RAPID COMMUNICATIONS

PHYSICAL REVIEW A **81**, 060704(R) (2010)

Formation of ultracold polar molecules in a single quantum state

Robin Côté,[1] Elizabeth Juarros,[1] and Kate Kirby[2,3]
[1]*Physics Department, University of Connecticut, 2152 Hillside Rd., Storrs, Connecticut 06269-3046, USA*
[2]*ITAMP, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138, USA*
[3]*American Physical Society, One Physics Ellipse, College Park, MD 20740, USA*

(Received 18 January 2010; published 16 June 2010)

We compute the formation rate of a polar molecule, LiH, into the lowest triplet electronic state, $a\,^3\Sigma^+$, via population of the intermediate excited electronic state, $b\,^3\Pi$, followed by radiative decay. We find large formation rates into the single rovibrational bound state ($v=0, J=0$) of the $a\,^3\Sigma^+$, which can be explained by the unusually large overlap of its wave function with those of the two upper-most bound levels of the $b\,^3\Pi$. With conservative parameters, we estimate that over 10^4 molecules/s could be produced in the single rovibrational level of the $a\,^3\Sigma^+$ state. We also discuss scattering properties of LiH triplet molecules and their relevance to ultracold chemical reactions.

DOI: 10.1103/PhysRevA.81.060704 PACS number(s): 34.20.−b, 33.80.−b, 31.50.−x, 34.50.−s

Over the last several years, the successful formation of ultracold molecules [1] has led to the realization of molecular Bose-Einstein condensates (BECs) [2]. There is also considerable interest in ultracold gases of polar molecules [3], such as the bi-alkali-metal molecules KRb, RbCs, or LiCs, in which new physics due to strong anisotropic dipole-dipole interactions [3,4] can be probed. In addition, schemes using ultracold polar molecules for quantum-information processing (QIP) have been proposed [5]. Other applications of polar molecules range from testing fundamental symmetries based on high-precision spectroscopy [6] to the attempts to detect the time variation of fundamental constants [7]. Such molecules could also be used in the study of ultracold chemistry, where state-to-state reactions could be followed in detail, and where the effect of the fermionic or bosonic nature of the reactants on the chemical reactivity could be tested [8–10]. Many of those applications require dense samples of ultracold polar molecules in the lowest rovibrational state.

In this article, we examine the possibility of forming large amounts of polar molecules in a single rovibrational state. The point is to demonstrate "proof of principle" rather than to provide absolute formation rates. We study the case of alkali-metal hydride molecules (XH, where X stands for Li, Na, K, Rb, or Cs) in their lowest triplet electronic state $a\,^3\Sigma^+$; all are predicted to sustain only one vibrational level [11,12]. Although we focus our attention on LiH and its isotopomers, the general results apply to other alkali-metal hydrides [13]. We consider atoms and molecules prepared in purely stretched spin states by an external magnetic field so that only the triplet manifold participates in the process. Spin-polarized atoms, Li and H, approaching each other along the triplet molecular ground-state asymptote, in the presence of an optical field, can make a transition into a bound level v' of the excited $b\,^3\Pi$ molecular electronic state (see Fig. 1).

The corresponding photoassociation rate coefficient $K_{v'} = \langle v_{\rm rel}\sigma_{\rm PA}\rangle$ (for a laser $L=\{I,\Delta\}$ of intensity I and detuning Δ from a bound level v', J') is [14,15]

$$K_{v'}(T,L) = \left\langle \frac{\pi v_{\rm rel}}{\kappa^2}\sum_{\ell=0}^{\infty}(2\ell+1)|S_{\ell,v'}(\varepsilon,L)|^2\right\rangle, \tag{1}$$

