Cs₂ in its X'Σ_g^+ ground state in the lowest vibrational level v=0 (hereafter referred to as the X state), to create ultracold Cs₃ molecules. We assume first that PA is performed with a laser frequency close to the 6s-6p transition, so that the PA dynamics is controlled by the long-range interaction between Cs(6p) and a rotating Cs₂(X) molecule. Following our previous works [45] this interaction is conveniently characterized by the standard multipolar long-range expansion of the potential energy V(R):

$$V(R) = \frac{1}{4\pi\varepsilon_0} \sum \frac{f_{\ell,m}\mathcal{Q}^{\ell,m}_{\ell,m}}{R^{\ell+1}} Q_a^{\ell,m} Q_a^{\ell,m},$$  (1)

where $R$ is the distance between the atom and the center-of-mass of the molecule. The $2\ell$-pole moment $Q_a^{\ell,m}$ are expressed in the body-fixed frame, and $f_\ell$ is a numerical factor [45]. As the atom is excited and the molecule is rotating (with angular momentum quantum number $N$), the lowest order contribution is the quadrupole-quadrupole term behaving like $C_5/R^5$ determined at the 1st-order of the perturbation theory. The second order yields the usual van der Waals interaction varying as $C_6/R^6$. The main task consists here in determining precise values of the quadrupole moment and dynamic polarizabilities of the Cs₂ molecule, relying on elaborated quantum chemistry calculations performed in our group [46]. In the present case, for a given value of $N$ and $\ell$ (=1 for the Cs(6p) atom) one obtains $(2N+1)\times(2\ell+1)$ long-range potential energy curves (PECs) $\varepsilon(R)$ expressed as:

$$\varepsilon(R) = B_0 N(N+1) + \frac{C_5^{(i)}}{R^5} + \frac{C_6^{(i)}}{R^6},$$  (2)

where $B_0$ is the rotational constant of the ground state Cs₂ molecule in $v=0$. As the potential energy can have the same magnitude than the rotational energy of the Cs₂ molecule, it is necessary to perform the final calculations of the PECs in the framework of the second-order degenerate perturbation theory [47], also taking in account the spin-orbit interaction on the excited atom [48]. We found that while $C_5$ values are either positive or negative, most $C_6$ values are negative, so that the latter contribution will dominate the interaction when distance is getting shorter. Note that this asymptotic model is valid for distances larger than the characteristic distance $R_{LR}$ – namely the LeRoy radius [49]- where exchange energy becomes significant (around $R_{LR}=45$ a.u. [45]).
Following the approach developed in Ref. [26] the rate $R_{PA}$ for a PA laser frequency $\nu_{PA}$ detuned by $\Delta$ to the red of the atomic frequency $\nu_a$ is given by

$$R_{PA} = A(g,e,e_{PA}) \left( \frac{3}{2\pi} \right)^{3/2} \frac{\hbar}{2} n_{mol} A^3 e^{-\Delta/\hbar \nu_{PA}} \Omega^2 \left| \langle \Psi_g | \Psi_e \rangle \right|^2$$

where $\Psi_g$ and $\Psi_e$ are respectively the initial (continuum) and the final (bound) radial wave function of the Cs-Cs$_2$ complex, and $A$ is an angular factor involving degeneracies of the initial ($g$) and final ($e$) states, and the chosen laser polarization $\varepsilon_{PA}$. As the process occurs mainly at large distances the transition dipole moment involved in the Rabi frequency $\Omega$ is assumed to be $R$-independent and equal to the atomic $6s \rightarrow 6p$ one. The atom-molecule pair density is assumed to be the molecular density $n_{mol}$ (which is most often smaller than the atomic one), and the associated deBroglie wavelength for the atom-molecule complex is denoted $\Lambda$.

Figure 2: Experimental proposal for the observation of Cs$_3^*$ in the framework of an experimental setup similar to the one used in [50], based on an optical lattice. The successive steps of the experimental implementation are represented: a) creation of a Mott insulator (MI) phase for Cs atoms with a two atoms per lattice site in the center of the optical lattice. Using magnetoassociation ground state Cs$_2$ molecules are formed in highly rovibrational levels, after that a four laser STIRAP technique is used to transfer the population to the rovibrational ground state of the molecules. b) The intensity of the optical lattice laser is decreased adiabatically to drive the MI to superfluid (SF) quantum phase transition for Cs atoms whereas the Cs$_2$ molecules remain in a MI state with one molecule per lattice site. c) The intensity of the optical lattice is increased adiabatically to drive a SF to MI transition of Cs atoms with one atom per lattice site and finally the PA laser is applied over the system. d) Cs$_3^*$ molecules are formed and they can be detected as loss of Cs atoms by fluorescence imaging technique.

