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Laser synthesis of ultracold alkali metal dimers: optimization and control

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The review concerns the potential of modern high-resolution laser spectroscopy and state-of-the-art *ab initio* electronic structure calculations used to obtain comprehensive information on the energy and radiative properties of strongly coupled rovibronic diatomic states. The possibility of deperturbation treatment of the intermediate electronically excited states at the experimental (spectroscopic) level of accuracy is demonstrated taking alkali metal dimers as examples. The deperturbation analysis is of crucial importance to optimize multistep laser synthesis and stabilization of ultracold molecular ensembles in their absolute ground level.
The bibliography includes 227 references.

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I. Introduction

The development of efficient methods for the synthesis of stable atom – molecule ensembles with an internal temperature (T) of less than 10^{-6} K belongs to the key research avenues in modern chemical physics and physical chemistry.[1–8] Fundamental interest in the synthesis and investigation of this new form of matter (so-called molecular Bose – Einstein condensate), in which the thermal de Broglie wavelength (λ_{dB})

$$\lambda_{dB}(T) = \sqrt{\frac{h^2}{2\mu k_B T}} \quad (1)$$

(h is the Planck constant and k_B is the Boltzmann constant) is longer than the distance between the interacting particles characterized by the reduced mass μ, is first of all due to dual — wave – particle — nature of matter at ultralow temperatures.

The short but eventful history of the research on laser cooling of particles down to ultralow temperatures is marked by three Nobel prizes in physics: for development of methods to cool and trap atoms with laser light in 1997; for the achievement of Bose – Einstein condensation in dilute gases of alkali metal atoms, and for early fundamental studies of the properties of the condensates in 2001; and for ground-breaking experimental methods that enable measuring and manipulation of individual quantum systems

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in 2012. Impressive advances made in the last two decades in the field of cooling and control of atom–molecule ensembles down to the temperature of Bose–Einstein condensation suggest the advent of an era of experiments with quantum matter that will have serious implications for not only fundamental research, but also progress of new technologies and metrology.

Unlike atoms, molecules are characterized by a more complicated structure and dynamics because they possess additional (rotational and vibrational) degrees of freedom that are closely related to one another and to the electronic structure of the molecule. Besides, stable ensembles of polar molecules with large (>1 a.u.) permanent dipole moments at ultralow temperatures represent systems with unique anisotropy of long-range forces[9–11] that can be controlled by external electromagnetic field.[12] Potential applications of ensembles of ultracold molecules are governed by their internal structure and chemical reactivity, and span a wide range from quantum optics to studies of the kinetics of barrierless reactions guided by laboratory magnetic and/or electric field.

Taking into account unique spatial confinement of ultracold particle ensembles, they can be treated as a specific class of quantum systems.[10,11] This may offer the frequency (energy) measurements with an unprecedented accuracy that is necessary to probe fundamental physical theories beyond the Standard Model,[13] namely:

— possible variations of physical constants on the cosmological time scale (in particular, the proton-to-electron mass ratio m_p/m_e and the fine structure constant α);

— the existence of permanent electric dipole moment of an electron; and

— violation of the parity conservation law.

Advances in the studies of ultracold molecules can have a critical impact on not only the development of fundamental concepts in physics, chemistry and astronomy, but also solution of application problems, *e.g.*, the design of ultra high accurate time and frequency standards and high-precision global navigation systems, the development of optical (contactless) methods for measuring the strength of external electric and magnetic fields, *etc*. Carrying out reactive scattering at collision energies that are comparable with the energy of external fields seems to be the most important application in chemical kinetics. This will enable highly sensitive coherent control[14,15] of the elementary steps and rate of chemical reactions at temperatures of at most a few hundreds nanokelvins using external electric and(or) magnetic field,[12] as well as detailed studies of the intramolecular interactions by partial-wave collisions at low orbital angular momentum values ($l = 0$, 1 and 2).[2,3] Besides, studies on low-temperature chemical reactions under laboratory conditions are of importance for understanding gas-phase processes in interstellar clouds at temperatures below 10 K.

Even more versatile are the possible applications of strongly polar ultracold molecules.[16–18] It was proposed to use long-range electric dipole–dipole interactions between polar molecules for the design of optical quantum systems, while the internal degrees of freedom of polar molecules will be used as regenerable carriers of quantum information.[19] The synthesis and storage as well as manipulation of such molecules in optical lattices created by high-power laser field allows one to construct unique molecular prototypes of quantum computers.[20–22]

The most common, although not the one and only, method of effective laser cooling of atoms down to ultralow temperatures is based on a multistep closed optical scheme which allows one to produce a sufficiently large number of atoms in a specified quantum state by multiple repetition of the absorption–emission cycle. Progress of laser cooling of atomic ensembles led to the establishment of a new temperature standard which was used to define the notions 'cold matter' and 'ultracold matter' in the late 1990s. They correspond to temperatures above and below $\sim 10^{-3}$ K, respectively. It should be noticed that the concept of global thermodynamic equilibrium is inappropriate for laser cooling processes, so by the local temperature is meant a quantity given by

$$T \approx \frac{E_{kin}}{k_B}$$

where E_{kin} is the kinetic energy of translational motion of atoms and (or) molecules.

When considering molecular systems (not atoms!), it seems to be more correct to determine the temperature for translational, vibrational and rotational kinds of motion separately.[23] For instance, weakly bound molecules (in fact, these are atomic pairs existing at long internuclear distances) formed upon photoassociation[24,25] and (or) magnetoassociation[26–30] have a very low translational and rotational temperature. Usually, they are distributed in a nonequilibrium manner over a wide range of excited vibrational states, thus being vibrationally 'hot'. The weakly bound molecules have sufficiently high internal (in this case, vibrational) energy, which can be released with ease upon inelastic collisions[31,32] and thus entirely heat the molecular ensemble.

Compared to laser cooling of atoms, laser synthesis of ultracold molecular ensembles is a much more complicated task because the electronically excited states of molecules (in contrast to those of atoms) can undergo radiative (and/or non-radiative) decay to a variety of vibrational-rotational states with lower (or equal) energies. Thus, various schemes of laser cooling of atoms often lose their efficiency when applied to molecules owing to high dissipation of internal energy, namely, a number of absorption cycles lead to population of a variety of rovibronic levels. In this connection, special efforts were made to develop fully controllable optical methods for cooling of molecules.[33]

This review concerns modern laser spectroscopy techniques and electronic structure calculations, which provide information on the energy and radiative properties of mixed electronically excited diatomic states. This information is required to optimize multistep laser synthesis and to stabilize ultracold molecular ensembles in their lowest rovibronic ground state. Combination of the results of ultrahigh-resolution laser spectroscopy and state-of-the-art *ab initio* calculations to predict the energy and radiative properties of spin–orbit coupled molecular states in a wide range of vibrational-rotational excitations will be illustrated taking homo- and heteronuclear alkali metal dimers as examples. Particular examples are taken from original papers reported in the last fifteen years including publications of the authors of this review. We have demonstrated the possibility and crucial importance of constructing comprehensive deperturbation models describing intermediate excited molecular states at the experimental (spectroscopic) level of accuracy

in order to optimize laser synthesis and coherent control of quantum states of stable (with minimum possible internal energy) ensembles of alkali metal dimers (first of all, polar ones). The present review differs from the other reviews [2, 34 – 36] in that the latter mainly concern specific features of photoassociation and magnetoassociation as precursors for synthesis of ultracold molecules in unstable vibrationally excited states.

II. Laser synthesis of ultracold molecules: methods

Modern methods for production of cold molecules can be divided into two groups, *viz*., direct and indirect ones. Molecules treated as 'hot' in the usual sense can be cooled to rather low temperatures (from 1 K down to 1 mK) by the direct methods that include:

— expansion to a supersonic molecular beam;

— collision with pre-cooled atoms of a buffer gas; and

— decelerating of a molecular beam by external electric field (for polar molecules).

Indirect methods of formation of ultracold molecules with temperatures from 1 mK to 1 μK are based on the assembly of molecules from ultracold atoms confined in magneto-optical traps (MOT). Two main processes used in this case are photoassociation [24, 25] and magnetoassociation.[26, 27, 29, 30] In turn, photoassociation (PA) is a two-step process.

In the first step, two cooled atoms involved in a slow elastic collision absorb a photon $h\nu$ and go to electronically excited molecular state AB*

$$A + B + h\nu \longrightarrow AB^* \text{ (photoassociation)}$$

Then, spontaneous or stimulated emission causes the unstable excited molecule to go to a lower-lying electronic state with a typical radiative lifetime of the order of a few tens of nanoseconds

$$AB^* \longrightarrow AB + h\nu \text{ (radiative stabilization)}$$

Magnetoassociation is an alternative to photoassociation. It occurs in an external homogeneous magnetic field and involves stabilization of paramagnetic atoms participating in a slow elastic collision resulting in the formation of so-called Feshbach resonances of considerable width.

In the last decade, there has been made considerable progress in theoretical foundations of PA and MA technologies. This makes it possible to produce dense metastable ensembles of diatomic molecules from ultracold atomic gas.

Initially, photoassociative laser synthesis was proposed and successfully used to produce ultracold homonuclear alkali metal dimers.[2, 34 – 36] Then, laser cooling was adapted to heteronuclear diatomic molecules. For instance, stable ensembles of ultracold polar molecules with high particle density (molecular Bose – Einstein condensate) were obtained for a number of heteronuclear alkali metal dimers, *e.g*., KRb,[11] LiCs,[18] RbCs,[38] and NaCs.[39]

Molecules synthesized by photoassociation and magnetoassociation have a very low translational and rotational temperature that is comparable with the kinetic energy of the initial atomic pairs. However, these molecules are formed in highly excited and, therefore, metastable vibrational states lying in the vicinity of the dissociation threshold. Thus, the main problem in the laser synthesis of stable

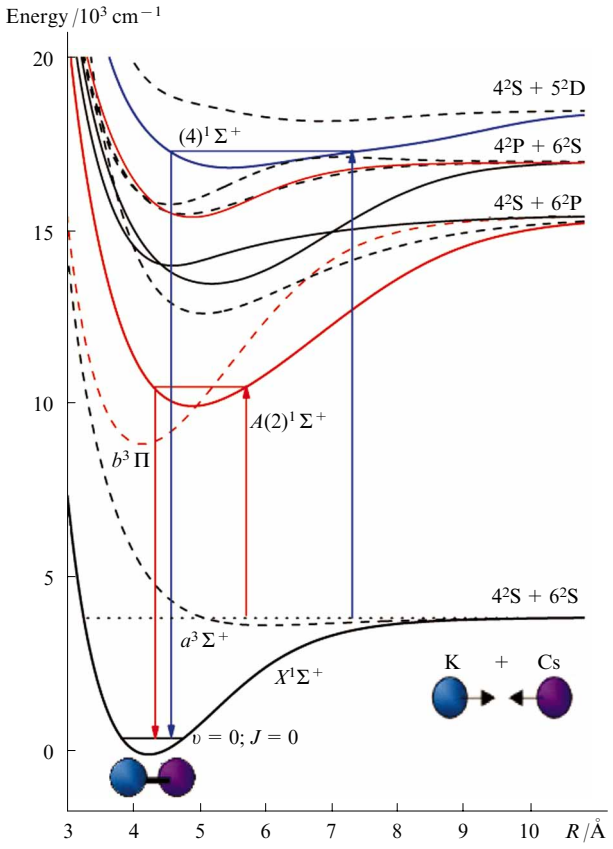


Figure 1. Potential energy curves for low-lying electronic states of KCs molecule from *ab initio* calculations.[37]
R is the internuclear distance; υ and J are the vibrational and rotational quantum number, respectively; solid lines correspond to singlet states, dashed lines correspond to triplet states, dotted line denotes the initial level of weakly bound atomic pair.
Upward arrows denote photoassociation of ultracold K and Cs atoms resulting in intermediate excited states of KCs molecule. Downward arrows denote possible stimulated and/or spontaneous transitions of KCs molecules to the lowest rovibronic level ($\upsilon = 0$; $J = 0$) of the $X^1\Sigma^+$ ground state.

ensembles of ultracold molecules from ultracold atoms is to bridge the gap between very long interatomic distances of colliding atoms (usually, they are of the order of a few micrometres) and the equilibrium bond length in a stable diatomic molecule (typically, of the order of a few Ångströms) [26, 29] (Fig. 1).

