Possibility of applying laser-cooling techniques to the observation of collective quantum effects

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Obtaining ultracold atomic gases is now possible because of laser cooling, and it has been proposed to search for collective quantum effects in these gases. In this paper, I show that the observation of such effects seems unlikely in alkali-metal vapors, at least in a noncondensed phase. Finally, I discuss briefly the effects of radiative trapping and long-range resonance dipole interactions on laser cooling at high atomic densities, and I show that this phenomenon introduces severe limitations of the maximum attainable density, at least for the most elementary laser-cooling scheme.

I. INTRODUCTION

Laser cooling[1] and laser confinement[2] or magnetic trapping[3] of alkali-metal atoms has been achieved recently. Such experiments have many goals, the most interesting one probably being ultrahigh-resolution spectroscopy. Another goal[2,3] is the observation of collective quantum effects exhibited by dense and cold atomic gases such as spin-polarized hydrogen.

In this paper, I want to point out that if the spin-polarized hydrogen-atom interaction is attractive but too weak to hold any bound level,[4] the corresponding interaction between alkali-metal atoms is considerably stronger and because of the larger masses, there are many bound levels.

The content of this paper is a brief description of the present knowledge of the $^3\Sigma_u^+$ states of alkali-metal molecules, the evaluation of their dissociation constant as a function of temperature, and a discussion of the kinetic[5] of dimer formation in the gas phase. In the final section, we discuss some other important points concerning laser cooling of high-density vapors.

II. POTENTIAL CURVES OF THE $^3\Sigma_u^+$ STATES OF HOMONUCLEAR ALKALI-METAL MOLECULES

Many calculations of alkali-metal-molecule potential curves have been made, but few of them appear to be very accurate for the slightly bound $^3\Sigma_u^+$ states dissociating in two ground-state atoms. In the published literature, there are accurate data concerning Li$_2$ (Refs. 5 and 6) and Na$_2$ (Refs. 7 and 8) and slightly less accurate data concerning Cs$_2$.[9] These $^3\Sigma_u^+$ states are attractive because of multipolar long-range interaction and mainly because of the leading $-C_6/R^6$ term, and they are repulsive at short distance because of exchange interaction. The C_6 term is well known and Table I presents values of this quantity

TABLE I. C_6 in atomic units. All values are taken from Ref. 12. The accuracy can be estimated of the order of 1% for Li and 20% for Cs (see Refs. 13 and 14).

Atom	H	Li	Na	K	Rb	Cs
C_6	6.50	1390	1580	3820	4600	7380

for hydrogen and the alkali-metal atoms. The exchange interaction is well understood also,[10] but not very easy to evaluate.[11]

This table shows clearly that the long-range interaction is considerably stronger for alkali-metal atoms than for hydrogen. Moreover, it is well known that long-range interactions dominate the properties of molecular bound levels close to the dissociation limit,[15] and a strong long-range interaction means many bound levels. Table II presents the available data concerning Li$_2$, Na$_2$, and Cs$_2$. In the first two cases, both experiment and theory are available while Cs$_2$ data is mainly theoretical.

The following comments can be made.

(i) The well depth D_e does not depend strongly on the alkali-metal (being in the range 150–350 cm^{-1}) and is considerably larger than for H [$D_e = 4.49$ cm^{-1} (Ref. 16)].

(ii) Although we have no direct information on K$_2$ and Rb$_2$, their properties should be similar (this is verified in the case of NaK for which the spectroscopy of the $^3\Sigma_u^+$ state is known[17(a)] and in the cases of various interalkali molecules for which information on this $^3\Sigma_u^+$ state has been deduced from differential spin exchange scattering experiments[17(b)]).

(iii) The number of rovibrational bound levels increases very rapidly with the atomic mass.

Up to this point, we have used a molecular point of view. We can use also the point of view of condensed matter, i.e., the quantum theorem of corresponding states [(QTCS), see Ref. 18 and references therein]: a fundamental parameter characterizing the interaction between two atoms is the quantum parameter $\eta = \hbar^2/(m\sigma^2 D_e)$, where σ is the collision diameter and m the mass. Table III shows that this parameter is small for spin-polarized alkali metal and accordingly one does not expect significant quantum behavior for the alkali-metal spin-polarized systems (at least in the range of reduced temperature $k_B T/D_e$ where QTCS has been tested). This was already noted in Ref. 18.

Finally, it is easy to link these two points of view: For instance, from Wentzel-Kramers-Brillouin (WKB) arguments, one shows easily that the numbers of vibrational and rotational levels [N_v, $N_j(v=0)$] are both proportional to $\eta^{-1/2}$.