where $\varepsilon = \hbar^2\kappa^2/2\mu = \mu v_{\rm rel}^2/2$, μ is the reduced mass, $v_{\rm rel}$ is the relative velocity of the colliding pair, and $S_{\ell,v'}$ represents the scattering matrix element for producing the state v' from the continuum state. Averaging over $v_{\rm rel}$ is implied by $\langle\cdots\rangle$. At ultracold temperatures, only the s wave ($\ell=0$) contributes, and assuming that the width $\gamma_{v'}$ of the bound level ($v', J'=1$) is much larger than the stimulated width γ_s from the continuum initial state, we can approximate $|S_{\ell=0,v'}|^2 \simeq 2\pi\gamma_s(I,\varepsilon,v')\delta(\varepsilon-\Delta)$ [14], where $\gamma_s(I,\varepsilon,v') = \pi I|D_{v'}(\varepsilon)|^2/\epsilon_0 c$ [16]. Here, ϵ_0 is the vacuum permittivity and c the speed of light, while $|D_{v'}(\varepsilon)|^2 \equiv |\langle v'|D(R)|\varepsilon\rangle|^2$ is the square of the dipole transition matrix element between the continuum initial state $|\varepsilon,\ell=0\rangle \equiv |\varepsilon\rangle$ and the target state $|v',J'=1\rangle \equiv |v'\rangle$, with $D(R)$ being the corresponding molecular dipole transition moment connecting the $b\,^3\Pi$ and $a\,^3\Sigma^+$ states.

Assuming a Maxwellian velocity distribution characterized by the temperature T, the maximum value $K_{v'}^{\rm max}$ of $K_{v'}(T,L=\{I,\Delta\})$ at ultralow T becomes [15,16]

$$K_{v'}^{\rm max}(T,I) = \frac{4\pi^2}{h}\frac{I}{\epsilon_0}\frac{e^{-1/2}}{Q_T}C_{v'}\sqrt{\frac{k_BT}{2}}\,, \tag{2}$$

where $Q_T = (2\pi\mu k_BT/h^2)^{3/2}$ (k_B is the Boltzmann constant). Here, we assumed $|D_{v'}(\varepsilon)|^2 = C_{v'}\sqrt{\varepsilon}$ in accordance with Wigner's threshold law [17], and that the maximum value of $K_{v'}$ occurs at $\Delta = k_BT/2$ [15]. The above approximation is not valid when the intensity I becomes large, at which point saturation needs to be considered [16]. In particular, the rate coefficient cannot be larger than the saturation limit (independent of the level v' considered) obtained when $|S_{\ell,v'}|^2 = 1$, namely [16],

$$K^{\rm limit}(T) = \frac{k_BT}{hQ_T} = \frac{h^2}{(2\pi\mu)^{3/2}}\frac{1}{\sqrt{k_BT}}\,. \tag{3}$$

The above expressions neglect the light polarization. A rate $\mathcal{R}$ of molecules formed per second is obtained if we multiply $K_{v'}$ by the densities of the atomic species, n_X and $n_{\rm H}$ (X represents the alkali-metal atom), and by the volume V illuminated by the laser beam: $\mathcal{R}_{v'} = n_X n_{\rm H} K_{v'} V$ [15].

Once a $b\,^3\Pi$ vibrational level ($v', J'=1$) is populated, it will decay by spontaneous emission. As the $a\,^3\Sigma^+$ state has only one vibrational level, the decay occurs only into that level or into the continuum. We note that since the transition takes place from an s-wave collisional state ($\ell=0$) with even parity,

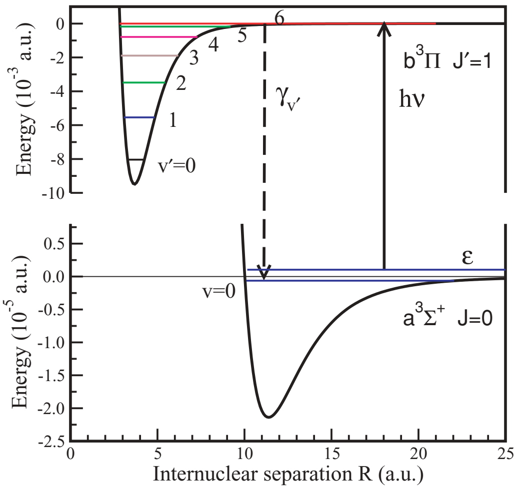

FIG. 1. (Color online) Schematics: a pair of colliding atoms with energy ε absorbs a photon of frequency ν to form a molecule in an excited electronic state which spontaneously decays partly into the bound level of the lower electronic state.

