Resonant Coupling in the Formation of Ultracold Ground State Molecules via Photoassociation

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We demonstrate the existence of a new mechanism for the formation of ultracold molecules via photoassociation of cold cesium atoms. The experimental results, interpreted with numerical calculations, suggest that a resonant coupling between vibrational levels of the 0_u^+ $(6s + 6p_{1/2})$ and $(6s + 6p_{3/2})$ states enables formation of ultracold molecules in vibrational levels of the ground state well below the $6s + 6s$ dissociation limit. Such a scheme should be observable with many other electronic states and atomic species.

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Efficient formation of long-lived cold molecules, via single-color photoassociation (PA) of a cold atom pair followed by spontaneous emission, has recently been observed for Cs_2 [1]. The formation process relies upon particular double-well features in Cs_2 excited potential curves, as was also observed for Rb_2 [2]. A more elaborate two-color PA scheme is required to achieve a comparable efficiency in K_2 [3]. In the present paper, we propose for Cs_2 the existence of a more general formation mechanism.

In the quoted experiments, the first step is a PA reaction between a pair of atoms of relative kinetic energy $E_k = k_B T$ (at a temperature $T \sim 10^{-4}$ K), which for cesium can be expressed as

$$2\mathrm{Cs}(6s) + E_k + h(\nu_0 - \Delta_L) \rightarrow \mathrm{Cs}_2^*(\Omega_{u,g}(6s + 6p_j; v, J)), \quad (1)$$

where ν_0 is the frequency of the $6s \rightarrow 6p_j$ resonance line $(j = 1/2, 3/2)$ and Δ_L (>0) is the red detuning of the laser. Reaction (1) can be understood as a vertical transition from the continuum of the ground molecular state to a rovibrational level (v, J) of the excited state $\Omega_{u,g}$. Because of the $-C_3/R^3$ long-range behavior of this potential and the ultralow temperature of the atoms, the transition occurs mostly at a large interatomic distance $R_L \sim (C_3/h\Delta_L)^{1/3}$, corresponding to the outer turning point of the excited potential, where the vibrational wave function is mainly localized [see Fig. 1(a)]. In most cases, this short-lived photoassociated molecule decays back, by spontaneous emission of a photon of frequency $\nu_0 - \Delta_2$, into a pair of atoms:

$$\mathrm{Cs}_2^* \rightarrow 2\mathrm{Cs}(6s) + E_k' + h(\nu_0 - \Delta_2). \quad (2)$$

The gain in relative kinetic energy $[E_k' - E_k = h(\Delta_2 - \Delta_L) > 0]$ generally allows both atoms to escape from the trap. The stabilization into a ground state molecule with a binding energy $E_{v''} = h(\Delta_L + \Delta_3) - E_k$,

$$\mathrm{Cs}_2^* \rightarrow \mathrm{Cs}_2(^{1,3}\Sigma_{g,u}^+(6s + 6s; v'', J'')) + h(\nu_0 + \Delta_3), \quad (3)$$

requires a favorable overlap between the vibrational wave functions of both the excited and ground molecular states. Because of the shorter range of the asymptotic $-C_6/R^6$ ground state potential, only the uppermost levels of the ground state can be populated via reaction (3) [4,5]. Efficient mechanisms for formation of cold molecules in lower vibrational levels are offered by the double-well structure [Fig. 1(b)] of the Cs_2^* 0_g^- or 1_u $(6s + 6p_{3/2})$ long-range potentials, where the vibrational wave function can display a high probability of presence both at large ($R >$ 100 a.u.) and intermediate ($R \approx 15$–25 a.u.) internuclear distances [6,7].

Following recent work on channel coupling between the $0_u^+(ns + np_j)$ states of the heavy alkali dimers [8,9], we discuss in this paper the efficiency of a new scheme taking advantage of this coupling. For small detunings Δ_L below the $6s + 6p_{1/2}$ limit, PA can proceed from the continuum of the $X^1\Sigma_g^+$ ground state to a vibrational level of the $0_u^+(6s + 6p_{1/2})$ state. Because of the coupling with the $0_u^+(6s + 6p_{3/2})$ state, a resonance phenomenon can occur between the two vibrational series and is manifested, close to the $6s + 6p_{1/2}$ dissociation limit, by a vibrational wave function showing a noticeable density probability at intermediate distances as well as at large distances [Fig. 1(c)]. Such a behavior favors spontaneous emission towards lower-energy bound levels of the $X^1\Sigma_g^+$ state.