In order to compute $\Psi_g$ and $\Psi_e$ the long-range PECs must be extrapolated to short distances. Assuming in the present model that the short-range interaction only plays a limited role in the PA dynamics, we matched the curves above around $R=45$ a.u. to a Lennard-Jones potential with a depth $D_{LJ}$ much larger than the potential energy for $R>R_{LR}$, i.e. $D_{LJ} >> 1$cm$^{-1}$ [44]. For a detuning of about 1 cm$^{-1}$ and under typical MOT for Cs (say, for T=140$\mu$K) [30], the PA rate – expressed in cm$^2$ when it is scaled by the photon flux and by the particle density [27] for the sake of comparison with available experimental results - is found about one order of magnitude smaller than the observed PA rate for Cs atoms, which reflects the “heteronuclear” character of the Cs-Cs$_2$ system. This situation is in turn more promising if we consider experimental conditions of the Innsbruck group for their Cs degenerate quantum gas set up [50], namely a gas density which could be two orders of magnitude higher than under MOT conditions. The PA rate is thus found at the same level or higher than in the PA
experiment performed by Hulet et al. [51]. This lead us to formulate the experimental proposal described in Figure 2, in relation with possible developments of the experiment in Innsbruck, to observe the creation of photoassociated Cs$_3^+$ molecules.

3. Long-range interactions between polar alkali-metal diatoms

The recent production of ultracold heteronuclear alkali-metal dimers in their lowest rovibronic [52, 35] and hyperfine level opens new ways for studying anisotropic interactions in ultracold gases, referred to as dipolar gases [53, 9]. Indeed such molecules, nowadays denoted as polar molecules, possess a permanent electric dipole moment (PEDM) $d_0$ in their body-fixed frame which allows for orienting them with external electric fields. The most spectacular experimental achievements on ultracold dipolar molecular gases have been performed on KRb molecules [42, 43] which motivated a wealth of theoretical investigations on this species [54-57].

Just like in the previous section, the dynamics of the dipolar gas is conditioned by the long-range dipole-dipole interaction $V_{dd}(R)$ which now depends on the orientation ($\theta, \phi$) of the molecules with respect to the intermolecular axis, $R$ being the distance between their center of mass:

$$V_{dd}(R) = \frac{d_0^4}{R^6} (2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\phi_2 - \phi_1)).$$

As stated in Ref. [58] the energy of the mechanical rotation between the two molecules, and thus the corresponding rotational couplings, are small compared to the van der Waals (vdW) interaction and to the rotational energy of the individual molecules, so that the main features of the system can be captured in the frame fix to bimolecular complex.

We first calculate the long-range interaction between two polar ground state molecules in their lowest rovibrational level ($v=0, j=0$) in free space. In this case their mutual interaction is isotropic, and is obtained at the second order of perturbation theory to determine the relevant $C_6$ coefficients of the vdW interaction. The $C_6$ coefficients are related to dynamic polarizabilities in imaginary frequencies [58] which require, as already quoted, the accurate computation of molecular properties like PECs and transition dipole moments (TDM) [46]. Detailed numerical results for such polarizabilities are provided for the ten heteronuclear bialkali species in Ref. [60] and will be the subject of a forthcoming paper. The resulting $C_6$ values (Figure 3) vary dramatically with the species, ranging from a few thousands atomic units for LiNa and KRb, up to a few millions for NaCs. Such differences ensue from the contribution of the transitions within levels of the ground state to the dynamic polarizability, such that $C_6$ can be expressed to a good approximation [58] as $C_6 \approx \frac{d_0^4}{6B_0}$ for eight species (thus except KRb and LiNa) which possess a strong PEDM. Our results are in satisfactory agreement with other published values [61-63].