the excited state $(v', J' = 1)$ with odd parity must decay into an even-parity state ($J = 0$ discrete or $\ell = 0$ and 2 continuum states). Thus, only $(v = 0, J = 0)$ triplet alkali-metal hydride molecules can be populated with a formation rate simply given by

$$\mathcal{R} = r_{v=0}^{v'} \mathcal{R}_{v'} = r_{v=0}^{v'} n_X n_{\rm H} K_{v'} V. \qquad (4)$$

Here, $r_{v=0}^{v'} = A_{v=0}^{v'} \tau_{v'}$ is the branching ratio between an excited level $(v', J' = 1)$ and the ground state $(v = 0, J = 0)$, where $A_{v=0}^{v'}$ is the spontaneous width (or Einstein A coefficient) from $(v', J' = 1)$ to $(v = 0, J = 0)$, and $\tau_{v'} \equiv 1/A_{\rm Tot}^{v'}$ is lifetime of the level $(v', J' = 1)$ [15].

To compute the LiH formation rate, we used the *ab initio* potential curves for the $a\,^3\Sigma^+$ state from Gadéa and coworkers [18], and the $b\,^3\Pi$ state from Boutalib and Gadéa [19]. The $b\,^3\Pi$ potential was joined smoothly to the long-range form $-C_6/R^6 - C_8/R^8$ with $C_6 = 84.327$ a.u. and $C_8 = 14794$ a.u. from Zemke *et al.* [20]. The dipole transition moment $D(R)$ between those two states was obtained from Docken and Hinze [21].

TABLE I. Binding energy of rovibrational levels $(v = 0, J)$ in $a\,^3\Sigma^+$ for LiH isotopomers in hartree, cm^{-1}, and kelvin. All other states are not bound.

	Level	E_b		
Isotopomer	$(v = 0, J)$	(10^{-7} a.u.)	(cm^{-1})	(K)
^{7}LiH	$J = 0$	3.148	0.0691	0.0994
^{6}LiH	$J = 0$	2.710	0.0595	0.0856
^{7}LiD	$J = 0$	23.05	0.5059	0.7279
	$J = 1$	8.768	0.1924	0.2769
^{6}LiD	$J = 0$	21.44	0.4706	0.6770
	$J = 1$	7.0142	0.1539	0.2215

The $a\,^3\Sigma^+$ state supports only one vibrational level $(v = 0)$ [22], and depending on the isotopomer, the rotational states $J = 0$ and 1. In Table I, we list these binding energies in units of hartree, cm^{-1}, and kelvin. Although these levels are very close to the dissociation limit, collision energies of many tens of mK would be necessary to cause dissociation. The excited $b\,^3\Pi$ state can support several bound levels [22]: in Table II, we give their energy in cm^{-1} for the various isotopomers. We also computed the lifetime of those levels, including the contributions from both bound-bound and bound-free decays in a manner similar to Ref. [23]. As the level v' increases, $\tau_{v'}$ decreases monotonically until it reaches a value close to the atomic lifetime of 27.104 ns for Li(2p) [24]. This trend reflects the general overlap of the wave functions for excited levels of the $b\,^3\Pi$ with that for the $a\,^3\Sigma^+$ bound state (see Fig. 2 and discussion below).