The experimental setup was described in detail in Refs. [1,6]. To summarize, a magneto-optical trap is loaded with about 5×10^7 cesium atoms, at a density of $n_{\mathrm{at}} = 4 \times 10^{10}$ cm^{-3} and temperature of 130 ± 10 μK. PA is achieved by continuously illuminating the cold Cs atoms with the beam ($\sim$200 W/cm^2) of a Ti:sapphire laser pumped by an argon-ion laser, slightly red-detuned from the $6s(f = 4) \rightarrow 6p_{1/2}(f' = 4)$ atomic transition ($\lambda = 894$ nm). This method is now well established for long-range molecular PA spectroscopy [7,10].

Two detection methods are used to monitor the PA process. First, we measure the fluorescence yield, collected by a photodiode, from the trapped atoms. Variations in the

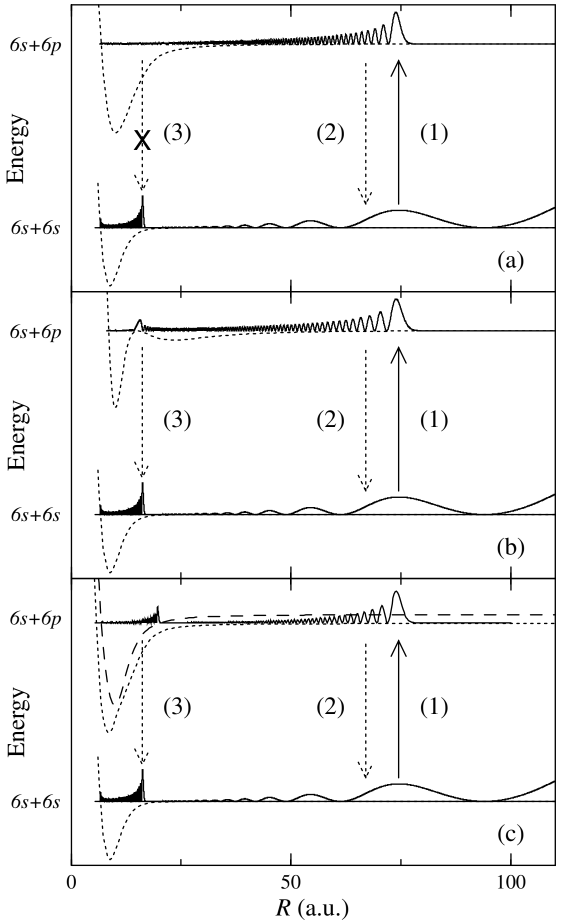

FIG. 1. Photoassociation from the cesium $6s + 6s$ continuum [reaction (1)] to (a) a typical potential; (b) a double-well potential [e.g., $0_g^-(6s + 6p_{3/2})$]; (c) two coupled states [e.g., $0_u^+(6s + 6p_{1/2,3/2})$]. The system decays by spontaneous emission either back to the continuum [reaction (2)] or to a bound level of the ground state [reaction (3)]. For case (a), reaction (3) is usually unlikely.

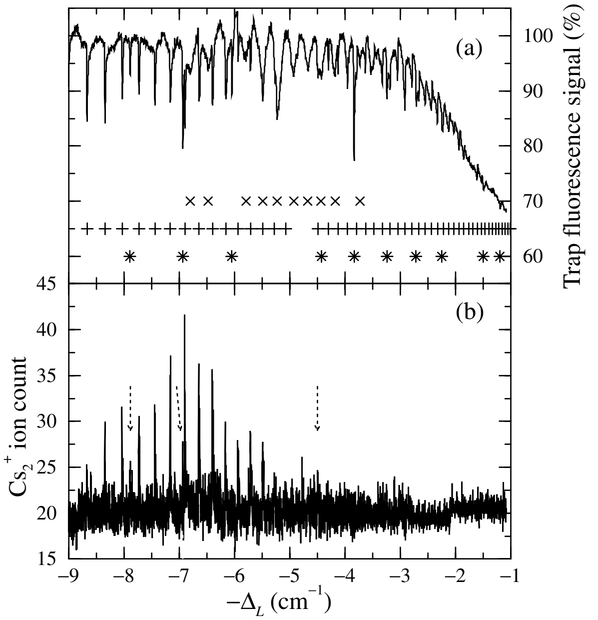

FIG. 2. Photoassociation spectra as a function of the laser detuning Δ_L below the $6s + 6p_{1/2}$ dissociation limit. (a) Trap loss spectrum. Markers indicate peaks assigned to the 0_g^- (*), 0_u^+ (+), and 1_g (×) states. (b) $\mathrm{Cs_2}^+$ ion signal resulting from the ionization of cold ground state molecules. Arrows indicate peaks associated to the $0_g^-(6s + 6p_{1/2})$ state.