![Figure 3: van der Waals $C_6$ coefficients between two identical ground-state heteronuclear alkali-metal diatoms in their lowest rovibrational level ($v=0, j=0$), as a function of their permanent electric dipole moment in their body-fixed frame. Red squares (resp. blue circles) denote those species for which the transitions within the ground state dominate (resp. do not dominate) the contributions to the $C_6$ magnitude (see text). The value for the interaction between two ground state Cs$_2$ molecules in given for the sake of comparison (open triangle).]
dimensional traps for the ultracold quantum gas. In addition to those of $V_{dd}(R)$ (eq. 4), the matrix elements of the field molecule interaction Hamiltonian are evaluated in the basis $|j_1m_1j_2m_2>$ containing the quantum numbers of the individual molecules ($m_i$ is the projection of $j_i$ on the intermolecular axis), for a given $M=m_1+m_2$ and for a given parity $p=(-1)^{(j_1+j_2)}$. In analogy with two atoms, the PECs resulting from the diagonalization are labeled $|M_{g/u}^{\sigma}(g)|$ where $\sigma$ is the symmetry with respect to a plane containing the intermolecular axis. More details on the calculations and on the PECs are available in Ref. [58]. Note that all species could be considered in a single calculation by rescaling distances and electric fields with the characteristic quantities $[58]$

$$R^* = \left(\frac{d_0^2}{\varepsilon_0}\right)^{1/3}; \quad \varepsilon^* = \frac{\varepsilon_0}{d_0}$$

which equals -3 if the interaction is of dipole-dipole type, and -6 if it is of vdW type. Figure 4 displays the expected variation of the dipole-dipole interaction ($n^*=3$) at large distances, which is attractive due to a head-to-tail approach in a parallel field, and repulsive due to a side-by-side approach in a perpendicular field (not shown in the figure in logarithmic scale). In a perpendicular field the competition between the repulsive dipole-dipole interaction and the attractive vdW interaction induces a change in the sign of the potential energy around $R^*$, which causes the divergence of $n^*$ (not shown in the figure).

![Figure 4](https://example.com/figure4.png)

**Figure 4**: Leading exponent $n^*(R, \varepsilon)$ of the interaction between two ground-state heteronuclear molecules in their lowest rovibrational level, for parallel and perpendicular electric field. Distance are in scaled units, and $\varepsilon=\varepsilon^*/10$.

This variation is even understood with Figures 5 and 6 below where we computed the induced dipole moment for molecule $i$ $d_i(R, \varepsilon)$ (in units of $d_0$) along the electric field axis and the averaged value $s(R, \varepsilon)$ of the scalar product of the two dipole moments which reflects their mutual alignment at short distances as well as a strong alignment along the electric field in the parallel case only. At large distances no alignment is visible so that despite their $R^{-3}$ interaction the two molecules. For the moderate parallel field considered here, the dipole moment strongly varies with $R$: it changes from $d/d_0=0.18$ at $R/R^*=0.74$ up to $d/d_0=0.81$ at $R/R^*=0.45$. For the five species (NaK, NaRb, NaCs, KCs, and RbCs) among the ten heteronuclear bialkali molecules which are found stable against ground state collisions [64], this feature suggests that one-photon-assisted formation of ultracold polar tetramers could be possible by stimulated radiative association process along the lines proposed in Ref. [65]. In contrast, such an association process cannot occur when the electric field is perpendicular to the intermolecular axis since the individual dipole moments are zero. Thus we predict that this mechanism is strongly anisotropic, and that electric fields could be used to control the association of...
the tetramers, in a similar way than the one used to reduce the collisional rate of ultracold KRb molecules in the JILA experiment.

![Figure 5](image1.jpg)  
**Figure 5:** Dipole moment (in units of $d_0$) of the individual molecules induced by the external electric field as a function of $R$ in scaled units (see text), which expresses the alignment along the electric field.

![Figure 6](image2.jpg)  
**Figure 6:** Scalar product of the dipole moments of the interacting molecules as a as a function of $R$ in scaled units (see text), which expresses the mutual alignment of the molecules.

### 4. Conclusions

In this paper we have theoretically considered two photo-assisted collisional processes between ultracold particles namely between an atom and a molecule, or between molecules, in order to create ultracold trimers or tetramers. Such processes represent basic elements of a novel ultracold chemistry which is dominated by the long-range interactions between the reacting particles. In the former case the photoassociation rate for creating excited trimers is found promising providing that the experiment will be realized under condition close to the ones of quantum degenerate gases. In the latter case, the long-range interactions between identical bialkali molecules is such that in the presence of an electric field parallel to the intermolecular axis the photoassociation of the molecule pair into an ultracold tetramer seems favourable. Both situations are treated assuming that the short-range part of the interaction between particles does not play a significant role. This is actually an open question, addressed in two recent theoretical papers from JILA [66, 67] which suggest that the large amount of resonances of a triatomic or of the tetrameric complex with a wave function mainly located at short distances may trap the incoming particles just like if they would hit a single resonant state. The detection of PA along the lines of the present paper may provide an experimental insight onto the role of these numerous resonances in the dynamics.