Weakly bound rovibronic states of ultracold polar molecules formed as a result of photoassociation at long internuclear distances are hardly suitable for practical applications. Indeed, molecules in these states are (i) less polarized owing to marked decrease in the electric dipole moment and (ii) unstable because of high efficiency of inelastic collisions. Therefore, it is crucially important to convert photoassociated molecules to a maximally stable state, the rovibronic ground state characterized by zero vibrational and rotational quantum numbers being the best candidate.

One of the most promising laser methods for conversion of short-lived, translationally-rotationally cold weakly bound atomic pairs to the rovibronic ground state level

$X^1\Sigma^+(v = 0; J = 0)$ is based on the use of multistep optical cycles involving intermediate excited rovibronic states [*e.g.*, $A(2)^1\Sigma^+ \sim b(1)^3\Pi$; $(4)^1\Sigma^+$]. The simplest two-step scheme of laser assembling (see Fig. 1) shows that in the first step (upward arrows) resonant absorption of a photon by weakly bound K⟷Cs atomic pairs occurs at long and moderate internuclear distances in full agreement with the classical Franck–Condon principle. The second step of the cycle corresponds to a spontaneous or stimulated emission of electronically excited molecules at short internuclear distances to the longest-lived level of the ground electronic state. This leads to the desired decrease in the internal (electronic-vibrational) energy of atomic pairs by optical transformation from long to short (equilibrium) internuclear distances. The PUMP and DUMP steps involve rovibronic transitions with the maximum values of the Franck–Condon factors (FCF) and, as can be seen in Fig. 1, by turning the laser frequency one can smoothly vary the distance between the colliding atoms corresponding to maximum FCF values.

Optical cycles used in the case of alkali metal dimers usually involve perturbed excited states having 'mixed' singlet–triplet character owing to pronounced influence of both local and regular intramolecular spin–orbit interaction.[26, 38]

The first successful experiments using two-photon PUMP and DUMP processes were carried out taking K_2 (Ref. 40) and RbCs (Ref. 41) molecules as examples. As applied to heteronuclear alkali metal dimers, possible implementation of PA methods was analyzed[42] for nine polar dimers including KRb (this was studied in most detail), LiNa, LiK, LiRb, LiCs, NaK, NaRb, NaCs and KCs. Since then, the two-photon cycle was successfully implemented for $^{87}Rb_2$,[43] $^{40}K^{87}Rb$,[10] and $^{41}K^{87}Rb$.[44]

An alternative and experimentally more simple method realizes molecular photoabsorption to strongly bound electronically excited states at short internuclear distances in spite of much lower photoassociation rates. A significant advantage of the photoabsorption at short distances consists in spontaneous decay of the excited intermediate level to lower-lying vibrational-rotational levels of the ground electronic state, including the ground state level $X^1\Sigma^+(v = 0; J = 0)$. The method proved itself in producing stable ensembles of K_2,[40] NaCs,[39, 45] KRb,[46] LiCs,[18] and RbCs molecules.[47] In particular, a one-step scheme of laser excitation *via* a $(2)^3\Pi_0(v' = 10)$ 'intermediate' state followed by spontaneous decay to the $X^1\Sigma^+(v = 0)$ state was practically implemented.[47] The results provided convincing proofs of the need for (i) detailed spectroscopic information in order to choose an optimum optical pathways and (ii) high resolution studies of the intermediate excited states. In particular, the optimum vibrational level of the $(2)^3\Pi$ intermediate state was chosen[47] based on the high-precision energies measured[48] by PA spectroscopy of ultracold RbCs molecules excited to the $(2)^3\Pi$ state.

In the simplest-design one-step scheme of laser excitation of the intermediate level followed by spontaneous emission, the formation rate of molecules in the rovibronic ground state is proportional to the product

$$\left(\lambda_{\mathrm{dB}}^3\, n_{\mathrm{A}\leftrightarrow\mathrm{B}}\right)\left(\frac{2\pi I^{\mathrm{PUMP}}}{c}\, M_{i\to f}^2\right) R_{f\to\mathrm{X}} \qquad (2)$$

where λ_{dB} the thermal de Broglie wavelength defined by Eqn (1), $n_{\mathrm{A}\leftrightarrow\mathrm{B}}$ is the initial concentration of the weakly bound atomic pairs produced by photoassociation or magnetoassociation, I^{PUMP} is the laser pump intensity, $M_{i\to f}$ is the matrix element (ME) of the dipole moment of the PUMP transition, $R_{f\to\mathrm{X}}$ is the branching ratio for the decay from the photoassociated state to the $X^1\Sigma^+(v = 0, J = 0)$ rovibronic ground state ($R_{f\to\mathrm{X}}$ is proportional to the product $A_{f\to X}\,\tau_f$, where $A_{f\to X}$ is the Einstein coefficient of spontaneous emission) and τ_f is the radiative lifetime of the intermediate level f.

The undesired spontaneous transitions to excited rovibronic levels of lower-lying states are suppressed using the pulse of the second laser (so-called DUMP, or anti-Stokes, laser), which is in phase with the PUMP laser in order to generate coherent population–depopulation of the intermediate level. The technique called stimulated Raman adiabatic passage (STIRAP, see Fig. 2) enables almost full control of the population of internal degrees of freedom.[8, 14, 49, 50] This makes it possible to suppress undesired transitions from the intermediate level and to attain a 100% optical conversion.

The STIRAP technique is based on the three-level optical scheme which employs virtual excited states created upon the action of high-power laser radiation on the stable rovibronic level f of the intermediate state. The key parameters of this scheme are the so-called Rabi frequencies

$$\hbar\Omega^{\mathrm{PUMP}} = \sqrt{\frac{2\pi I^{\mathrm{PUMP}}}{c}}\,|M_{i\to f}|\,, \qquad (3)$$

$$\hbar\Omega^{\mathrm{DUMP}} = \sqrt{\frac{2\pi I^{\mathrm{DUMP}}}{c}}\,|M_{f\to X}|$$

and the laser frequency detunings (frequency differences) Δ^{PUMP} and Δ^{DUMP} from the intermediate state. They are directly related to the matrix elements $M_{i\to f}$ and $M_{f\to X}$ of the moments of the corresponding rovibronic transitions $i\to f$ and $f\to X$, as well as to the radiative lifetime τ_f.

Optical conversion rate of atomic pairs can be governed using pico- or femtosecond chirped laser pulses with specif-

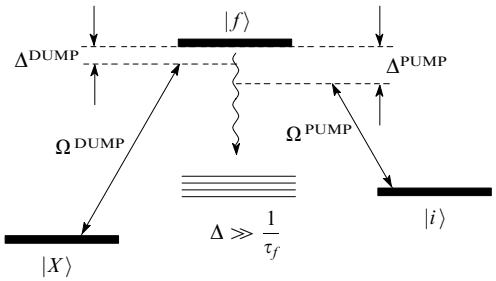


Figure 2. A scheme of coherent two-photon laser conversion of ultracold weakly bound atom pairs to the lower-lying rovibronic ground state using stimulated Raman adiabatic passage (STIRAP).[14]

ically chosen chirp parameters. In this case, the probability of coherent pump and stimulated emission increases owing to creation of an optimum shape of vibrational wave packets and to control of the motion dynamics in the intermediate excited state.[15]

Thus, the search for the most efficient channels of laser transformation requires calculations of the total probabilities of the optical cycle

$$P^{\text{tot}} \sim \left[P_{i\to f}^{\text{PUMP}}\right]\left[P_{f\to X}^{\text{DUMP}}\right] \tag{4}$$

which includes the probabilities of stimulated absorption

$$P_{i\to f}^{\text{PUMP}} \sim \nu_{i\to f} M_{i\to f}^2$$

from highly excited vibrational levels of the initial state i to rovibronic levels of the intermediate electronically excited state f with the wavenumber $\nu_{i\to f}$, as well as stimulated emission with the wavenumber $\nu_{i\to X}$

$$P_{i\to f}^{\text{DUMP}} \sim \nu_{f\to X} M_{f\to X}^2$$

to the ground rovibronic level X ($\upsilon = 0$, $J = 0$) (see Figs 1 and 2).

Clearly, the search for optimum (maximum) P^{tot} values requires highly accurate data on the structure and dynamics of all combining electronic states in a maximally wide range of excitation energies. Theoretically, to solve the problem is to construct rigorous quantum chemical models suitable for the description (interpolation) and subsequent prediction (extrapolation) of the energy and radiative properties of the interacting electronic states with experimental (spectroscopic) accuracy. Constructing physically correct, non-phenomenological models requires high-level spectroscopic data, results of high-precision *ab initio* calculations and a detailed deperturbation analysis of intramolecular interactions.

The necessary experimental data (energy properties of electronically excited molecular states) for the alkali metal dimers considered in this review were obtained by analyzing high-resolution absorption spectra, photoassociation spectra of ultracold molecules, as well as laser-induced fluorescence (LIF) spectra. Often, the transition wavenumbers measured in the visible and IR spectral regions are determined to 0.003 cm^{-1}, but this accuracy is limited from above by the Doppler effect of the order of 0.01 cm^{-1}. Although the structure of the valence shell of alkali metal atoms seems to be simple, prediction of the total energies of rovibronic levels at the experimental level of accuracy using *ab initio* electronic structure calculations is impossible because the uncertainty in the potential energy of the excited states is a few hundreds of reciprocal cenitimetres. In contrast to simulation of the energy properties, that of the radiative properties requires determination of the corresponding transition dipole moments, which can be obtained from *ab initio* calculations with nearly experimental accuracy of about 5% – 10%. Reliability of these estimates was substantiated by agreement of the results obtained independently by different computational methods.