intensity of this yield are due to trap losses induced by the PA process. Second, $\mathrm{Cs_2}^+$ ions are detected in a time-of-flight mass spectrometer, after photoionization of the cold $\mathrm{Cs_2}$ molecules produced by reaction (3). The ionizing photons are provided by a pulsed dye laser ($\lambda \sim 716$ nm, 7 ns duration, 1.5 mJ/pulse) pumped by the second harmonic of a Nd:YAG laser. The resonance-enhanced multiphoton ionization (REMPI) process uses as the intermediate step the vibrational levels of an electronic molecular state correlated to the $6s + 5d$ dissociation limit. As in previous experiments [1], we have verified that $\mathrm{Cs_2}^+$ ions are still produced a few ms after the PA laser has been turned off, indicating that the signal comes from molecules in the ground state and not in the short-lived ($\sim$20 ns) excited state.

Both spectra thus obtained are shown in Fig. 2, as a function of the detuning Δ_L of the PA laser below $6s + 6p_{1/2}$, in the range $1 \leq \Delta_L \leq 9$ cm^{-1} (no signal is recorded for $\Delta_L < 1$ cm^{-1} as the PA laser then strongly perturbs the atom trap). In the trap fluorescence signal (already shown for $\Delta_L \leq 14$ cm^{-1} in Ref. [11]), normalized to the total number of atoms, vibrational progressions corresponding to the 1_g, 0_u^+, and 0_g^- attractive states are identified by their energy spacing and calculated width due to the hyperfine structure, 3 GHz, 200 MHz, and 200 MHz, respectively. The position of the 0_g^- lines has been fitted using the semiclassical LeRoy-Bernstein law [12], which confirms that due to the cancellation of the C_3 coefficient, the leading term in the multipolar expansion of the $0_g^-(6s + 6p_{1/2})$ potential is $-C_6/R^6$, with $C_6 = 99\,900 \pm 6300$ a.u., in good agreement with the theoretical value of $C_6 = 94\,480$ a.u. [13].

For detunings $4 \leq \Delta_L \leq 9$ cm^{-1}, we detect up to 40 molecular ions per photoionization laser pulse, emerging from a background of about 20 ion counts [14]. Three small peaks of the ion spectrum are assigned to PA into $0_g^-(6s + 6p_{1/2})$ levels, at $\Delta_L = 4.5$, 6.9, and 7.9 cm^{-1}, and will not be considered in this paper. As noted above, the $-C_6/R^6$ behavior of this state, similar to that of the ground state, makes reaction (3) in Fig. 1(a) more probable. A series of 14 other peaks are identified as corresponding to $0_u^+(6s + 6p_{1/2})$ levels.

For the theoretical interpretation, Born-Oppenheimer potentials for $\mathrm{Cs_2}$ were constructed from *ab initio* curves (for $R \lesssim 25$ a.u.) [15] connected to an asymptotic part (for $R \gtrsim 30$ a.u.) obtained from C_3, $C_6, \ldots$, coefficients [16], with an R-dependent spin-orbit coupling [15] for the $0_u^+(6s + 6p_j)$ states. The vibrational wave functions are calculated using the mapped Fourier grid Hamiltonian method, which is particularly well suited for the calculation of highly elongated bound levels located just below the dissociation limits as well as resonant levels [17]. Because of the very low kinetic energy of the atoms, we describe the motion of the atom pair in reaction (1) by a single continuum wave function $|\chi(k_B T)\rangle$, calculated using standard Numerov integration, for an energy of $E/k_B = T = 140\ \mu$K above $6s + 6s$. A small shift of the repulsive wall of the $0_u^+(6s + 6p_{3/2})$ potential (up to $R = 8.3$ a.u.) by $+0.01$ a.u. allows one to reproduce correctly the observed energy value of the corresponding vibrational levels. The effects of the hyperfine structure are neglected and rotation is not considered.