### References

[1] Carr L D and Ye J. 2009 *New J. Phys.* 11:055009  
[2] Dulieu O and Gabbanini C. 2009 *Rep. Prog. Phys.* 72:086401  
[3] Jin D S and Ye J 2012 Chem. Rev. 112 4801  
[4] Blume D 2012 *Rep. Prog. Phys.* 72:086401  
[5] Bloch I, Dalibard J and Nascimbène S 2012 *Nature Phys.* 8 276  
[6] Galitski V and Spielman I B 2013 *Nature* 494 49  
[7] Krems R V 2008 *Phys. Chem. Chem. Phys.* 10 4079  
[8] Micheli A, Brennen G K, and Zoller P 2006 *Nature Phys.* 2 341  
[9] Lahaye T, Menotti C, Santos L, Lewenstein M, and Pfau T 2009 *Rep. Prog. Phys.* 72 126401
[10] Pasquiou B, Maréchal E, Vernac L, Gorceix O, and Laburthe Tolra B 2012 Phys. Rev. Lett. 108 045307
[11] Bahns J T, Stwalley W C, and Gould P L 1996 J. Chem. Phys. 104 9689
[12] Shuman E S, Barry J F, and DeMille D 2010 Nature 467 820
[13] Di Rosa M D 2004 Eur. Phys. J. D 31, 395
[14] Van de Meerakker S Y T, Bethlem H L, Vanhaecke N, and Meijer G 2012 Chem. Rev. 112 4828
[15] Narevicius E and Raizen M G 2012 Chem. Rev. 112 4879
[16] Weinstien J D, deCarvalho R, Guillet T, Friedrich B, and Doyle J M 1998 Nature 395 148
[17] Rangwala t, Junglen T, Rieger T, Pinkse P W H and Rempe G 2003 Phys. Rev. A 64 043406
[18] Mudrich M, Biinermann O, Stienkemeier F, Dulieu O and Weidemüller M 2004 Eur. Phys. J. D 31 291
[19] Thorsheim H R, Weiner J and Julienne P S 1987 Phys. Rev. Lett. 58 2420
[20] Jones K M, Tiesinga E, Lett P D and Julienne P S 2006 Rev. Mod. Phys. 78 483
[21] Fioretti A, Comparat D, Crubellier A, Dulieu O, Masnou-Seeuws F and Pillet P 1998 Phys. Rev. Lett. 80 4402
[22] Timmermans E, Tommasini P, Hussein M and Kerman A 1999 Phys. Rep. 31 230
[23] Heinzen D J, Wynar R, Drummond P D and Kheruntsyan K V 2000 Phys. Rev. Lett. 84 502
[24] Tiesinga E, Verhaar B J and Stoof H T C 1993 Phys. Rev. A 47 4114
[25] Chin C, Grimm R, Julienne P and Tiesinga E 2010 Rev. Mod. Phys. 82 122
[26] Pillet P, Crubellier A, Bleton A, Dulieu O, Nosbaum P, Mourachko I and Masnou-Seeuws F 1997 J. Phys. B: At Mol. Opt. Phys. 30 2801
[27] Côté R and Dalgarno A 1999 Phys. Rev. A 58 498
[28] Bohn J L and Julienne P S 1999 Phys. Rev. A 60, 414
[29] Azizi S, Aymar M and Dulieu O 2004 Eur. Phys. J. D 31 195
[30] Drag C, Tolra B L, Dulieu O, Comparat D, Vatasescu M, Boussen S, Guibal S, Crubellier A and Pillet P 2000 IEEE J. Quantum Electron. 36 1378
[31] Kraft S D, Mudrich M, Staudt M U, Lange J, Dulieu O, Wester R, and Weidemüller M 2005 Phys. Rev. A 71 013417
[32] Stwalley W C and Wang H 1999 J. Mol. Spectrosc. 195 194
[33] Gabbanini C, Fioretti A, Lucchesini A, Gozzini S and Mazzoni M 2000 Phys. Rev. Lett. 84 2814
[34] Wang D, Qi J, Stone M F, Nikolayeva O, Wang H, Hattaway B, Gensemer S D, Gould P L, Eyler E E and Stwalley W C 2004 Phys. Rev. Lett. 93 243005
[35] Deiglmayr J, Grochola A, Repp M, Mörtbauer K, Glück C, Lange J, Dulieu O, Wester R and Weidemüller 2008 Phys. Rev. Lett. 101 133004
[36] Sage J M, Sainis S, Bergeman T and DeMille D 2005 Phys. Rev. Lett. 94 203001
[37] Viteau M, Chotia A, Allegrini M, Bouloufa N, Dulieu O, Comparat D and Pillet P 2008 Science 321 232
[38] Zahzam N, Vogt T, Mudrich M, Comparat D and Pillet P 2006 Phys. Rev. Lett. 96 023202
[39] Staanum P, Kraft S D, Lange J, Wester R and Weidemüller M 2006 Phys. Rev. Lett. 96 023201
[40] Hudson E R, Gilfoy N B, Kotochigova S, Sage J M and DeMille D 2008 Phys. Rev. Lett. 100 203201
[41] Deiglmayr J, Repp M, Dulieu O, Wester R and Weidemüller M 2011 Eur. Phys. J. D 104 99
[42] Ospelkaus S, Ni K K, Wang D, de Miranda M H G, Neyenhuis B, Quéméner G, Julienne P S, Bohn J, Jin D S and Ye J 2010 Science 327 853
[43] de Miranda M H G, Chotia A, Neyenhuis B, Wang D, Quéméner G, Ospelkaus S, Bohn J L, Ye J and Jin D S 2011 Nature Phys. 7 502
[44] Pérez-Ríos J, Lepers M and Dulieu O to be submitted
[45] Lepers M, Dulieu O and Kokooine V 2010 Phys. Rev. A 82 042711
[46] Aymar M and Dulieu O 2005 J. Chem. Phys. 122 204302
[47] Lepers M and Dulieu O 2011 Eur. Phys. J. D 65 113 ; Lepers M, Vexiau R, Bouloufa N, Dulieu
O and Kokoouline V 2011 Phys. Rev. A 83 042707