TABLE II. This table gives for the $^3\Sigma_u^+$ state of each molecule the well depth D_e, the equilibrium distance r_e, the vibrational (ω_e), and rotational (B_e) constants. N_v is the number of bound vibrational levels and $N_j(v=0)$ is the number of bound rotational levels for $v=0$. These values are taken from (or calculated thanks to) Refs. 5 and 6 for Li_2, Refs. 7 and 8 for Na_2, and Ref. 9 for Cs_2.

Molecule		$^6Li_2$	$^{23}Na_2$	Cs_2
D_e (cm^{-1})	Theor.	341. (15)	180.2	290 (30)
	Expt.	336.0 (5.4)	174.45 (36)	
r_e (Å)	Theor.	4.11 (12)	5.206	6.4
	Expt.	4.13 (8)	5.0911	
ω_e (cm^{-1})		73.0 (1.4)	24.47 (21)	11
B_e (cm^{-1})		0.329 (13)	0.0565	0.0062
N_v		9	17	50
N_j $(v=0)$		32	53	216

III. DISSOCIATION CONSTANT

If the atoms electronic spins are totally polarized, it is impossible to form ground-state singlet molecules. This remark was made by Kastler[19] and this prediction was verified experimentally by Alzetta, Gozzini, and Moi in 1972.[20] Therefore we consider that the only species in the gas are spin-polarized atoms A (density n_A) and $^3\Sigma_u^+$ molecules A_2 (density n_{A_2}). At equilibrium the densities verify

$$\frac{n_A^2}{n_{A_2}} = K(T) .$$

The dissociation constant $K(T)$ has the dimension of a molecular density and its value can be easily calculated using Boltzmann statistics (see, for example, Ref. 21),

$$K(T) = 2^{-3/2}\Lambda(T)^{-3}\frac{Z_A^2}{Z_{A_2}}e^{-D_e/k_B T} ,$$

where $\Lambda(T)$ is the thermal de Broglie wavelength for atom A at temperature T [$\Lambda(T)=(2\pi\hbar^2/mk_B T)^{1/2}$], and Z_A and Z_{A_2} are the atomic and molecular partition functions (the energy zero being the atomic ground-state and the bottom of the molecular well, respectively). The exact evaluation of Z_{A_2} demands some care (because of problems of quasidegeneracy and of nuclear spins). However, within factors of a few unities, $Z_A=1$ and $Z_{A_2}=\exp(-\omega_e/2k_B T)$ in the low-temperature regime $k_B T \ll B_e$ and $Z_{A_2}\simeq(k_B T/B_e)\exp(-\omega_e/2k_B T)$ in the intermediate-temperature regime $B_e \ll k_B T \ll \omega_e$ (where ω_e and B_e are the vibrational and rotational constants of the $^3\Sigma_u^+$ state). In the low-temperature regime, one obtains

$$\frac{n_A}{n_{A_2}} \simeq \frac{e^{-D_0/k_B T}}{n_A\Lambda(T)^3} ,$$

where $D_0=D_e-\omega_e/2$ is the dissociation energy of the level $^3\Sigma_u^+ v=0$.

TABLE III. The collision diameter σ and the quantum parameter η for spin-polarized H, Li, Na, and Cs atoms.

Atom	H	Li	Na	Cs
σ (Å)	3.69	3.4	4.28	5.5
η	0.55	1.5×10^{-3}	4.6×10^{-4}	3×10^{-5}

This equation proves that in the region of collective quantum effects, i.e., in the region $n_A\Lambda(T)^3\simeq1$, the ratio n_A/n_{A_2} is of the order of $\exp(-D_0/k_B T)$. This ratio is extremely small. It is given by $\exp(-432/T)$ for Li_2, $\exp(-233/T)$ for Na_2, $\exp(-410/T)$ for Cs_2 (T in kelvin).

From this, we deduce that at equilibrium, the atomic fraction is negligible in the temperature range where one can search for collective quantum effects. However, we have considered only the atom-dimer equilibrium and because of the low value of the quantum parameter η, these systems should have an ordinary phase diagram and be in solid phase at equilibrium at very low temperature. Nevertheless, it is interesting to evaluate the speed of dimer formation in the gas phase as it will given an idea of the metastability of this phase.

IV. DIMER FORMATION IN THE GAS PHASE

This process, also called recombination, is due to three-body collisions: $A+A+M\rightarrow A_2+M$. The order of magnitude of the rate of three-body collisions can be evaluated thanks to an argument due to Bodenstein.[22] One compares the number $k_3 n^3$ of three-body collisions to the number $k_2 n^2$ of two-body collisions. This ratio is equal to the ratio of the collision diameter σ to the mean-free path λ_c. This gives $k_3=\sqrt{2}\pi^2\sigma^5 v_r=10^{-31}$ cm^6 s^{-1} (using $\sigma=5$ Å and mean relative speed $v_r=3\times10^4$ cm/s).