We computed $K_{v'}^{\rm max}$ into excited levels $(v', J' = 1)$ of the $b\,^3\Pi$ state. The results for the various isotopomers are depicted in Fig. 3 for a laser intensity $I = 50$ W/cm^2 at a temperature $T = 1$ mK. This laser intensity was chosen so that the rate coefficient would be safely below $K^{\rm limit}$ for all isotopomers: the largest rate coefficient shown is for $v' = 6$ of ^{7}LiH with 2.12×10^{-10} cm^3/s, 20 times lower than its limiting value of 4.25×10^{-9} cm^3/s. We note that the deuterides, because of their larger reduced masses, have two more bound levels than the corresponding hydrides. We also find that $K_{v'}^{\rm max}$ is very large for the two upper-most levels v' in the $b\,^3\Pi$ state, and follows an exponential trend as a function of v'. This behavior reflects the overlap of the initial continuum wave function

TABLE II. Energy levels and lifetimes of LiH isotopomers in $(v', J' = 1)$ of $b\,^3\Pi$. Square brackets imply power of 10.

	E_b (cm^{-1})				$\tau_{v'}$ (ns)			
v'	^{7}LiH	^{6}LiH	^{7}LiD	^{6}LiD	^{7}LiH	^{6}LiH	^{7}LiD	^{6}LiD
0	1.76[3]	1.76[3]	1.84[3]	1.84[3]	107	107	111	111
1	1.22[3]	1.21[3]	1.41[3]	1.40[3]	82.0	81.5	90.7	90.1
2	7.64[2]	7.55[2]	1.04[3]	1.02[3]	62.8	62.2	74.1	73.4
3	4.15[2]	4.04[2]	7.18[2]	7.00[2]	48.3	47.8	60.6	59.8
4	1.74[2]	1.65[2]	4.57[2]	4.37[2]	37.8	37.4	50.1	49.2
5	3.93[1]	3.47[1]	2.52[2]	2.37[2]	30.6	30.3	41.4	40.7
6	3.18[−1]	3.05[−2]	1.12[2]	9.92[1]	25.9	26.5	34.7	34.1
7	–	–	3.07[1]	2.39[1]	–	–	29.9	29.4
8	–	–	1.83[0]	7.18[−1]	–	–	26.9	26.7

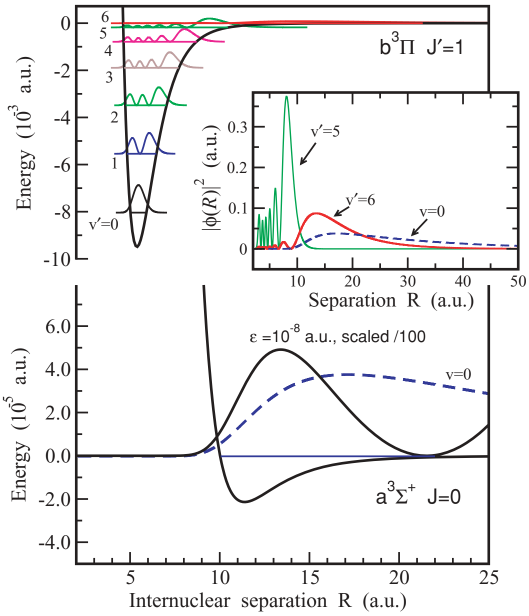

FIG. 2. (Color online) Probability densities of the bound states of $b\,^3\Pi$ and $a\,^3\Sigma^+$ of ^{7}LiH. Also shown is the (scaled) continuum wave function for $\varepsilon/k_B \sim 3$ mK. The inset shows the overlap of the two uppermost levels v' with $v = 0$ of $a\,^3\Sigma^+$.

with the bound levels v': except for the highest level v', the overlap takes place deeply in the classically forbidden region, where the amplitude of the continuum wave function decreases exponentially (see Fig. 2). The poor overlaps also explain the long lifetimes (see Table II).

To obtain the total formation rate $\mathcal{R}$ into $(v = 0, J = 0)$ of the $a\,^3\Sigma^+$, we also calculated the branching ratio $r_{v=0}^{v'}$ [see Eq. (4)]. Figure 4 shows the branching ratio from various excited levels v' for all isotopomers: for the two uppermost levels of all isotopomers, $r_{v=0}^{v'}$ reaches large values ranging from 1% to 95%. These values and exponential trend are again well explained by the wave function overlaps (see Fig. 2 and its inset).