[48] Lepers M and Dulieu O 2011 Phys. Chem. Chem. Phys. 13 19106

[49] LeRoy R J 1974 Can. J. Phys. 52, 246

[50] Danzl, J. G., Haller E, Gustavsson M, Mark M J, Hart R, Bouloufa N, Dulieu O, Ritsch H, and Nägerl H C 2008 Science 321, 1062

[51] Prodan I D, Pichler M, Junker M, Hulker R G and Bohn J L 2003 Phys. Rev. Lett. 91, 080402

[52] Ni, K.-K., Ospelkaus S, de Miranda M H G, Pe’er A, Neyenhuis B, Zirbel J J, Kotochigova S, Julienne P S, Jin D S and Ye J 2008 Science 322, 231

[53] Baranov M A 2007 Phys. Rep. 464 71

[54] Byrd J N, Montgomery Jr J A, and Côté R 2012 Phys. Rev. Lett., 109 083003

[55] Idziaszek Z and Julienne P S 2010 Phys. Rev.Lett., 104 113202

[56] Quéméner G and Bohn J L 2010 Phys.Rev. A, 81 022702

[57] Quéméner G and Bohn J L 2010 Phys. Rev. A,81 060701

[58] Lepers M, Vexiau R, Aymar M, Bouloufa-Maafa N and Dulieu O 2013 Phys. Rev. A, 88, 032709

[59] Derevianko A, Porsev S G and Babb J F 2010 At.Data Nucl. Data Tables, 96 323

[60] Vexiau R. PhD thesis, Université Paris-Sud, Orsay, France

[61] Quéméner G, Bohn J L, Petrov A and Kotochigova S 2011 Phys. Rev. A, 84 062703

[62] Byrd J N, Montgomery Jr J A, and Côté R 2012 J. Chem. Phys. 136 014306

[63] Żuchowski P, Kosicki M, Kodrycka M, and Soldán P. Phys. Rev. A, 87:022706

[64] Żuchowski P and Hutson J M 2010 Phys. Rev. A, 81 060703

[65] Juarros E, Pellegrini P, Kirby K and Côté R 2006 Phys. Rev. A, 73 041403

[66] Mayle M, Ruzic B P and Bohn J L 2012 Phys. Rev. A 85, 062712

[67] Mayle M, Quéméner G, Ruzic B P and Bohn J L 2013 Phys. Rev. A 87, 012709.

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