III. The energy and radiative properties of intermediate excited states

A correct description of the energy and radiative properties of excited states of a molecule at the experimental level of accuracy implies taking account of intramolecular perturbations that depend on the particular procedure for separation of the total Hamiltonian of the molecule. Namely, translational and rotational motion can be separated on going to the coordinate system with the origin at the centre of mass of the molecule. Assuming no external fields, the total electronic-vibrational-rotational Hamiltonian of a diatomic molecule is given by [51]

$$\mathbf{H} = [(\mathbf{H}_{\text{e}} + \mathbf{H}_{\text{so}}) + \mathbf{H}_{\text{r}}] + \mathbf{H}_{\text{v}} \tag{5}$$

where $\mathbf{H}_{\text{e}} + \mathbf{H}_{\text{so}}$ is the electronic Hamiltonian in the Born – Oppenheimer (BO) approximation [the sum of the 'adiabatic' Hamiltonian $\mathbf{H}_{\text{e}}$ and the spin – orbit coupling (SOC) operator $\mathbf{H}_{\text{so}}$]. In contrast to most quantum chemical studies, here the term 'adiabatic' means that, within the framework of the adiabatic BO approximation, (i) $\mathbf{H}_{\text{e}}$ does not include spin-dependent interactions within the group of low-lying electronic states under study and (ii) these spin-dependent interactions are described by the operator $\mathbf{H}_{\text{so}}$. In the text below the term 'adiabatic electronic states' refers to the eigenstates of $\mathbf{H}_{\text{e}}$. The operator $\mathbf{H}_{\text{r}}$ corresponds to rotational component of the kinetic energy of atomic nuclei and the operator

$$\mathbf{H}_{\text{v}} = -\frac{\hbar^2 \text{d}^2}{2\mu \text{d}R^2}$$

corresponds to the kinetic energy of nuclear vibrations; μ is the reduced mass of the molecule.

Intramolecular perturbations corresponding to interactions between different adiabatic states are mainly governed by the operator of the spin – orbit and electronic-rotational coupling. The energy of spin – orbit coupling in electronically excited states of alkali metal dimers is comparable with the energy of vibrational quanta for molecules containing heavy atoms, Rb and Cs. Although the strong spin – orbit coupling can be observed experimentally, its energy is much lower than that of Coulomb interaction and therefore the SOC effect can be treated as a perturbation when solving the BO electronic problem.

The total wavefunction of the perturbed electronic states can be represented by a linear combination

$$\Psi_j = \sum_i \phi_i \varphi_i$$

where φ_i are the basis electronic-rotational wavefunctions and i is the number of the interacting electronic states included explicitly into the consideration. The expansion coefficients ϕ_i depending on R are components of the multicomponent (nonadiabatic) vibrational function

$$\Phi_j \equiv \|\phi_i\|,$$

which is the solution to the coupled-channel (CC) equation [51]

$$\left(-\mathbf{I}\frac{\hbar^2 \text{d}^2}{2\mu \text{d}R^2} + \mathbf{V}(R,\mu,J) - \mathbf{I}E_j^{CC}\right)\Phi_j(R) = 0 \tag{6}$$

where **I** is the identity matrix, $\mathbf{V}(R, \mu, J)$ is the symmetric potential energy matrix [the corresponding matrix elements are continuous functions of the internuclear distance R and parametrically (in explicit form) depend on the reduced mass of the molecule μ and on the rotational quantum number J]; and E_j^{CC} is the nonadiabatic (total) energy of the jth rovibronic level.

To construct the potential energy matrix, one should determine the nonzero matrix elements of the zero-order BO Hamiltonian in the basis set of electronic-rotational wavefunctions namely:

— the potential energy curves (PECs) of isolated (adiabatic) electronic states;

— the electronic matrix elements of nonadiabatic interaction, first of all, spin–orbit and electronic-rotational coupling as explicit functions of R.

The required functions can be obtained either from *ab initio* calculations or by processing of experimental data and, then specified in tabulated form or analytically. The choice between these representations is based on the reliability and accuracy of the theoretical and experimental data, on the one hand, and on the need to fit parameters of the deperturbation model on the other hand.

Mathematically, the most rigorous method of deperturbation analysis is based on direct solution of the system of coupled radial equations since Eqns (6) enable [one to describe most intramolecular interactions in explicit form. The influence of the remote electronic states can be taken into account in the framework of the van Vleck contact transformations.[51] Obvious advantages of the CC method are as follows:

— independency of the accuracy of calculated energy and wavefunction on the strength and type of intramolecular interactions because the CC method is equally applicable to calculated strong local and weak regular perturbations;

— the possibility to accomplish simultaneous treatment of the dynamic and energy properties of the bound, continuum and quasi-bound vibrational levels of electronic states using the same set of deperturbation parameters;

— joint description of the energy and radiative properties of all isotopologues in the framework of a unified deperturbation model (this ensures minimum correlation effects and, therefore, maximum reliability of the fitted parameters); and

— clear physical meaning of the deperturbed molecular parameters: they are exactly the electronic matrix elements of the electronic Hamiltonian obtained during *ab initio* calculations under BO approximation.

Practical implementation of CC method requires an initial set of molecular parameters in the form of continuous functions of the internuclear distance, which possess correct interpolation and extrapolation properties. The CC method is labour-consuming multiple numerical solution of the system of radial equations (6), which is dramatized by the lack of physical clarity of the level labelling due to violation of the conventional oscillation theorem for the multi-channel (mixed) perturbed states.

An alternative method of deperturbation analysis, which is free from the shortcomings mentioned above, is based on expansion of the total wavefunction in a basis set of vibrational wavefunctions of isolated (adiabatic) electronic states. A fundamental difference of the method of effective electronic-vibrational Hamiltonian from the CC method consists in the assumption of weak dependence of the electronic matrix elements on R compared to the strongly oscillating behaviour of the vibrational wavefunctions in the same range of internuclear distances. This allows one to approximate the off-diagonal electronic elements by a constant or a linear function of R. The next important assumption used in the effective Hamiltonian approach is associated with the possibility to factorize diagonal elements of the potential energy matrix in explicit form by the Dunham expansion [51]

$$\sum_{l,m} Y_{lm}\left(\upsilon + 1/2\right)^t \left[J(J+1)\right]^m$$

where Y_{lm} are conventional spectroscopic constants unambiguously related to parameters of the internuclear potential.

The Dunham expansion is mathematically justified only for rovibronic levels far from the dissociation limit (in fact, a Taylor expansion of the potential is valid only in this region). Also, centrifugal force constants strongly correlate with the vibrational-rotational constants and thus cannot be treated as independent parameters of the model. The major drawback of the method of effective Hamiltonian consists in a large (in the limit case, infinite) dimension of the variation problem because each electronic state possesses an infinite set of vibrational wavefunctions. Taking into account the truncation of the basis set on the energies and wavefunctions is a non-trivial task, especially for highly excited levels lying near the dissociation limit. Apparently, variational estimates of the calculated energies represent the upper bounds of exact eigenvalues whereas the quality of the corresponding nonadiabatic wavefunctions cannot be assessed *a priori* at all.

The method of effective Hamiltonian is successfully used to calculate the energy of locally and regularly excited rovibronic states of alkali metal dimers [52–68] containing lithium, sodium and potassium atoms. It should be noted that attempts to use the same method for alkali metal dimers containing rubidium and caesium atoms failed because of the difficulty to separate rovibronic levels into the locally and regularly perturbed ones. It was found that the effective Hamiltonian is not ideally suitable in this case since the need to introduce a huge number of fitting parameters leads to a significant decrease in the accuracy of description of experimental data owing to unavoidable truncation of the dimensionality of the variation problem. Therefore, in the last decade researchers have preferred to use the CC method, which is based on direct solution of the system of coupled radial equations (6).

The transition probability between rovibronic energy levels upon absorption or emission defines the radiative properties of molecules. The intensities in experimental spectra are proportional to the populations of the initial level, which are known with certainty only in the case of local thermodynamic equilibrium. The absolute concentration of excited molecules is unknown; therefore, the relative intensity distributions measured. into the vibrational structure of the emission spectra can be estimated as

$$I \sim \nu_{i\to f}^4 |M_{i\to f}|^2$$

where $\nu_{i\to f}$ are the wavenumbers of the rovibronic transition, $M_{i\to f} = \langle \phi_i | d_{if}^{\mathrm{el}} | \phi_f \rangle$ are the matrix elements of the

rovibronic transitions moment, $|\phi_i\rangle$, $|\phi_f\rangle$ are the vibrational wavefunctions of the combining electronic states and $d_{if}^{\rm el}(R)$ is the function of the electronic transition dipole moment (ETDM).

The radiative lifetimes ($\tau_i^{\upsilon' J'}$) of excited states are governed by the corresponding Einstein coefficients for spontaneous emission ($A_{i\to f}^{\upsilon' J'\to \upsilon'' J''}$)

$$\frac{1}{\tau_i^{\upsilon' J'}} = \sum_f \sum_{\upsilon''} \sum_{J''} A_{i\to f}^{\upsilon' J'\to \upsilon'' J''} \tag{7}$$

If there is more than one decay channel from the upper rovibronic level to lower-lying electronic states, the relative intensity of transition to the level of interest can be evaluated using the vibronic branching ratios ($R_{i\to f}^{\upsilon' J'}$) given by

$$R_{i\to f}^{\upsilon' J'} = \tau_i^{\upsilon' J'} \left(\sum_{\upsilon''} \sum_{J''} A_{i\to f}^{\upsilon' J'\to \upsilon'' J''} \right) \tag{8}$$

The probabilities of rovibronic transitions involving excited states depend strongly on the degree of intramolecular mixing. Therefore, they can serve as highly sensitive probe of the deperturbation model used.

For both regular and local spin – orbit interactions, spin-forbidden transitions (so-called intercombination transitions) are possible. For instance, in the case of a regular moment of the singlet – triplet transition $d_{\rm st}^{\rm el}$ can be represented by a linear combination of the dipole moments of the spin-allowed triplet – triplet transitions $d_{\rm tt}^{\rm el}$

$$d_{\rm st}^{\rm el}(R) \approx \sum_i C_i(R) d_{\rm tt}^{\rm el}(R)$$

where C_i are the coefficients of spin – orbit mixing between the interacting singlet – triplet states, which can be determined by diagonalization of the matrix of the electronic Hamiltonian ($\mathbf{H}_{\rm e} + \mathbf{H}_{\rm so}$). In fact, this procedure corresponds to a transition from *a* to *c* Hund's coupling case [51] where the quantum numbers of the electron spin projection (Σ) and the orbital angular momentum of the electron (Λ) are no longer 'good' quantum numbers and one deals with the selection rule $\Delta\Omega = 0, \pm 1$, where $\Omega = \Lambda + \Sigma$.

In the case of local SOC effect the total nonadiabatic wavefunction includes the singlet and triplet components in explicit form; therefore, both singlet – singlet and triplet – triplet transitions from the same excited level are allowed. The probability of each vibronic transition can be evaluated using the spin-allowed transition moments:

$$\langle \phi_{\rm s}^{J'} | d_{\rm ss}^{\rm el}(R) | \chi_{\rm s}^{J''} \rangle \text{ and } \langle \phi_{\rm t}^{J'} | d_{\rm tt}^{\rm el}(R) | \chi_{\rm t}^{J''} \rangle$$

where $|\phi_{\rm s,t}\rangle$ are the multicomponent vibrational wavefunctions of perturbed electronic state and $|\chi_{\rm s,t}\rangle$ are the adiabatic vibrational wavefunctions of isolated electronic states.