Using conservative experimental values ($n_{\rm Li} = n_{\rm H} = 10^{11}$ cm^{-3} and $V = 10^{-6}$ cm^3), and assuming $K^{\rm max} \sim 2 \times 10^{-10}$ cm^3/s and a branching ratio between 1% and 50%, we get a total formation rate $\mathcal{R}$ ranging from 2×10^4 to 10^6 molecules/s (with $I = 50\,{\rm W/cm^2}$ and $T = 1$ mK). Much larger rates for the same conditions can be obtained by saturating the transition to $K^{\rm limit}$, a gain of about 20. Larger rates can also be reached simply by increasing the densities n or the volume V, or by reducing the temperature: far from saturation, $K_{v'}^{\rm max}$ scales like T^{-1}, while $K^{\rm limit}$ scales like $T^{-1/2}$. We note that since the formation rate is large for the uppermost level v', the laser frequency necessary for this process is very close to the $2s \to 2p$ atomic transition of Li, making it very easy to realize. We note that since the other alkali-metal hydrides have very similar properties (electronic potentials, dipole moments, etc.), the same general results are to be expected: the formation of large quantities of molecules in a single rovibrational level of the $a\,^3\Sigma^+$ excited state.

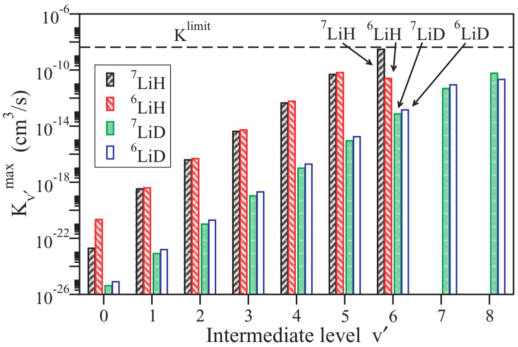

FIG. 3. (Color online) Rate coefficient $K_{v'}^{\rm max}$ with $I = 50\,{\rm W/cm^2}$ and $T = 1$ mK. The horizontal dashed line shows the value of $K^{\rm limit} = 4.25 \times 10^{-9}$ cm^3/s for ^{7}LiH: it is, respectively, 4.38, 1.79, and 1.89 ($\times 10^{-9}$ cm^3/s), for ^{6}LiH, ^{7}LiD, and ^{6}LiD.

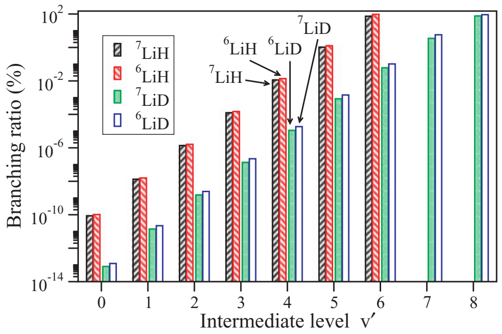

FIG. 4. (Color online) Branching ratios $r_{v=0}^{v'}$ for the various isotopomers. Large ratios (1% to 95%) occur for the two top levels v'.

Forming large amounts of alkali-metal hydride molecules in a single quantum state may allow the study of chemical reactions governed by the fermionic or bosonic nature of the constituents [8–10]. For example, if LiH, formed in a trap with spin-polarized Li and H, collides with spin-polarized H, we have the following processes:

$$
{\rm LiH} + {\rm H} \longrightarrow \begin{cases} {\rm LiH} + {\rm H}, & \text{elastic,} \\ {\rm Li} + {\rm H} + {\rm H}, & \text{requires } \varepsilon \geqslant E_b, \\ {\rm Li} + {\rm H}_2, & \text{impossible.} \end{cases}
$$

Unless the collision energy is large enough to break LiH (with the smallest E_b being 86 mK for ^{6}Li, see Table I), only elastic collisions can occur: LiH cannot quench to lower levels (there are none), and a reaction to form H_2 is prohibited, since the total spin projection of the purely stretched system is conserved and H_2 is not bound in the triplet state. The same is true for all of the isotopomers.