The PA rate per atom to a vibrational level $|v(0_u^+)\rangle$ populated at a detuning Δ_L below $6s + 6p_{1/2}$ is obtained from a perturbative approach [18],

$$\mathcal{R}_{\rm PA}(\Delta_L) = \left(\frac{3\lambda_{\rm th}^2}{2\pi}\right)^{\frac{3}{2}} \frac{h}{2}\, n_{\rm at} K^2 \mathcal{A}\, |\langle v(0_u^+) \,|\, \chi(k_B T)\rangle|^2, \tag{4}$$

in the current experimental conditions, with $\lambda_{\rm th} = h\sqrt{1/(3\mu k_B T)}$ the thermal de Broglie wavelength (μ is the reduced mass of the system), $2K = 9.9 \times 10^9\ {\rm s}^{-1}$ the atomic Rabi frequency (in effect considering an R-independent transition dipole moment) for a PA laser intensity $I = 200\ {\rm W/cm}^2$, and $\mathcal{A} = 35/3888$ is an angular factor including hyperfine degeneracies [11,18]. The cold molecule formation rate per atom is then obtained by considering the branching ratio to the bound levels $|v''(X^1\Sigma_g^+)\rangle$,

$$\mathcal{R}_{\rm mol}(\Delta_L) = \mathcal{R}_{\rm PA}(\Delta_L) \sum_{v''} |\langle v(0_u^+) \,|\, v''(X^1\Sigma_g^+)\rangle|^2, \tag{5}$$

where the sum runs over all vibrational levels of the $X^1\Sigma_g^+$ state, again neglecting the R dependence of the transition dipole moment.

Results for $0_u^+(6s + 6p_{1/2})$ as the lone excited state and for the two coupled $0_u^+(6s + 6p_j)$ states [corresponding to Fig. 1(a) and Fig. 1(c), respectively] are given in Fig. 3(a). We see an oscillation in the rate value attributable to the oscillations of $|\chi(k_B T)\rangle$, the minima at $\Delta_L \approx 12.8\ {\rm cm}^{-1}$ and $3.4\ {\rm cm}^{-1}$ corresponding to the nodes of $|\chi(k_B T)\rangle$ at $R \approx 61.2$ a.u. and 95.4 a.u., respectively; PA can take place between those minima.

Calculations indicate that two vibrational levels of the $0_u^+(6s + 6p_{3/2})$ state lie in the region $0 \le \Delta_L \le 20\ {\rm cm}^{-1}$, at $\Delta_L \approx 18\ {\rm cm}^{-1}$ and $7\ {\rm cm}^{-1}$, almost coinciding with maxima in the PA rate to the $0_u^+(6s + 6p_{1/2})$ state. The wave functions of $0_u^+(6s + 6p_{1/2})$ vibrational levels coupled to a level of the $0_u^+(6s + 6p_{3/2})$ state show an important probability density at the outer turning point of the latter [Fig. 1(c)], allowing a better overlap with the bound levels of the $X^1\Sigma_g^+$ state, which raises the ratio of reaction (3) over reaction (2) in the spontaneous decay of the excited molecules. Moreover, we see in Fig. 4, for PA at $\Delta_L \approx 7\ {\rm cm}^{-1}$, that ground state molecules formed through a resonantly coupled vibrational level can be found well below the dissociation limit (bound by 1 to $50\ {\rm cm}^{-1}$), while only the uppermost, highly elongated ($\sim$100 a.u.) vibrational levels, bound only by a fraction of ${\rm cm}^{-1}$, are reached after spontaneous emission from an uncoupled $0_u^+(6s + 6p_{1/2})$ state, as was expected [4]. The maximum predicted in Fig. 3(a) for $\Delta_L < 2\ {\rm cm}^{-1}$, unaffected by the coupling, is due to the good long-range overlap of the excited wave function with $|\chi(k_B T)\rangle$, resulting in a higher PA rate. Here again, molecules are formed only in the uppermost levels of the ground state.