Thus, calculations of the intensities of intercombination transitions require not only the dipole moment functions, but also the electronic matrix elements of SOC interactions determined in a wide range of internuclear distances (ideally, from 0 to ∞). They can be obtained from high-level *ab initio* calculations since the alternative experimental methods are often limited by values of corresponding FC factors.

III.1. *Ab initio* electronic structure calculations

Ab initio calculation of the adiabatic potential energy curves and the matrix elements of spin – orbit coupling implies one or another model for the relativistic Hamiltonian ($\mathbf{H}_{\rm e} + \mathbf{H}_{\rm so}$) of the electronic subsystem of the molecule under study (recall that the exact expression for this Hamiltonian is unknown). The most popular models are the relativistic pseudopotentials (RPP).[69 – 72] They explicitly treat only the subsystem of valence (and, usually, subvalence) electrons. The interaction of these electrons with the core shells is simulated by the pseudopotential operators which in the simplest case represent superpositions of atomic one-particle components, *i.e.*, sets of potentials that are distinguished for different values of the total angular momentum and orbital momentum of an electron. The RPP model is characterized by (i) low computational cost of approximate determination of eigenstates of the Hamiltonian due to exclusion of the core shells from explicit treatment and (ii) simplicity of separation of the Hamiltonian into two components:

— spin-independent scalar relativistic Hamiltonian $\mathbf{h}_{\rm sc}$ obtained by replacing the total pseudopotentials by the operators averaged over mutual orientations of the spin and orbital momentum; and

— one-particle effective SOC operator $\mathbf{h}_{\rm so}$.

The operator $\mathbf{h}_{\rm sc}$ has high non-relativistic symmetry and is as simple in operation as the non-relativistic Hamiltonian within the pseudopotential model. The operator $\mathbf{h}_{\rm so}$ has a lower symmetry, does not include two-particle terms, is characterized by small amplitudes in the problems of interest. Thus, $\mathbf{h}_{\rm so}$ can be included in calculations perturbatively, without a catastrophic increase in computational cost. It should be noted that in the case of small amplitudes the operator $\mathbf{h}_{\rm so}$ can be identified with the operator $\mathbf{H}_{\rm so}$ [see Eqn. (5)].

Ab initio calculations [73, 74] of low-lying states of homonuclear rubidium and caesium dimers as well as RbCs and KRb molecules were carried out using the basic relativistic electronic structure model determined by the Dirac – Coulomb Hamiltonian and thus implied the explicit dependence of the wavefunctions on the coordinates of all electrons and the description of one-particle states by four-component spinors. It should be noted that separation of the scalar component of this Hamiltonian is possible but not so simple as in the RPP model.[75] The approximation of the Hamiltonian can be discretized in the finite one-particle basis sets that are usually comprised of contracted Gaussian functions (conventional basis sets augmented with diffuse functions necessary to describe excited states). The basis set for representation of the Dirac – Coulomb Hamiltonian in Refs 73 and 74 was constructed from solutions of the Dirac – Fock problem for free atoms and Sturm functions.

The potential energy curves are obtained from calculations of the eigenvalues of the total (spin-dependent) relativistic Hamiltonian. They are not adiabatic in the sense mentioned above [see notes to Eqn (5)] since there is no unambiguous procedure for going from these eigenvalues to the matrix elements of the operator $\mathbf{H}_{\rm so}$ and to the eigenvalues of $\mathbf{H}_{\rm e}$. However, if the amplitudes of spin-dependent interactions for low-lying electronic states are relatively small (this holds for all molecules in question), the adiabatic

states can be defined as being the closest to the eigenvectors of the scalar Hamiltonian $\mathbf{h}_{sc}$. In order to further simplify the situation one can ignore the shift of the adiabatic potential energy functions due to the spin-dependent interactions with higher states (including continuum-bound ones) and to identify (i) adiabatic PECs with the eigenvalues of the scalar relativistic Hamiltonian $\mathbf{h}_{sc}$ and (ii) effective spin–orbit coupling in the potential energy matrix [see Eqn (6)] with the matrix elements of $\mathbf{h}_{so}$.

Quantitative estimation of excited state properties of alkali metal dimers requires a correct description of electron valence–subvalence $[(n-1)s^2\ (n-1)p^6]$ correlation. Otherwise, the energy differences as well as the charge and spin density distributions in the valence area will be distorted. This yields the incorrect description of the SOC effect. Specific features of the low-lying electronic states of dimers with dominant configurations differing in the valence electron distributions are taken into account in the design of correlation treatment schemes. In particular, it is natural to use the formalism of effective (intermediate) Hamiltonians [76] in the model spaces spanned by the configurations with filled subvalence orbitals and different distributions of two valence electrons over the active orbitals. The choice of particular orbital generation procedure seems not to be critically important; often, this is done by solving the molecular state-average multiconfiguration self-consistent field or fractional occupancy Fock–Nesbet equations.

The effective Hamiltonians were constructed [77–80] in the framework of the second-order multipartitioning perturbation theory (MPPT) [81, 82] and taking into account the effective spin–orbit terms only within the model space.[83] Note that the latter limitation should lead to a uniform underestimation of the SOC amplitudes because the electronic configurations with holes in the sub-valence shell $(n-1)p^6$, which contribute largely to these amplitudes, are outside the model space. The problem was solved by scaling the operators included in $\mathbf{h}_{so}$; the scale factors for each value of the orbital momentum were chosen by means of the condition for exact reproduction of atomic spin–orbit splittings at the dissociation limit.

Quite recently, the accuracy of calculations of the intermediate effective Hamiltonian and, correspondingly, adiabatic PECs was significantly improved [84, 85] using the Fock space coupled cluster method [86, 87] with scalar relativistic Hamiltonian; however, the method is suitable to obtain only adiabatic PECs.

A well-established method for constructing the effective Hamiltonian for two valence electrons takes into account their interactions with the subvalence shells (including valence shell polarization and correlation effects) by introducing electrostatic-field-dependent terms called the core polarization potentials (CPPs) [88–90] into the Hamiltonian. This scheme is usually designed as semiempirical one, *i.e.*, some parameters of the CPPs and effective SOC are determined from conditions of reproduction of the atomic spectra. Most part of the theoretical data on low-lying electronic states of alkali metal dimers [91–99] was obtained using this scheme.

A considerable part of the *ab initio* data was also obtained by the multireference configuration interaction (MRCI) method. Calculations were carried out using both non-relativistic [100] and full relativistic Hamiltonians.[73, 74, 101, 102] As in the cases considered above, the particular way of generating one-electron functions (molecular orbitals or spinors) used to build the configurations are of no particular importance; a number of successful MRCI calculations were performed in the basis set of configurations constructed directly from atomic spinors.[101, 102] A specific feature of the problems in question consists in that the wavefunctions are mainly composed of configurations with no holes in the subvalence shell. This circumstance greatly simplifies construction of the reference set.

It should be noted that the MRCI method implies calculations of approximate wavefunctions of the states under study in explicit form, whereas construction of the effective Hamiltonian and determination of its eigenvectors only provides information on components of the wavefunctions lying within the model space. That is why the coupled cluster method for the effective Hamiltonian in the scalar approximation was coupled with calculations of the spin–orbit matrix elements obtained from the MRCI calculations.[84, 85]

These approaches give a highly accurate description of the energy of alkali metal dimers. The potential energy curves of low-lying electronic states with respect to the energy of free ground-state atoms obtained from different calculations usually coincide within 1%–2%. However, the absolute error in the electronic energy calculations can be as large as a few hundreds of reciprocal centimetres. This is equivalent to several vibrational quanta for rubidium- and (or) caesium-containing molecules. It is basically not sufficient for unambiguous assignment of vibrational levels. Meanwhile, in most *ab initio* calculations at fixed internuclear distance R the energy differences between states appear to be much more accurate than the absolute energies themselves owing to compensation of systematic errors, in particular, the superposition error of atom-centred basis sets. In this situation, the refined PECs of excited electronic states $U_i^{\mathrm{dif}}(R)$ can be obtained by combining the highly accurate empirical potential of the $U_X^{\mathrm{exp}}(R)$ ground electronic state and the calculated energy differences between the ground $U_X^{ab}(R)$ and excited $U_i^{ab}(R)$ states at each R value

$$U_i^{\mathrm{dif}}(R) = U_X^{\mathrm{exp}}(R) + \left[U_i^{ab}(R) - U_X^{ab}(R)\right] \qquad (9)$$

The results presented in Table 1 show how close can be equilibrium parameters of the difference-based potentials as compared to their initial analogues calculated using various *ab initio* methods.

When calculating the functions of permanent electric dipole moment of electronic states and the matrix elements of the electronic transition dipole moments (ETDM) between them using the schemes of solution of the many-electron problem mentioned above, one can use the finite-field approach or directly calculate the matrix elements of the dipole moment operator (as applied to transition matrix elements, one can say about the dipole length representation). In most cases, when these two approaches become inequivalent (this does occur for almost all widely used approximations), the former technique seems to be more preferable. Since the schemes involving construction of the intermediate effective Hamiltonian are not aimed to get the explicit form of the many-electron wavefunctions, direct calculations of the matrix elements imply taking account of the correlations of the valence and subvalence electrons to the one-body spin-free transition density matrices [77–79] or

Table 1. Electronic energies (T_e) and equilibrium internuclear distances (R_e) obtained for the $A^1\Sigma^+$ and $b^3\Pi$ states of NaRb molecule using original *ab initio* potentials U^{ab} and their deference-based analogues U^{dif} [see Eqn (9)].

Method	$A^1\Sigma^+$ state		$b^3\Pi$ state		Ref.
	T_e/cm^{-1}	R_e/Å	T_e/cm^{-1}	R_e/Å	
Ab initio potentials					
RPP – CPP	11396	4.47	11303	3.70	95
RPP – CPP	11680	4.38	11308	3.61	103
RPP – MPPT	11708	4.25	11060	3.65	77
RPP – MRCI	12109	4.24	11012	3.63	104
Deference-based potentials					
RPP – CPP	11630	4.38	11300	3.63	95
RPP – CPP	11619	4.39	11309	3.64	103
RPP – MPPT	11596	4.40	11288	3.65	77
RPP – MRCI	11769	4.43	11242	3.65	104

to the effective operator of dipole moment defined in the model space. This operation can be done easily within the framework of perturbation theory methods[77] and can hardly be performed in the case of multiconfiguration coupled cluster methods (that is why the MRCI method is used to calculate the ETDMs[84, 85]).

A possible alternative to direct construction of the effective operator of dipole moment or the transition density matrix is to use the finite-field methods to calculate the ETDM functions.[105] According to theoretical analysis[106] and numerical experiments, the ETDM values can be determined quite accurately using the eigenvectors of the effective Hamiltonian (in other words, only components of wavefunctions in the model space are required) and their variations upon switching on the external field. In practice, ETDM calculations are sometimes carried out ignoring the difference between the conventional and effective operators of dipole moment.[37, 88] This causes systematic error of the order of 3% to 7%, but never has a strong effect on the specific features of the ETDM functions, which are significant for further use in the integration procedure with vibrational wavefunctions of the combining electronic states. Such features include the regions characterized by abrupt changes in the matrix elements on R, positions of maxima, *etc*. This supports physical correctness of the two-electron model space used; indeed, the valence component of the wavefunctions governs the behaviour of the dipole moment functions. However, even a qualitatively correct determination of the wavefunction decomposition requires taking account of electron correlation between the valence and subvalence shells.