Collisions of LiH with Li lead to the following channels:

$$
{\rm LiH} + {\rm Li} \longrightarrow \begin{cases} {\rm LiH} + {\rm Li}, & \text{elastic,} \\ {\rm Li} + {\rm Li} + {\rm H}, & \text{requires } \varepsilon \geqslant E_b, \\ {\rm Li}_2(v', J') + {\rm H}, & \text{reaction.} \end{cases}
$$

Again, no quenching or breakup (at low energy) can occur for all isotopomers: however, reactions could take place to form $\rm Li_2$, which has several bound levels in the $a\,^3\Sigma_u^+$ state. By analogy with Feshbach molecules, the very extended $a\,^3\Sigma^+$ bound level of LiH (see Fig. 2) would appear, to an approaching spin-polarized Li atom, as a pair of almost free Li and H atoms in stretched spin states. The scattering of Li by the H atom in LiH will result in an elastic process (elastic or resonant exchange collisions: no other outcome is possible). The s-wave scattering (at low energy) with the Li atom in LiH will depend on the fermionic or bosonic nature of Li. For fermionic ^{6}Li, s-wave scattering is suppressed [8], and we expect the reaction rate to be small, and thus ^{6}LiH to be a rather stable system in a spin-polarized environment. Naturally, if the system is not spin polarized or if there is significant spin-orbit coupling [13], spin-flip collisions would lead to the the formation of H_2 and Li_2 singlet molecules. The same conclusions would be true if we consider D instead of H. However, if bosonic ^{7}Li is used instead, the suppression of collisions between the Li atoms will not take place, and we expect large chemical reaction rates. Thus, one could study chemical reactions that depend on Fermi or Bose statistics.

If the density of LiH molecules becomes large, collisions between these molecules will take place, leading to

$$\mathrm{LiH} + \mathrm{LiH} \longrightarrow \begin{cases} \mathrm{LiH} + \mathrm{LiH}, & \text{elastic}, \\ \mathrm{Li}_2 + \mathrm{H}_2, & \text{reaction}, \end{cases}$$

where again no quenching or breakup (at low energy) of LiH is possible. If the molecule is fermionic, i.e. ^{6}LiH or ^{7}LiD, then the s-wave scattering will be suppressed, and so will the reaction rates. If the molecules are bosonic, we expect large reaction rates. However, recent theoretical studies [10] predict that if a bosonic dimer is composed of two fermions with very different masses, then reactions would also be suppressed. Such is the case for ^{6}LiD. Thus all dimer-dimer reactions of LiH isotopomers are suppressed except for ^{7}LiH. Considering all the possible reaction partners above, we can thus expect that ^{6}LiH should be very stable at ultracold temperatures.

In conclusion, we have shown that large amounts of triplet LiH molecules could be formed into a single rovibrational state using photoassociation of Li and H into the $b\,^3\Pi$ followed by radiative decay. Rate coefficients up to the saturation limit can easily be reached at moderate laser powers, due to the unusually large overlap of the uppermost levels of the $b\,^3\Pi$ with both the continuum and bound levels of the $a\,^3\Sigma^+$. We also discussed the relevance of alkali-metal hydride molecules to ultracold chemistry. Finally, we point out that because all alkali-metal hydrides have very similar properties, the LiH results can be generalized to other alkali-metal hydrides and their isotopomers [13].

The work of E.J. and R.C. was supported in part by the Department of Energy, Office of Basic Energy Sciences.

---

[1] J. Doyle *et al.*, Eur. Phys. J. D **31**, 149 (2004), and references therein.

[2] S. Jochim *et al.*, Science **302**, 2101 (2003); M. Greiner, C. A. Regal, and D. S. Jin, Nature (London) **426**, 537 (2003); M. W. Zwierlein *et al.*, Phys. Rev. Lett. **91**, 250401 (2003).

[3] L. D. Carr and J. Ye, New J. Phys. **11**, 055009 (2009), and references therein.