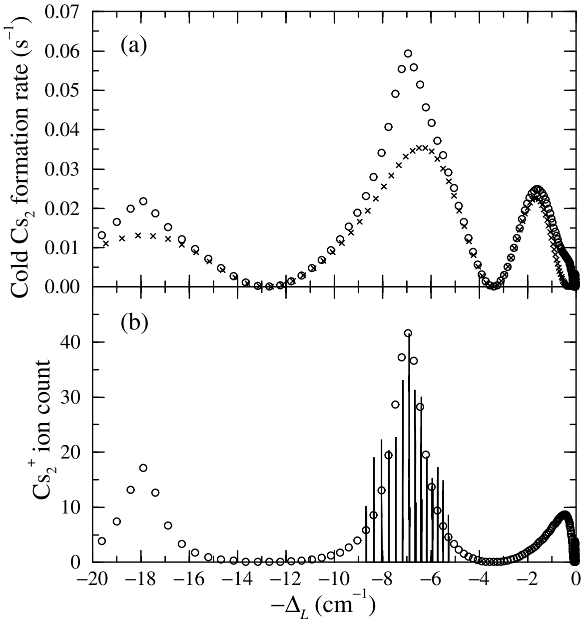

FIG. 3. (a) Ultracold ground state Cs$_2$ formation rate $\mathcal{R}_{\rm mol}$ (per second per atom) through the $0_u^+(6s + 6p_{1/2,3/2})$ electronic states, with detuning Δ_L given with respect to the $6s + 6p_{1/2}$ dissociation limit. Circles: calculated values, starting from the $X^1\Sigma_g^+$ continuum at $T = 140\ \mu$K; crosses: same without the coupling between the 0_u^+ channels. (b) Cs$_2{}^+$ ion count for molecules formed through the coupled channels. Solid line: experimental signal (±5 uncertainty); circles: calculated $\mathcal{R}_{\rm ion}$ values (arbitrarily scaled).

The computed rates for $\Delta_L \approx 7\ {\rm cm}^{-1}$, $\mathcal{R}_{\rm mol} \approx 0.03\ {\rm s}^{-1}$ and $0.06\ {\rm s}^{-1}$ without and with coupling, respectively (the corresponding PA rate is $\mathcal{R}_{\rm PA} \approx 1\ {\rm s}^{-1}$), are comparable to those obtained, under equivalent conditions, for PA in the $0_g^-(6s + 6p_{3/2})$ state ($\mathcal{R}_{\rm mol} \approx 0.2\ {\rm s}^{-1}$, $\mathcal{R}_{\rm PA} \approx 3\ {\rm s}^{-1}$) [11]. Our calculations predict a smaller value of $\mathcal{R}_{\rm mol}$ for $\Delta_L = 18\ {\rm cm}^{-1}$ and the resulting molecules may be barely visible experimentally.

We simulate the Cs$_2{}^+$ ion spectrum by calculating the $v''(X^1\Sigma_g^+) \rightarrow v'(^1\Pi_u(6s + 5d))$ transition probability, assuming a uniform ionization probability for all v' in the second step of the REMPI process. We thus have

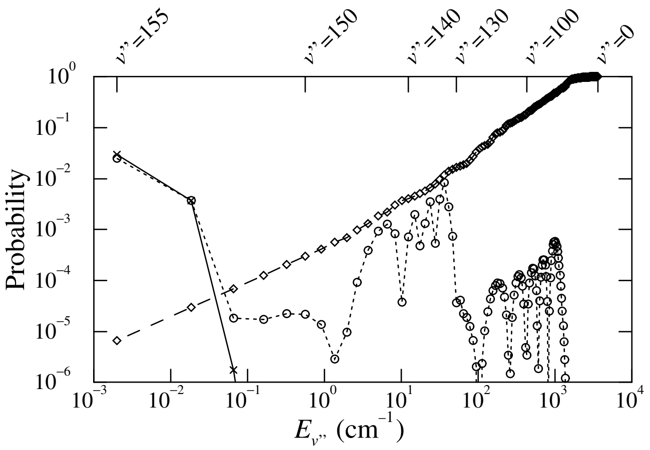

FIG. 4. Diamonds: ionization probability $\mathcal{P}_{\text{ion}}(v'')$ of the $X^1\Sigma_g^+$ vibrational levels. Circles: Franck-Condon factors between the $0_u^+(6s + 6p_j)$ vibrational level at $\Delta_L \approx 7\ \text{cm}^{-1}$ and levels of $X^1\Sigma_g^+$. Crosses: same as circles, but for $0_u^+(6s + 6p_{1/2})$ in the absence of coupling.

$$\mathcal{P}_{\text{ion}}(v'') = \sum_{v'} |\langle v'(^1\Pi_u)\,|D|\,v''(X\,^1\Sigma_g^+)\rangle|^2 f(\nu_{v'',v'}), \quad (6)$$