The experience in *ab initio* electronic structure calculations for excited states of homo- and heteronuclear alkali metal dimers shows that spin – orbit coupling and the dipole moments of electronic transitions can be estimated with an accuracy of a few per cent. This is sufficient for unambiguous vibrational assignment of highly excited levels of singlet – triplet complexes. However, the absolute error in the determination of the electronic energies of excited states can be as high as a few vibrational quanta. The explicit consideration of the heterogeneous electronic-rotational interactions which govern, *e.g*., the Λ-doubling effect in degenerate electronic states requires calculations of the L-coupling matrix elements, which can be obtained in the framework of the above computational schemes with an accuracy of 2% – 3%.[107, 108]

III.2. Laser spectroscopy of excited electronic states

In recent decades, the rovibrational structure of the ground and excited diatomic electonic states has been intensively studied by laser-induced fluorescence (LIF) spectra recorded on high-resolution Fourier transform (FT) spectrometers. Progress in this research is due to the design of commercially available tunable single-mode lasers as well as high-resolution robust FT spectrometers operating in a wide spectral range.

Monochromatic laser radiation at a specified frequency tuned in resonance with a particular molecular transition (usually, started from the ground state) provides a rather selective population of the v', J' vibrational-rotational levels of the electronically excited state, which induces fluorescence to a lower-lying electronic states. This fluorescence is focused on the input aperture of a FT spectrometer. Taking into account a relative simplicity of LIF spectra and using a high-resolution FT spectrometer operating with a typical uncertainty of the order of 0.001 – 0.004 cm^{-1} for the determination of line positions, one can study the rotationally resolved structure of diatomic states with high accuracy.

Note that FT LIF spectroscopy becomes efficient if fluorescence signals are sufficiently strong. A convenient method to improve signal/noise ratio is to use long metallic heat-pipes to create high concentrations of gas-phase molecules under study. This enables operation at high temperatures (this is crucial for studies on molecules containing atoms of refractory elements, *e.g*., calcium and strontium). In the heat-pipes, metal vapours are surrounded by inert gas to prevent their condensation on optical windows. A laser beam propagates along the heat-pipe axis, and feedback LIF is observed along the direction of laser beam propagation. Laser-induced fluorescence is collected from a larger volume of metal vapours, thus ensuring a high intensity of the signals being measured.

The technique appeared to be particularly useful in studies of the ground electronic state, *e.g*., the $X^1\Sigma_g^+$ ground states of homonuclear alkali metal dimers including K_2,[109 – 111] Na_2,[112, 113] Rb_2,[114] Cs_2 (Ref. 115) and the $X^1\Sigma^+$ states of heteronuclear dimers including NaK,[116] NaRb,[117, 118] NaCs,[119] KCs,[120 – 122] RbCs,[123 – 125] KRb,[125 – 128] LiCs,[129] NaLi,[130] KLi (see Refs 131 and 132), as well as the ground states of alkaline-earth metal dimers, namely, Ca_2 (Refs 133 and 134) and Sr_2 (Ref. 135). All these molecules are of particula interest for production of stable ultracold molecules.

In a number of works Fourier transform LIF spectroscopy was used to study low-lying excited electronic states by means of direct excitations to higher-lying states. As a rule, the LIF progressions to the state under study and to the ground electronic state were recorded simultaneously. By analyzing the LIF transitions to well-known ground state one can determine the term value and rotational quantum number of the excited (upper) level and thus identify the rovibronic levels of the state under investigation. This optical scheme was applied to heteronuclear [NaK,[136, 137] KRb,[138 – 140] KCs,[141] RbCs (Refs 142 and 143)] and homonuclear [K_2,[144] Na_2,[145, 146] Rb_2 (Refs 147 –

149)] molecules. It should be noted that one-step excitation of the upper intermediate state of homonuclear molecules led to observation of only even (g) states in the LIF spectra owing to the parity selection rules ($g \nleftrightarrow u$). Odd states (u) of, *e.g.*, Rb_2 were studied [150–153] using two-step (and two-photon) excitation.

As mentioned above, FT LIF spectroscopy is the most efficient tool to study the ground electronic state. The selective excitation of particular levels v', J' of the upper state makes investigations of excited states by direct optical excitation less informative and labour-consuming. However, the efficiency of the LIF method can be significantly improved using higher pressures of inert gas in the heat-pipe. Collisions of excited molecules with atoms of the inert gas lead to redistribution of the initial population of the optically excited level over neighbouring rotational and in some cases vibrational levels. This leads to the appearance of satellite transitions in the LIF spectra. The number of satellite levels J' due to rotational relaxation can be as large as a few dozens; this offers the possibility for the excited-state rotational structure to be studied systematically. The collisionally-induced fluorescence (CIF) was applied to investigate excited states of NaRb,[154, 155] NaCs,[156–158] KCs,[141, 159–162] RbCs,[143, 163, 164] LiCs,[165] Rb_2,[153] Ca_2 [166] and Sr_2 [167] molecules. The accuracy in determination of the upper-state energy in the case of direct laser excitation in thermal vapours is mainly limited by the Doppler effect because the laser frequency can deviate from the centre of the absorption line. The typical line width is $0.01-0.02$ cm^{-1} depending on the molecular mass and on the energy of the state being excited.

Polarization labelling spectroscopy is an alternative, highly informative method of investigation of electronically excited states. Detailed analysis of various modifications of the method goes beyond the scope of this review. Mention may only be made of a technique that has been successfully used by researchers from Poland;[168–184] it involves the V-type optical-optical double resonance with two independent lasers. Weak polarized radiation of the probing laser is passed through vapours of the molecule under study in a heat-pipe placed between two crossed polarizers. A detector of the intensity of the probing laser beam passed through the heat-pipe and crossed polarizers supplies a zero signal. The frequency of the probe laser is tuned to a particular transition from the labelled level v'', J'' of the ground state to fixed rovibronic level of another excited electronic state. Radiation of a second laser (higher-power pump laser) is directed quasi-collinearly to the first laser beam, so both beams overlap in the heat-pipe. The frequency of the second laser is tuned within the excitation band of the electronic state under study. At some frequency, the second laser induces absorption from the labelled level, thus causing optical anisotropy for the probe beam which changes its polarization. This allows the probe laser to pass through the crossed polarizers and the detector supplies a signal corresponding to transition from the labelled level to the state under study. High sensitivity of the polarization method enables detection of very weak transitions. By varying the mutual polarization of the probing and pump lasers one can vary the intensity ratios for different kinds of transitions;[168] this significantly simplifies the assignment (identification) of the spectra. The method was used to investigate the excited states of alkali metal dimers including Li_2,[169, 170] Na_2,[168, 171, 172] K_2,[173] NaLi,[174] KLi,[175–177] NaK,[178] NaRb,[179, 180] LiCs,[181] NaCs,[182] and KCs.[183, 184]

Rovibronic levels lying near the dissociation threshold are studied by photoassociation spectroscopy of colliding atoms. Photoassociation has long been known (for historical backgroound, see Refs 185–187); however, photoassociation spectroscopy became of particular importance for obtaining high-precision data on diatomic molecules upon combining with methods of assembling ultracold molecules.[4] The kinetic energies of atoms in such systems are very low; as a consequence, the frequency of laser radiation which can induce photoassociation is narrow and corresponds to the natural linewidth that is governed by the decay time of the excited molecular state. The translation temperature of atomic gas (T) should be lower than Γ/k_B, where Γ is the natural linewidth (for many atomic systems this corresponds to $T \leqslant 0.5$ μK).

Progress in methods of production of ultracold atoms with temperatures below 1 μK [188] led to the situation when the photoassociative transition frequency scatter due to the initial kinetic energy of colliding atoms can be even smaller than the natural width of the rovibrational level of an electronically excited state of the molecule. In this case, free-bound transitions manifest themselves as narrow resonances resembling resonance transitions in sub-Doppler spectroscopy of atoms and molecules.[189] These resonances can be detected using an auxiliary laser which induces transitions from the electronically excited states with a fixed vibrational-rotational level. Excited states are often investigated by photoionization followed by detection of molecular ions. In essence, the photoassociation spectrum characterizes the number of excited molecules in a particular state as function of the frequency of the tunable laser. An alternative method of counting photoassociated molecules involves detection of the 'loss' of cold atoms in a MOT [4] based on the decrease in the fluorescence signals of the atoms that did not escape the MOT.

The main advantage of photoassociation spectroscopy compared to traditional methods consists in measuring the absolute values of the binding energies of molecular levels. These values are determined by detuning (towards the long-wavelength region) from the energy of 'fixed' separated atoms (dissociation limit). The bindng energy of a molecule equals the energy difference between the photoassociation laser and the excited atom. A correction, k_BT/h, necessary to take into account the initial thermal (kinetic) energy of atoms is small, being about 20 MHz at $T = 1$ mK. Thus, photoassociation spectroscopy allows one to obtain information on the levels near the dissociation limit with unique accuracy. Also, the method enables production of very slowly rotating photoassociated molecules (usually, the rotational quantum number lies between 1 and 5). This significantly facilitates extrapolation to the rotationless energy of the molecule. Photoassociation spectroscopy was used to study various alkali metal dimers.[190] In particular, the following molecules were studied in detail: K_2,[191] Cs_2,[192] RbCs,[25, 32] KRb,[193, 194] NaCs,[195] and LiCs.[18] Besides, experiments with YbRb molecule were reported;[196] a particular interest in the molecule is due to the fact that it has a nonzero electric dipole moment and a nonzero magnetic dipole moment in the $X\,^2\Sigma^+$ ground electronic state.

III.3. The lifetimes and relative intensity distributions

Measurements of the time dependence of the LIF intensities (kinetics of spontaneous decay of rovibronic levels upon pulsed laser excitation) allow the decay rates of alkali metal dimers to be estimated with an accuracy of a few percent. Experimental values of the radiative and pre-dissociation lifetimes of homonuclear dimers ($B\,^1\Pi_u$ states of Na_2,[197, 198] K_2,[199, 200] and Cs_2 molecules;[201] $D\,^1\Pi_u$ and $C\,^1\Pi_u$ states of Rb_2 molecule [204]) and heteronuclear dimers [$B\,^1\Pi$, $D\,^1\Pi$ and $C(3)^1\Sigma^+$ states of NaK [105, 202, 203] and NaRb [78, 205, 206] molecules; $(3)^1\Pi$ and $(2)^1\Pi$ states of NaCs molecule [207]] are available for a limited number of rovibronic levels. The experimental lifetimes determined by the delayed coincidence and quantum beats methods are usually in good agreement with the theoretical predictions obtained from *ab initio* ETDM functions.