[4] L. Santos, G. V. Shlyapnikov, P. Zoller, and M. Lewenstein, Phys. Rev. Lett. **85**, 1791 (2000).

[5] D. DeMille, Phys. Rev. Lett. **88**, 067901 (2002); S. F. Yelin, K. Kirby, and R. Côté, Phys. Rev. A **74**, 050301(R) (2006); E. Kuznetsova, R. Côté, K. Kirby, and S. F. Yelin, Phys. Rev. A **78**, 012313 (2008).

[6] D. DeMille *et al.*, Phys. Rev. A **61**, 052507 (2000); J. J. Hudson, B. E. Sauer, M. R. Tarbutt, and E. A. Hinds, Phys. Rev. Lett. **89**, 023003 (2002).

[7] V. V. Flambaum and M. G. Kozlov, Phys. Rev. Lett. **99**, 150801 (2007).

[8] M. T. Cvitaš, P. Soldań, J. M. Hutson, P. Honvault, and J. M. Launay, Phys. Rev. Lett. **94**, 200402 (2005); **94**, 033201 (2005); J. P. D'Incao, B. D. Esry, and C. H. Greene, Phys. Rev. A **77**, 052709 (2008); J. P. D'Incao, S. T. Rittenhouse, N. P. Mehta, and C. H. Greene, *ibid.* **79**, 030501(R) (2009); D. S. Petrov, C. Salomon, and G. V. Shlyapnikov, *ibid.* **71**, 012708 (2005).

[9] E. R. Hudson, N. B. Gilfoy, S. Kotochigova, J. M. Sage, and D. DeMille, Phys. Rev. Lett. **100**, 203201 (2008).

[10] B. Marcelis, S. J. J. M. F. Kokkelmans, G. V. Shlyapnikov, and D. S. Petrov, Phys. Rev. A **77**, 032707 (2008).

[11] R. Côté, M. J. Jamieson, Z. C. Yan, N. Geum, G. H. Jeung, and A. Dalgarno, Phys. Rev. Lett. **84**, 2806 (2000).

[12] A. Derevianko, R. Côté, A. Dalgarno, and G. H. Jeung, Phys. Rev. A **64**, 011404(R) (2001); N. Geum *et al.*, J. Chem. Phys. **115**, 5984 (2001).

[13] Spin-orbit coupling for systems like RbH or CsH will mix the singlet and triplet manifolds, leading to larger inelastic cross sections involving singlet molecules.

[14] J. L. Bohn and P. S. Julienne, Phys. Rev. A **54**, R4637 (1996); R. Côté and A. Dalgarno, *ibid.* **58**, 498 (1998).

[15] E. Juarros, P. Pellegrini, K. Kirby, and R. Côté, Phys. Rev. A **73**, 041403(R) (2006).

[16] P. Pellegrini and R. Côté, New J. Phys. **11**, 055047 (2009).

[17] E. P. Wigner, Phys. Rev. **73**, 1002 (1948).

[18] F. X. Gadéa, T. Leininger, and A. S. Dickinson, Eur. Phys. J. D **15**, 251 (2001) ; we use the HB (without BSSE) data.

[19] A. Boutalib and F. X. Gadéa, J. Chem. Phys. **97**, 1144 (1992).

[20] W. T. Zemke, K. R. Way, and W. C. Stwalley, J. Chem. Phys. **69**, 402 (1978).

[21] K. K. Docken and J. Hinze, J. Chem. Phys. **57**, 4928 (1972).

[22] The $v = 1$ level would be bound if the $a\,^3\Sigma^+$ curve were 5.6 times deeper, much more than its estimated 1% uncertainty [18]; $b\,^3\Pi$ has the same 1% accuracy [19].

[23] E. Juarros, K. Kirby, and R. Côté, J. Phys. B **39**, S965 (2006).

[24] W. I. McAlexander, E. R. I. Abraham, and R. G. Hulet, Phys. Rev. A **54**, R5 (1996).