We have collected in Table IV some measured values of the recombination rate k_r. It appears that the order of magnitude of k_r is comparable to the three-body collisions rate. This proves that the efficiency of three-body collision for recombination is not small.

Many theoretical works have been made in order to understand the dependences of the rate k_r with A, M, and with the temperature T. Among the most important contributions, we may quote the works of Wigner,[27] Keck,[28] Bunker,[29] and Porter.[30] Nowadays, the two-step theory of Bunker[29] is commonly assumed to be valid.[31−33,25] In this theory, the first step is the formation of a collision complex (a classical orbiting trajectory or a quantum resonance): $A+A\rightarrow A_2^*$. This first reaction is assumed to be in equilibrium

$$n_{A_2^*} = K^*(T)n_A^2$$

$K^*(T)$ is the pseudoequilibrium constant for this reaction[32]

TABLE IV. Some measured values of the recombination rate k_r.

Reaction	T (K)	k_R $(cm^6 s^{-1})$	Reference
$2H + H_2 \rightarrow 2H_2$	300	$(7.5 \pm 1) \times 10^{-33}$	23
$2I + Ar \rightarrow I_2 + Ar$	298	$(8.0 \pm 0.8) \times 10^{-33}$	26
$Rb + 2Xe \rightarrow RbXe + Xe$	300	$(2.21 \pm 0.12) \times 10^{-31}$	24
$3Rb \rightarrow Rb_2 + Rb$	600	1.7×10^{-30}	25
$3Cs \rightarrow Cs_2 + Cs$	600	2×10^{-30}	25

$$K^*(T) = 2^{3/2} \Lambda(T)^3 g_A^{-2} \sum_i g_i (2J + 1) \exp(-E_i^r / k_B T)$$

[$\Lambda(T)$ is the atomic de Broglie wavelength, g_A the atomic degeneracy, E_i^r, J and g_i are the energy, J value, and nuclear spin degeneracy for resonance i].

The second step is the stabilization of A_2^* by a collision during which rotational or vibrational relaxation occurs:

$$A_2^* + M \rightarrow A_2 + M .$$
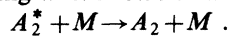
If $M \neq A$, the first step may be AM^* formation and the second step the reactive encounter $AM^* + A \rightarrow A_2 + M$. The rate of this second step being k_f, the recombination rate is then given by

$$k_r = k_f K^*(T) .$$

$K^*(T)$ has been studied in detail by Meyer;[33] it is maximum for a temperature of the order of the energy of the lowest resonance. Assuming a Lennard-Jones potential, he finds that this energy is given by $k_B T_0 \simeq 4 B_e^{3/2} D_e^{-1/2}$ and that $K^*(T)$ decreases with increasing temperature:

$$K^*(T) = 47.9 r_e^3 \left[\frac{D_e}{k_B T} \right]^{5/6} \left[\frac{B_e}{D_e} \right]^{1/2} ,$$

$$k_B T_0 \ll k_B T \ll D_e$$

and

$$K^*(T) = 45.7 r_e^3 \left[\frac{D_e}{k_B T} \right]^{3/2} \left[\frac{B_e}{D_e} \right]^{3/2} , \quad D_e \ll k_B T .$$

The rate of the second step is more difficult to evaluate. Roberts et al.[32] have used detailed calculation of the cross sections for rotational relaxation. Such cross sections usually increase at low collision energy.[34] This behavior is also exhibited by the cross section for complex formation or the "soft-sphere" cross section of Ref. 25 which are both proportional to $(C_6 / k_B T)^{1/3}$.

These theoretical results as well as the experimental results collected in Table IV suggest the following conclusions.

(i) The recombination rate constant k_r is sensitive to the long-range part of the interaction potential. This has two consequences: (i) k_r is large for the alkali metal and (ii) it is comparable for singlet or triplet state formation.

(ii) The calculated temperature dependence of the recombination rate is $k_r \propto T^{-7/6}$ (in the range $k_B T_0 \ll k_B T \ll D_e$ and using the soft-sphere cross section). Typical T_0 values are 0.06 K for Li, 2×10^{-4} K for Cs. This means that for heavy alkali metals like Cs, using this temperature dependence and the value of k_r measured at $T = 600$ K (see Table IV), we calculate a value of the recombination-rate constant of the order of 10^{-23} cm^6 s^{-1} at $T = 10^{-3}$ K and the recombination lifetime $\tau = k_r^{-1} n_A^{-2}$ will be quite small (or the order of 1 s for $n_A = 10^{12}$

cm^{-3}, of 1 μs for $n_A = 10^{15}$ cm^{-3}). For $T < T_0$, the above results suggest a rapid decrease of k_r but there is no real knowledge of k_r in this temperature range.