Measurements of the relative intensity distributions in LIF progressions [77, 104, 141, 153, 155, 158 – 160] provide unique information on the nodal structure (shape and node positions) of vibrational wavefunctions of electronically excited states, vibrational branching ratios and even on the R-dependence of the ETDM functions. In some cases, the relative intensity distributions make it possible to determine the absolute numbering of vibrational levels, which is of great importance for substantiation of the vibrational assignment of energy measurements.[208]

IV. Laser assembling of alkali metal dimers: optimization and control

Simulation of cyclic laser conversion of weakly bound atom pairs formed by photoassociation or magnetoassociation of cold alkali metal atoms to stable molecular states requires systematic calculations of the optical transition probabilities taking into account laser absorption from highly excited vibrational levels of the singlet and (or) triplet ground state to the 'intermediate' level of electronically excited state and subsequent spontaneous or stimulated emission to the singlet ground-state level $v'' = 0$, $J'' = 0$

$$\left[P_{X,a\to f}^{(v'',J''=0\to v',J'=1)}\right]\left[P_{f\to X}^{(v',J'=1\to v''=0,J''=0)}\right]$$

where $P_{X,a\to f}$ and $P_{f\to X}$ are the probabilities of individual rovibronic transitions; they are proportional to the products of the corresponding wavenumbers and squared matrix elements of the transition dipole moments [see Fig. 1 and Eqn (4)].

To simulate structural-dynamic characteristics of the mutually perturbed excited states, one should (i) construct deperturbation models that correctly take into account intramolecular interactions and (ii) develop efficient methods of solution of the direct and inverse spectroscopic problems. Solution of the direct spectroscopic problem is aimed to predict the experimentally observed properties the framework of the particular deperturbation model at fixed values of molecular parameters. To solve the inverse problem is to refine parameters of the model by experimental data (usually, from highly accurate term values). A block diagram of this procedure is shown in Fig. 3.

Practically, solution of the direct and inverse problems involves realization of the following algorithm.

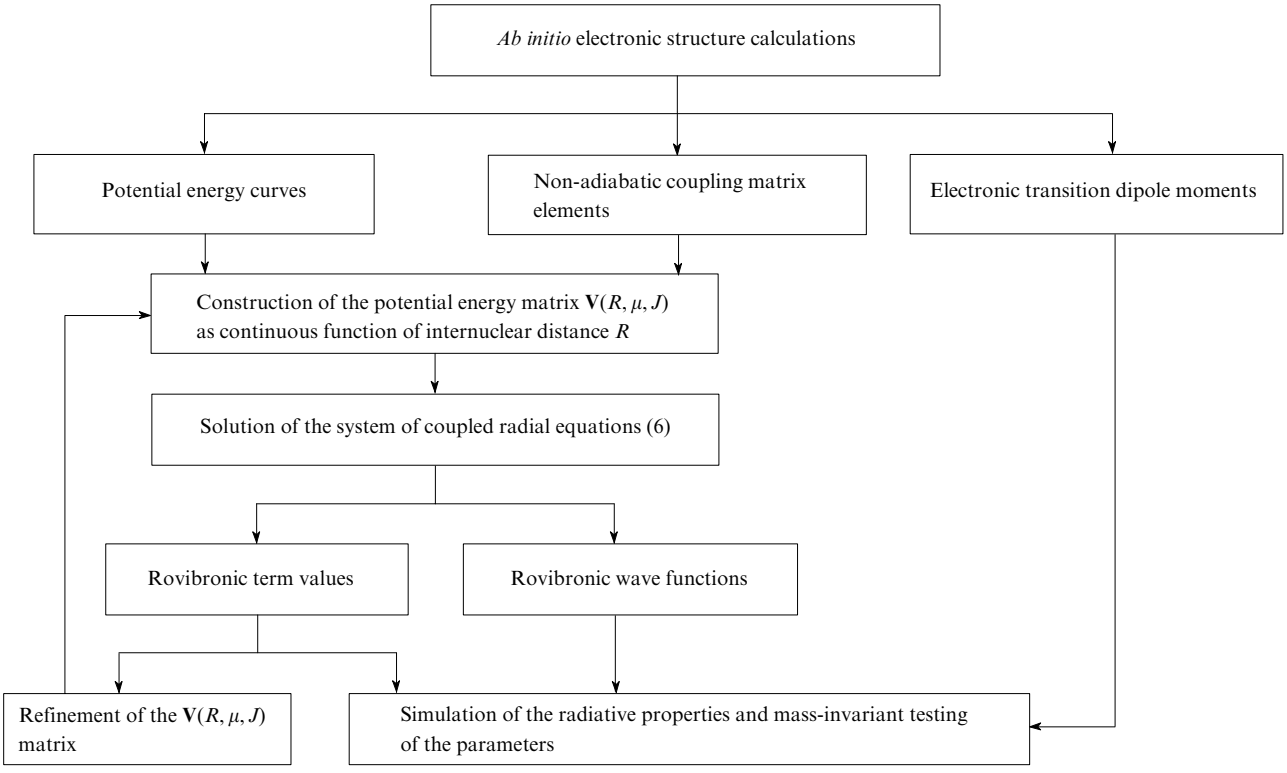


Figure 3. Block scheme of iterative procedure for solving the direct and inverse spectroscopic problems within the framework of the coupled-channel (CC) method.

1. *Ab initio* electronic structure calculations (solution of the electronic problem at fixed internuclear distance) in order to obtain the initial guess of the potential energy curves, electronic matrix elements of nonadiabatic (spin–orbit coupling and electronic-rotational interactions) and the electronic transition dipole moments for all electronic states under study in a wide range of internuclear distances. It should be noted that the quaility of *ab initio* calculations (reliability of the trial fitting parameters) to a great extent assures success of further nonlinear optimization, because solution of the inverse problem does not guarantee that the global minimum of the objective function will be found within the framework of nonlinear least squares method.

2. Calculations of rovibronic energies and vibrational wavefunctions of electronic states taking into account crucial intramolecular interactions. Iterative refinement of fitting parameters of the deperturbation models using experimental energies of (usually) the most abundant isotopologue.

3. Testing of the deperturbed molecular parameters by calculating the energies of other isotopologues and various radiative properties (including the relative intensity distributions in LIF spectra, branching ratios of spontaneous emissions, and radiative lifetimes) and comparison of the theoretical estimates with experimental data.

Iterative schemes for solving the direct and inverse spectroscopic problems were successfully used in a series of publications concerning deperturbation analysis of excited rovibronic levels of low-lying singlet and triplet states of alkali metal dimers.[141, 153, 155, 158–163] Particular interest in studies of the energy and radiative properties of the low-lying singlet–triplet complexes is due to the fact that, owing to strong spin–orbit coupling, the levels are characterized by strong singlet–triplet mixing, which determines the possibility of optical transitions involving both singlet ($X\,^1\Sigma^+$) and triplet ($a\,^3\Sigma^+$) electronic states.

To predict the radiative properties of electronically excited states, one should apparently know corresponding wavefunctions. The dependence of the mixing coefficients of adiabatic wavefunctions on the internuclear distance causes not only changes in the amplitudes of the corresponding vibrational functions, but also changes in their nodal structure (changes in positions and number of nodes of the vibrational wavefunctions). The latter is of crucial importance. Regarding this fact, we may expect sophisticated behaviour of the multichannel wavefunctions and probabilities of corresponding rovibronic transitions in the strongly perturbed states.

Indeed, numerous calculations of nonadiabatic wavefunctions of the spin–orbit complexes of alkali metal dimers confirmed a nontrivial dependence of their nodal structure on the strength of intramolecular interactions, energy of electronic-vibrational excitation, and on the shape and relative position of the PECs of combining electronic states. In particular, a trivial visual comparison of the wavefunctions calculated under conventional adiabatic approximation and with inclusion of intramolecular interactions (Fig. 4) for highly excited levels of the complex $A \sim b$ of KCs clearly demonstrates that the experimental intensity distribution cannot be reproduced in the framework of one-channel (adiabatic) approximation. An example in Fig. 4 *a*,*b* illustrates the relative intensity distribution in the full vibrational progressions starting with close-lying levels of the $A \sim b$ complex of the KCs molecule and

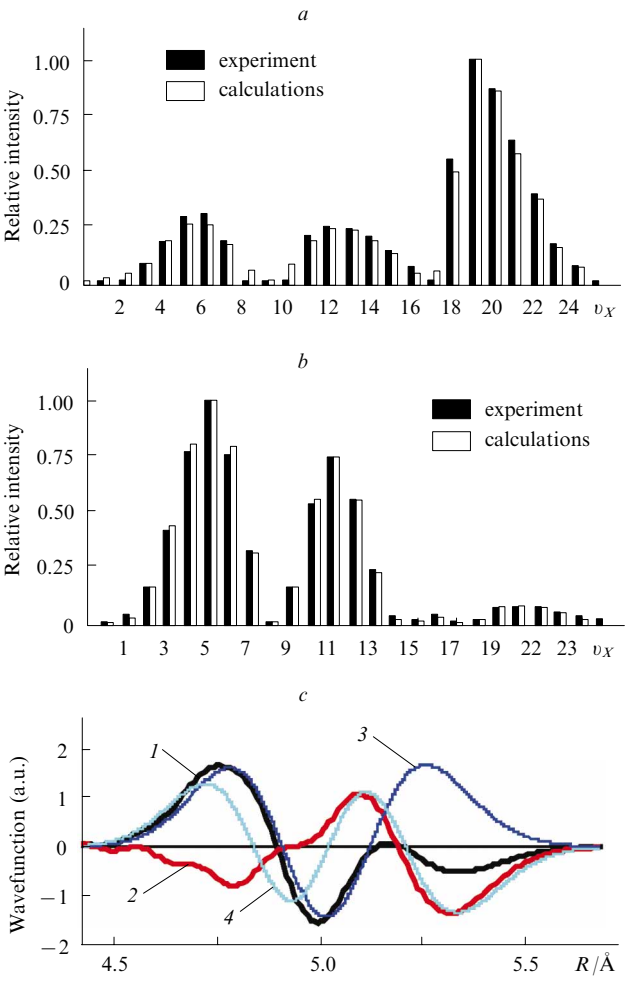


Figure 4. Relative intensity distributions in full $A \sim b \rightarrow X\,^1\Sigma^+(\upsilon_X)$ progressions in the LIF spectra of $^{39}K^{133}Cs$ molecule. The progressions begin with close-lying rovibronic levels of the singlet-triplet complex $A \sim b$ (see Ref. 159 and Fig. 1) and include different contributions of the $A\,^1\Sigma^+(P_A)$ singlet state (P_A is the fraction of the $A\,^1\Sigma^+$ state) (*a*, *b*).
Nonadiabatic (*1*, *2*) and adiabatic (*3*, *4*) wavefunctions corresponds to the vibrational levels with $\upsilon = 2$, 3 of the $A\,^1\Sigma^+$ state (*c*).
(*a*) Energy level ($J' = 44$) is 10227.038 cm^{-1}; $P_A = 0.48$;
(*b*) energy level ($J' = 49$) is 10255.412 cm^{-1}; $P_A = 0.74$;
(*c*) (*1*) ϕ_A ($J' = 49$); (*2*) ϕ_A ($J' = 44$); (*3*) χ_A ($\upsilon = 2$); (*4*) χ_A ($\upsilon = 3$).

characterized by slightly different rotational quantum numbers. In this case, one could expect (in the adiabatic approximation) a practically identical intensity distribution in LIF progression, but different extent of the SOC effect leads to dramatic changes in the nodal structure of nonadiabatic functions [curves (*1*) and (*2*), respectively, in Fig. 4 *c*], which manifests itself in the intensities (more exactly, in the overlap integrals of the corresponding vibrational wavefunctions). Moreover, calculations predict that the most pronounced changes in the nodal structure of wavefunctions are expected at internuclear distances near the crossing point of the interacting electronic states (see Fig. 1).