with D the R-dependent $6s + 6s \rightarrow 6s + 5d$ transition dipole moment [19] and $f(\nu_{v'',v'}) = \exp[-c(\nu_{v'',v'} - \nu_{\text{ion}})^2]$ accounting for the width of the ionizing laser [$c = \ln 2/(1.0\ \text{cm}^{-1})^2$, $\nu_{v'',v'}$ is the frequency of the $v''(X^1\Sigma_g^+) \rightarrow v'(^1\Pi_u)$ transition, and $\nu_{\text{ion}} = 14\,060\ \text{cm}^{-1}$ is the frequency of the ionizing laser used in the experiment]. We see in Fig. 4 that the detection probability of molecules in the last few bound levels of the ground state is almost nil. This means that cold molecules formed in the absence of a resonance will not be detected, as is the case for $\Delta_L < 2\ \text{cm}^{-1}$. Defining the $\text{Cs}_2{}^+$ production rate for a given Δ_L and ν_{ion} as

$$\mathcal{R}_{\text{ion}}(\Delta_L) = \mathcal{R}_{\text{PA}}(\Delta_L) \sum_{v''} \mathcal{P}_{\text{ion}}(v'') \times |\langle v(0_u^+)\,|\,v''(X^1\Sigma_g^+)\rangle|^2, \quad (7)$$

we are able to reproduce the observed $\text{Cs}_2{}^+$ ion signal, as shown in Fig. 3(b). In the absence of the resonant coupling, we obtain $\mathcal{R}_{\text{ion}} < 10^{-12}$ over the entire Δ_L range considered [using the same arbitrary scaling factor as in Fig. 3(b)].

In conclusion, we find a strong indication that resonant coupling allows for the efficient formation of cold molecules in vibrational levels well below the ground state dissociation limit (around $v'' = 132$, with $E_{v''} > 10\ \text{cm}^{-1}$). The resonant coupling mechanism appears fairly often as a non-Born-Oppenheimer interaction in molecular systems and should be exploitable using other excited electronic states as PA intermediates and applicable to the formation of different species of cold molecules, such as other alkali dimers.

Future work will focus on changes in the ionization process in order to enhance the detection of the ground state cold molecules, as molecules formed in the uppermost vibrational levels are not detected by the current REMPI scheme. We will also explore PA in the region of $\Delta_L \approx 18\ \text{cm}^{-1}$, where the next resonance between levels of the $0_u^+(6s + 6p_j)$ states is predicted.

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[1] A. Fioretti *et al.*, Phys. Rev. Lett. **80**, 4402 (1998).
[2] C. Gabbanini *et al.*, Phys. Rev. Lett. **84**, 2814 (2000).
[3] A. N. Nikolov *et al.*, Phys. Rev. Lett. **84**, 246 (2000).
[4] H. R. Thorsheim *et al.*, Phys. Rev. Lett. **58**, 2420 (1987).
[5] R. Côté and A. Dalgarno, J. Mol. Spectrosc. **195**, 236 (1999).
[6] A. Fioretti *et al.*, Eur. Phys. J. D **5**, 389 (1999).
[7] D. Comparat *et al.*, Eur. Phys. J. D **11**, 59 (2000).
[8] V. Kokoouline *et al.*, Phys. Rev. A **62**, 022504 (2000).
[9] V. Kokoouline *et al.*, Phys. Rev. A **62**, 032716 (2000).
[10] W. C. Stwalley and H. Wang, J. Mol. Spectrosc. **195**, 194 (1999).
[11] C. Drag *et al.*, IEEE J. Quantum Electron. **36**, 1378 (2000).
[12] R. J. LeRoy and R. B. Bernstein, J. Chem. Phys. **52**, 3869 (1970).
[13] M. Marinescu and A. Dalgarno, Phys. Rev. A **52**, 311 (1995).
[14] A. Fioretti *et al.*, Phys. Rev. Lett. **82**, 1839 (1999).
[15] N. Spies, Ph.D. thesis, Universtät Kaiserlautern, 1989.
[16] All coefficients are taken from Ref. [13], except for $C_3(6s + 6p) = 10.1$ a.u. obtained from local experiments and $C_6(6s + 6s) = 6510$ a.u. from C. Drag *et al.*, Phys. Rev. Lett. **85**, 1408 (2000).
[17] V. Kokoouline *et al.*, J. Chem. Phys. **110**, 9865 (1999).
[18] P. Pillet *et al.*, J. Phys. B **30**, 2801 (1997).
[19] We use the $^3\Sigma_u^+(6s + 6s) \rightarrow {}^3\Pi_u(6s + 5d)$ transition dipole moment taken from Ref. [15], connected to an asymptotic expansion for $R \geq 40$ a.u. [13]. We assume that the $^1\Sigma_g^+(6s + 6s) \rightarrow {}^1\Pi_g(6s + 5d)$ dipole moment will have a similar R dependence.