V. OTHER IMPORTANT PROCESSES

We want to discuss here some other processes which should be important in laser cooling and in laser confinement of a dense vapor.

A. Interaction between excited and ground-state atoms

This interaction is the well-known long-range resonance dipole-dipole interaction.[35] Its value is given by

$$V_{dd} = \frac{\hbar \Gamma}{2} \left[\frac{\lambda_0}{2 \pi r} \right]^3 \alpha ,$$

where $\alpha = \pm \frac{3}{2}$ for π states and $\alpha = \pm 3$ for Σ states arising from an S and a P state. Γ is the natural linewidth of the S-P transition and λ_0 is wavelength. The $+$ or $-$ sign of α depends on the u-g parity of the state. This expression has neglected the effect of electronic and nuclear spins. Taking account of this effect is straightforward and will change the values of α, but will not affect the magnitude of this interaction.

It is not easy to predict all the consequences of this large interaction. It seems that it will prevent laser cooling at large density for the following reasons:

(i) Radiative forces are very sensitive to the frequency distance between laser and the atomic line and an effect of V_{dd} is to shift the atomic line. The average value of the modulus of V_{dd} is roughly linear in the density n_A and comparable to $\hbar \Gamma$ if $n_A = (2\pi / \lambda_0)^3$.

(ii) Another consequence of this interaction is that, when an atom is excited, it is strongly attracted or repelled by its nearest ground-state neighbor and this will give an efficient heating process when the initial kinetic energy is sufficiently low so that spontaneous emission occurs during the collision.

As a consequence, it appears that by direct laser cooling, the density is limited to $n_A \leq (2\pi / \lambda_0)^3$ and the temperature to $k_B T \geq \hbar \Gamma / 2$. It is possible by an adiabatic expansion to cool further, but this will reduce the density and this will not increase the value of $n_A \Lambda(T)^3$ (as can be shown by Liouville theorem). In these conditions, $n_A \Lambda(T)^3$ is limited to

$$n_A \Lambda(T)^3 \leq \left[\frac{2\pi}{\lambda_0} \right]^3 \left[\frac{h}{m \Gamma} \right]^{3/2} .$$

We have evaluated this limit for hydrogen, lithium, and cesium (λ_0 and Γ pertaining to their first resonance line).

This limiting value of $n_A \Lambda(T)^3$ is close to 9 for hydrogen, 0.17 for Li, and 10^{-3} for Cs.

B. Radiation trapping

If the laser is resonant with a transition of considerable oscillator strength $(f \sim 1)$, the photon absorption cross section is of the order of λ_0^2. At very low temperature, the Doppler width is less or comparable to the natural width and this lowers considerably the radiation trapping threshold. If d is the dimension of a sample, radiation trapping occurs as soon as $n_A d \lambda_0^2 \sim 1$. Radiation trapping will diminish the effect of radiative cooling. Typically for a small sample $d \sim 10^{-3}$ cm, the threshold density is $n_A = 10^{13}$ cm^{-3} for hydrogen and $n_A = 3 \times 10^{11}$ cm^{-3} for alkali-metal atoms.

C. Collision processes involving one or two excited atoms

The collision of an excited atom A^* and a ground-state atom A may lead to recombination, by the inverse process of photodissociation. The collision of two excited atoms A^* can produce ions A^+ or A_2^+ or other excited states A^{**}. When exoergic, such processes (energy transfer collision, Penning ionization, associative ionization) have large rate constants. More precisely, as for rotational relaxation, the cross sections for such processes usually increase when the collision energy decreases but the rate decreases because of the relative speed term. These process-es may limit strongly the lifetime of a laser cooled or confined vapor.

VI. CONCLUSION

In this paper, I have shown that the equilibrium phase diagram of spin-polarized alkali metals should not present strong quantum effects because the quantum parameter is very small for these systems. I have verified directly that the equilibrium atomic fraction is negligible in the temperature and density regions where one could search for collective quantum effects. Moreover the recombination process whose detrimental effects have already been briefly discussed by Stwalley[36] and Pritchard[37] is calculated to be very fast down to very low temperatures. Finally I have pointed out that the interactions of excited atoms will make it difficult to maintain efficient cooling of a high density vapor.

All these results cast strong doubts on the possibility of observing collective quantum effects with laser-cooled alkali-metal vapors.

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