Thus, in the case of strong homogeneous interactions, the vibrational quantum numbers of the mutually perturbed

states are no longer 'good' quantum numbers and one can only make ambiguous vibrational assignment of interacting states. For instance, for two-component states the number of the eigenvalues $\upsilon \in (0, 1, 2...N)$ and the number of nodes of the corresponding vibrational two-component wavefunctions n_i, n_j obey the inequality $2\upsilon \geqslant n_i + n_j$, which should be treated as an analogue to the oscillation theorem for non-adiabatic states.[209] An increase in absolute value of non-adiabatic coupling causes the ϕ_i^υ and ϕ_j^υ wavefunctions to have identical nodal structures, being different in the amplitude only

$$\phi_i^\upsilon = \text{const}\ \phi_j^\upsilon$$

The relative arrangement and number of nodes of the two-component wavefunctions are determined by the rate of changes in the dimensionless parameter γ as function of internuclear distance

$$\gamma = \frac{U_i - U_j}{V_{ij}}$$

where U_i and U_j are the adiabatic potentials and V_{ij} are the matrix elements of nonadiabatic interaction (spin – orbit coupling). At the limit of the parameter $\gamma \to 0$, the corresponding nonadiabatic wavefunctions are interrelated:

$$\phi_i^\upsilon = \gamma\, \phi_j^\upsilon$$

and the number and coordinates of extrema of both wavefunctions coincide at those internuclear distances where one has

$$\frac{\mathrm{d}\gamma}{\mathrm{d}R} \longrightarrow 0$$

In particular, this is observed in the classically forbidden regions of motion of one of the combining states as well as near the common dissociation threshold, *i.e.*, at

$$U_i - U_j \longrightarrow 0$$

It should be noted that SOC effect between excited singlet and triplet states of light-weight alkali metal dimers, such as Li_2,[52–56] Na_2,[57–60] NaK,[61] and K_2 (Ref. 62 – 66) was intensively studied by high-resolution spectroscopic methods. A relevant deperturbation analysis of the complexes $A^1\Sigma^+ \sim b^3\Pi$ of homo- and heteronuclear dimers was performed within the framework of the method of effective Hamiltonian. Successful implementation of the method is due to two reasons:

— the possibility to exactly specify regions of local perturbations; and

— relatively small value of the electronic matrix element of spin – orbit coupling, *viz.*, $\xi_{so}^{el} = 0.114\ \text{cm}^{-1}$ for Li_2, $5.91\ \text{cm}^{-1}$ for Na_2, $15.64\ \text{cm}^{-1}$ for NaK and $18.4\ \text{cm}^{-1}$ for K_2.

In the molecules containing heavier alkali metal atoms (Rb and Cs) stronger spin – orbit coupling leads to almost complete mixing of the singlet and triplet levels, which can be correctly described only within the framework of the CC method.

According to electronic structure calculations, the matrix elements of spin – orbit coupling in alkali metal dimers depend strongly on the internuclear distance, the ξ_{Ab}^{so} value in the vicinity of the crossing point of the interacting states being comparable with the vibrational quantum. In this case, the relative SOC effect on the rovibronic structure of the complexes can be related to the dimensionless parameter

$$\gamma_{so} = \xi_{Ab}^{so}\left(\frac{1/\omega_e^A + 1/\omega_e^b}{2}\right)$$

where ω_e^A and ω_e^b are the harmonic vibrational frequencies of the $A^1\Sigma^+$ and $b^3\Pi$ states, respectively. Small deviation of γ_{so} values from unity (Table 2) indicates a pronounced 'intermediate' character of angular momentum coupling for the pairs of interacting states. It should be noted that even the use of the rigorous CC method to describe the states corresponding to the 'intermediate' (**a** – **b** – **c**) Hund's coupling case remains a non-trivial task owing to dramatic changes in the strength of intramolecular interactions as function of the internuclear distance and the extent of rotational excitation.

Based on the solution of the inverse spectroscopic problem and using empirically determined molecular parameters, systematic simulation of the energy (transition wavenumbers) and radiative properties (lifetimes and branching ratios) of excited electronic states of NaRb,[155] NaCs,[158] KCs[159] and RbCs[210] molecules were carried out in a wide range of electronic-vibrational excitations. For most LIF spectra observed, the theoretical intensity distributions matched their experimental counterparts within the uncertainty of measurements.

Thus, high-resolution spectroscopic methods and quantum chemical simulation of the energy and radiative properties of electronically excited states of alkali metal dimers provided the necessary energies and probabilities of rovibronic transitions with experimental accuracy; this is required for practical optimization of the optical conversion schemes in question. For instance, simulation of the two-step optical cycle

$$a^3\Sigma^+ \longrightarrow A^1\Sigma^+ \sim b^3\Pi \longrightarrow X^1\Sigma^+$$

of laser assembling of heteronuclear dimers NaRb,[155] NaCs,[158] KCs[159] and RbCs[210] involved systematic calculations of the wavenumbers $\nu_{a \to A \sim b}^{PUMP}$; $\nu_{A \sim b \to X}^{DUMP}$ and matrix

Table 2. Harmonic frequencies of the $A^1\Sigma^+$ and $b^3\Pi$ states (ω_e^A and ω_e^b, respectively), matrix element of the spin – orbit interaction ξ_{Ab}^{so} at the crossing point of the mutually perturbed states and the dimensionless parameter of the spin – orbit coupling γ_{so}.

Molecule	ω_e^A /cm^{-1}	ω_e^b /cm^{-1}	ξ_{Ab}^{so} /cm^{-1}	γ_{so}	Ref.
NaRb	64.9	106.0	40	0.5	155
LiCs	104.0	106.4	71	0.7	181
NaCs	60.1	100.3	95	1.3	158
KCs	51.8	71.6	80	1.3	159
RbCs	45.9	52.1	93	1.9	210
KRb	57.7	77.4	36	0.5	211
Rb_2	44.1	59.2	55	1.1	153
Cs_2	33.0	42.6	113	3.0	212

elements of the dipole moments of the spin-allowed vibronic transitions

$$M^{\mathrm{PUMP}}_{A\sim b-a} = \langle \phi_{b0}|d_{ba}|\chi_a\rangle \text{ and } M^{\mathrm{DUMP}}_{A\sim b-X} = \langle \phi_A|d_{AX}|\chi_X\rangle$$

in a wide range of electronic-vibrational excitations. The parameters v^{PUMP} and M^{PUMP} were determined for the last bound and first quasi-bound (virtual) vibrational levels (with an energy equal to the dissociation energy) of the $a^3\Sigma^+$ state. These initial levels lying in the vicinity of the dissociation limit correspond to photoassociative and magnetoassociative formation of ultracold molecular pairs. The relative accuracy of the calculated matrix elements M^{PUMP} and M^{DUMP} was about 5%–10%, being mainly limited by the accuracy of the relevant ETDM functions, $d_{ab}(R)$ and $d_{AX}(R)$, obtained from *ab initio* calculations. The accuracy of the calculated wavenumbers of the emission transition (DUMP) is comparable with the accuracy of reproduction of the rovibronic energy the $A\sim b$ complexes (about 0.01 cm^{-1}). The accuracy of prediction of the absorption wavenumbers (PUMP) is estimated at about 0.1 cm^{-1}, being equal to the uncertainty in the determination of the dissociation energy of the singlet ($X^1\Sigma^+$) and triplet ($a^3\Sigma^+$) ground states.

The efficiency (rate) of optical conversion was evaluated by means of the calculated radiative lifetimes $\tau_{A\sim b}$ of the intermediate levels of the complex $A\sim b$

$$\frac{1}{\tau_{A\sim b}} = \frac{8\pi^2}{3\hbar c}\left[\langle \phi_A|\Delta U^3_{AX}\, d^2_{AX}|\phi_A\rangle + \langle \phi_b|\Delta U^3_{ba}\, d^2_{ba}|\phi_b\rangle\right] \qquad (10)$$

and branching ratios, $R_{A\sim b}$, of spontaneous emission

$$R_{A\sim b} = \tau_{A\sim b}\left(\frac{8\pi^2}{3\hbar c} v^3_{A\sim b-X} M^2_{A\sim b-X}\right) \qquad (11)$$

to the rovibronic level of the $X^1\Sigma^+$ ground state. Here $\Delta U_{AX} = U_A - U_X$ and $\Delta U_{ba} = U_b - U_a$ are the differences between the adiabatic PECs of the combining electronic states. The $\tau_{A\sim b}$ and $R_{A\sim b}$ values were calculated with a help of the approximate sum rule,[213,214] characterize the intensity and selectivity of spontaneous emission resulting in population of the rovibronic ground-state by the simplest, one-step laser excitation [see Eqn (2)].

The resulting radiative properties corresponding to the strongest PUMP–DUMP transitions involving locally excited levels of the spin–orbit complex $A\sim b$ of KCs molecule are presented in Figs 5 and 6.[159] Clearly, the $\upsilon_A = 15$ vibrational level is optimum for both one-step excitation and two-step STIRAP scheme (see Figs 1 and 2).

Similar estimates made for other heteronuclear dimers[155,158,210] showed that the critical parameters of laser transformation *via* the levels of the complex $A\sim b$ are very weak absorption rates (PUMP) from the initial triplet state

$$a^3\Sigma^+ \longrightarrow A^1\Sigma^+ \sim b^3\Pi$$

This can be attributed to small values of the ETDM functions $d_{ba}(R)$ of $b^3\Pi \rightarrow a^3\Sigma^+$ triplet–triplet transition in the small and intermediate range of internuclear distances as well as with small values of corresponding FCFs $|\langle \phi_b|\chi_a\rangle|^2$ of the weakly bound levels *a*-state.

Practical implementation of the STIRAP scheme requires high-power laser radiation (~100 mW). At present, no laser pump of necessary power in the desired wavelength region is available. Nevertheless, commercially available diode lasers with fundamental wavelengths in the range 1.3–1.5 μm can be used instead. A relatively high efficiency of spontaneous and stimulated emission (DUMP) predicted for a number of low-lying levels of the complexes $A\sim b$ allows one to choose some intermediate vibrational levels that are suitable for realization of the most efficient optical conversion schemes. Stimulated emission can be induced by a tunable diode or a Ti-sapphire laser.

In addition to locally perturbed levels of the complexes $A\sim b$, laser assembling can be accomplished through regularly perturbed electronic states. For instance, a detailed analysis of the energy and radiative properties of the highly excited $(4)^1\Sigma^+$ states of RbCs[215] and KCs molecules[141,216] showed that these states can be utilized as 'intermediate' states in the two-step optical cycles

$$X^1\Sigma^+, a^3\Sigma^+ \longrightarrow (4)^1\Sigma^+(\upsilon') \longrightarrow X^1\Sigma^+(\upsilon'' = J'' = 0).$$

A specific 'shelf-like' shape of the PECs of the $(4)^1\Sigma^+$ states (see Fig. 1) for a number of rovibronic levels allows one to intensify transitions to the ground-state level ($\upsilon'' = 0$) and to highly excited $X^1\Sigma^+$ vibrational levels lying near the dissociation limit. In this case the pump and emission take place *via* the spin-allowed singlet–singlet transitions of ultracold atomic pairs formed at weakly bound vibrational levels of the $X^1\Sigma^+$ ground state. Then, regular spin–orbit interaction of the $(4)^1\Sigma^+$ states with close-lying $(3,4)^3\Pi$ states leads to the induced intercombination transitions

$$(4)^1\Sigma^+ \longrightarrow a^3\Sigma^+.$$

This means that the triplet state

$$a^3\Sigma^+ \longrightarrow (4)^1\Sigma^+ \longrightarrow X(\upsilon'' = 0, J'' = 0)$$

can also be involved in optical conversion cycles.

However, the probability of the spin-allowed transition is nearly 20 times higher than that of the spin-forbidden transition, as follows from the ratio of the absolute values of the ETDM functions.

It should be noted that the spin-allowed ETDM functions for KCs and RbCs molecules the are very close to each other while the probabilities of corresponding rovibronic transitions for RbCs are about ten times lower than those for KCs. This difference is caused by abrupt decrease in the FCF values with increasing absolute values of the quantum numbers of vibrational levels, *viz.*, $\upsilon_{\max} = 136$ for ^{85}RbCs and $\upsilon_{\max} = 104$ for ^{39}KCs. The most intense transitions come from the high-lying levels $\upsilon_X = 90$, $\upsilon_a = 7$ of the ^{39}KCs isotopologue and from $\upsilon_X = 102$ and $\upsilon_a = 11$ for the ^{85}RbCs isotopologue. Also, laser excitation from vibrational levels lying in the vicinity of the dissociation threshold ($\upsilon_X > 100$ for ^{39}KCs and $\upsilon_X > 134$ for ^{85}RbCs) is still feasible for the singlet channels are most efficient *via* vibrational levels of the $(4)^1\Sigma^+$ 'intermediate' state ($\upsilon' = 43–45$ for ^{39}KCs and $\upsilon' = 58–61$ for ^{85}RbCs).

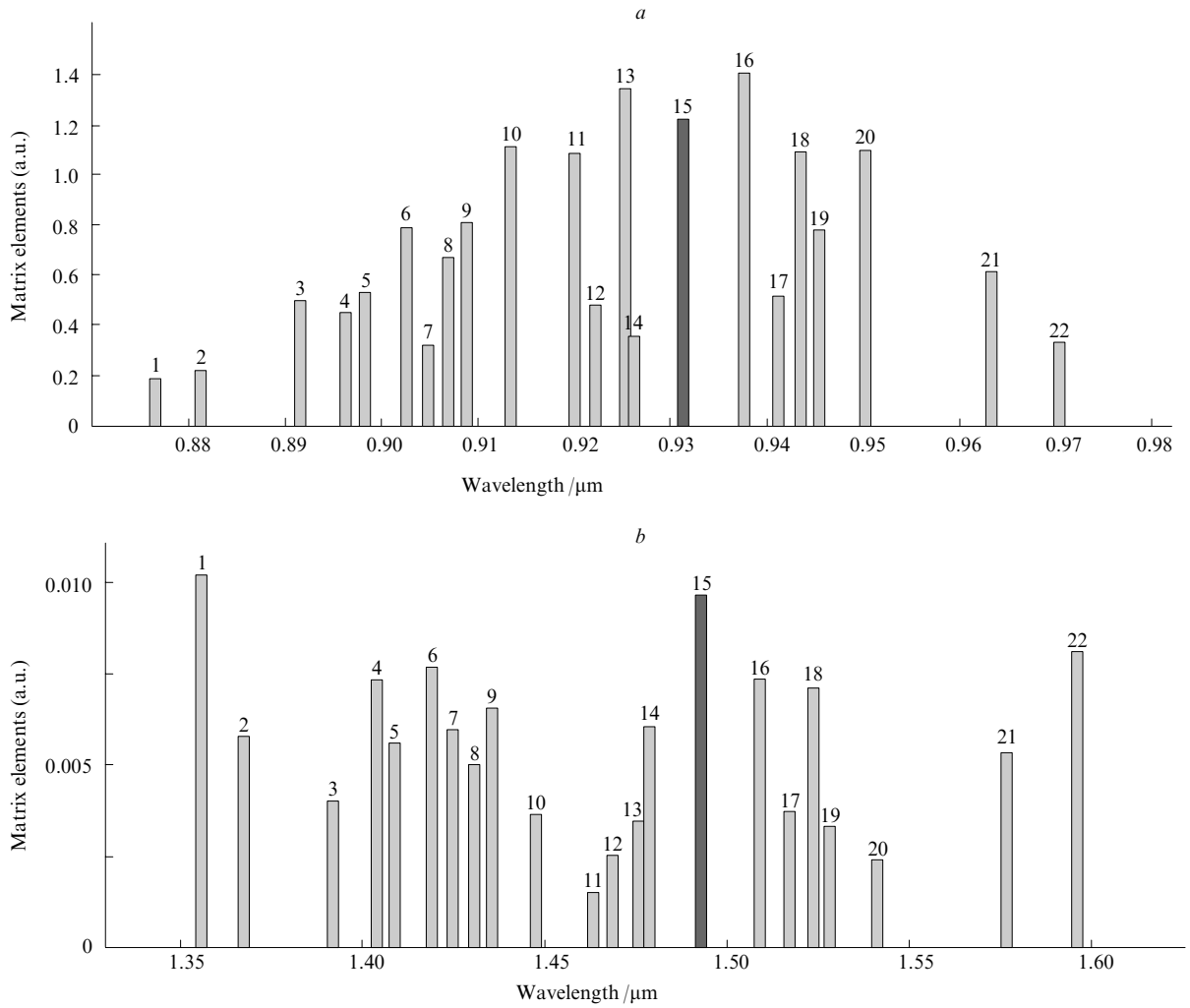


Figure 5. Calculated matrix elements of the dipole moments of PUMP – DUMP rovibronic transitions involving low-lying rovibronic levels of the spin – orbit complex $A \sim b$ of $^{39}K^{133}Cs$ molecule.[159]
(*a*) DUMP ($A \sim b \rightarrow X^1\Sigma^+$); (*b*) PUMP ($a^3\Sigma^+ \rightarrow A \sim b$). Numbers of the bars above correspond to the ordinal numbers of rovibronic level of the complex $A \sim b$.

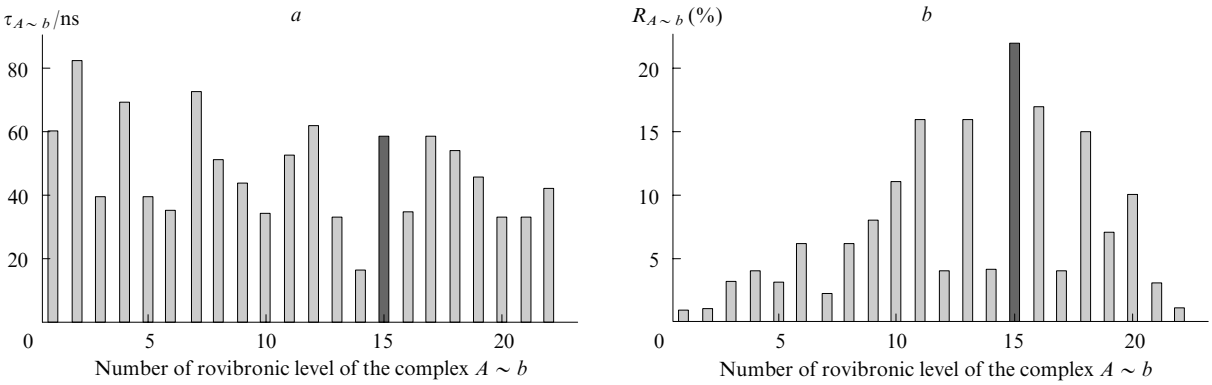


Figure 6. Radiative lifetimes $\tau_{A \sim b}$ (*a*) and vibrational branching ratios $R_{A \sim b}$ (*b*) calculated from Eqns (10) and (11), respectively, for low-lying levels of the spin – orbit complex $A \sim b$ of $^{39}K^{133}Cs$ molecule.[159]

V. Conclusion

A combination of photoassociation (magnetoassociation) and multistep laser assembling can offer optimal schemes for production of stable ensembles of quantum degenerate molecular gas in absolute (lowest) ground state. For instance, the two-step laser assembling of weakly bound ultracold atomic pairs of heteronuclear alkali metal dimers to the lowest singlet ground-state level ($\upsilon = J = 0$) could be efficiently realized by means of both locally and regularly perturbed levels of low-lying excited states. Optimization of laser synthesis is attained using high-precision deperturbation models constructed to reproduce the energy and radiative properties of excited electronic states within experimental accuracy, *viz*., 0.003 – 0.01 cm^{-1} for the energies of rovibronic terms and 5% – 15% for their radiative properties. Robustness of the deperturbation models is confirmed by the mass invariance of the fitting parameters obtained. The models developed can also be used to search for optical 'transparency windows' for spin-forbidden transitions and multistep (multiphoton) schemes of laser excitation and ionization of states of different multiplicity.

Progress in laser cooling and almost routine storage of ultracold atoms in magneto-optical traps led to significant extension of the range of molecular systems under study. Now we are not limited to alkali metal dimers. Pioneering results on ultracold molecules containing atoms of alkaline-earth metals [217, 218] and lanthanides [219] are available. These molecules seem to be more convenient systems for the applications of ultracold molecular ensembles and for achievement of record-high accuracy of measurements. For instance, the breakthrough in measuring of the electric dipole moment of an electron is associated with studies of an ultracold ensemble of YbRb molecules.[219]

Besides, an increase in the number of atoms can lead to significant complication of the mechanism of laser assembling of molecular systems. Recently reported experiments on photoassociation of ultracold trimers [220 – 223] are expected to help in simulating the potential energy surface with inclusion of higher-order multiple interactions. This might be considered to be a next step towards 'controllable' ultracold chemistry.

Prospects in the synthesis of ultracold molecular ensembles are associated with not only extension of the range of systems under study, but also further development of laser cooling and stabilization. A combination of photoassociation with Feshbach resonances [29, 224] seems to be most promising. In this scheme, initial quasi-bound states are modified by external magnetic and (or) electric field in order to shift the maximum of the density of vibrational wavefunctions towards short internuclear distances. This makes it possible to overcome the fundamental disadvantage of photoassociation, namely, very low probabilities of rovibronic transitions at long internuclear distances.

In addition to simulation of the energy and radiative properties of electronically excited molecular states, the search for optimal pathways of laser syntheses and control of ultracold molecules also requires high-precision information on the magnetic and electric properties of rovibronic states involved in the optical cycle. In particular, one should know the Lande factors (*g*-factors) of the 'intermediate' excited states when carrying out magnetoassociation experiments with the formation of Feshbach resonances in the initial electronic state. Coherent control of ultracold molecules in 'optical gratings' requires information on the permanent dipole moment and on the static and dynamic polarizability of the combining electronic states. The magnetic and electric properties molecular states are extremely sensitive to intramolecular perturbations;[225 – 227] this is the reason for unprecedentedly strict requirements for feasibility of deperturbation models that often should take into account hyperfine interactions in explicit form. Construction and tests of such models are in progress.

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