INSTRUMENTS AND METHODS OF INVESTIGATION

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Direct laser cooling of molecules

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Contents

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<u>Abstract.</u> The methods of laser cooling of atoms have long been applied to obtain cold and ultracold atomic gases, including degenerate states and the atomic Bose–Einstein condensate in particular. Until recently the application of laser cooling methods to molecules was assumed to be impossible because of the complex structure of molecular levels and the absence of closed cooling cycles for transitions between the electron levels of molecules in the general case. However, it has recently become clear that laser cooling can be performed for a large class of molecules, including not only the simplest diatomic molecules but also polyatomic molecules. We here present the general principles for identifying suitable molecules and discuss current studies on and further developments in the laser cooling of molecules.

Keywords: cold molecules, spectroscopy, laser cooling, electronic structure

1. Introduction

The cooling of atoms to temperatures considerably lower than 1 K is currently a well-developed technique widely used at research and even teaching laboratories. Studies with cold atoms have been described comprehensively in the literature, in particular, in textbooks and monographs. It should be explained what the definition 'cold' actually means with respect to atoms and molecules. The cooling and trapping of a considerable number of atoms or molecules is in itself a

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Received 14 September 2018, revised 18 December 2018 Uspekhi Fizicheskikh Nauk **190** (3) 313–328 (2020) Translated by M Sapozhnikov; edited by A M Semikhatov trivial task: it suffices to simply place a glass of water into a freezer to obtain a sample after some time with water molecules 'trapped' in a bounded volume with a density of about 10^{23} cm⁻³. However, the control of molecules in a piece of ice is, of course, absent even with respect to their nuclear subsystems: irregular defects in the crystal lattice, random hops of protons between vacancies, and other chaotic changes in the crystal lattice prevent the efficient control of the nuclear dynamics. If the aim is to completely control all the degrees of freedom of an individual atom or a molecule, including the external ones (so-called complete quantum control), this problem is far from trivial. One of the approaches to its solution in the case of neutral atoms is to use the gas of very cold atoms interacting with external laboratory electromagnetic fields. The atomic gas temperature should be low enough to confine atoms in so-called *atomic traps*, given by a combination of electric and magnetic fields, including the fields of laser beams capable of trapping atoms in a small spatial region (about a few cubic millimeters). Because the typical depth of widely used *magneto-optical atomic* traps is fractions of a kelvin, the atomic gas temperature should be noticeably lower than one kelvin.

Thus, to completely control the state of atoms, their considerable cooling is required, and the term *cold* atoms used in the special literature often means *completely controlled* atoms, including the control of their translational degrees of freedom. Similarly to atoms, molecules that can be confined in *molecular traps* after cooling to temperatures noticeably lower than 1 K can be naturally called cold molecules. As in the case of atoms, we relate cooling to the external degrees of freedom, i.e., to the decrease in the kinetic energy of a molecule as a whole¹. Besides the magneto-optical trap mentioned above, *magnetic molecular traps* [1] can also be

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¹ We note, however, that the energy of molecules related to the translational degrees of freedom does not necessarily depend on (or is equal to) the energy distributed among the internal (rotational and vibrational) degrees of freedom.

given as an example, capable of trapping molecules with temperatures below 0.4 K.

In a single review, it is impossible to completely describe the already existing and proposed techniques for obtaining cold molecules, even for direct methods. Some methods, for example, the Stark deceleration technique, are described in several multiple-page reviews. This review is devoted to the methods of direct laser cooling of molecules, which have been becoming more and more popular in recent years. These methods are at the initial stage of their development: the first successful results for diatomic molecules were obtained in 2010 [2], and in the very interesting case of polyatomic molecules, in 2017 [3]. The aim of this review is to attract the attention of molecular spectroscopists to this rapidly developing and, in our opinion, very promising research field. The laser cooling of molecules is closely related to the welldeveloped and comprehensively studied laser cooling of atoms. In the case of molecules, the cooling mechanism is similar to that for atoms if the molecule is properly chosen. The problem of choosing suitable molecules is discussed in a considerable part of the review.

We note that the number of molecules proposed for direct laser cooling increases very rapidly, and currently there are dozens of promising candidates (along with molecular cations and isotopic homologs), although this technique has been experimentally applied so far only for a few diatomic molecules (SrF, CaF, YbF, and YO) and two triatomic molecules (SrOH and YbOH). The close relation between the laser cooling of molecules and atoms makes it unnecessary to discuss all the features of the laser cooling technique, which are considered in numerous monographs, for example, in books [4] and [5] and review [6]. Some slight differences between laser cooling processes applied to molecules and atoms are discussed below whenever necessary. We also consider other molecular cooling schemes to a degree necessary for placing the laser cooling methods within the general picture.

Cold molecules are, on the one hand, an interesting and promising subject and, on the other hand, a powerful tool for studies. There are several reviews and even books devoted to the preparation and applications of cold molecules [7], in particular, in controllable chemistry studies [8], quantum computing [9, 10], the search for exotic interactions, including the search for dark matter [1], and many others.

We emphasize the outlook for ultraprecision spectroscopy with cold molecules, in particular, the search for effects of a 'new physics' that cannot be described by the Standard Model of elementary particles. One of the physical parameters most sensitive to the 'new physics' is the permanent electric dipole moment (EDM) of elementary particles (electron, proton, and neutron). The existence of the EDM would point to the presence of fundamental interactions noninvariant under both the reflection of spatial coordinate axes (i.e., breaking the \mathcal{P} -parity) and reversal time under (breaking the T-invariance). Polar molecules with a heavy atom are currently the most promising objects for searching for the EDM due to a strong enhancement of effects related to the presence of the EDM in them compared to the EDM of 'bare' elementary particles. For example, in the ThO molecule currently used by the ACME (Advanced Cold Molecule Electron EDM, http://www.electronedm.org/) collaboration to search for the electron EDM, the unpaired electrons are subjected to the action of the effective intramolecular electric field of the order of 7×10^{10} V cm⁻¹. However, producing a

permanent well-controllable electric field above 10^5 V cm⁻¹ is in fact impossible under laboratory conditions. The bound on the electron EDM at a level of 1.1×10^{-29} e cm (e is the elementary charge) imposed by the ACME collaboration limits the rest mass of some supersymmetric partners at a level above 30 TeV, exceeding the energy range of the Large Hadron Collider. In experiments with cold triatomic molecules, it is planned to move the mass bound for supersymmetric partners to petaelectronvolts. Below, we discuss the reasons for such a rapid increase in the sensitivity of molecular experiments in more detail.

2. First steps in the laser cooling of matter: laser cooling of atoms

It is worth saying a few words about the history of methods for the laser cooling of atoms. The idea of cooling atoms by electromagnetic radiation is in itself quite nontrivial, and the first discussions of such possibilities appeared in papers by Kastler [14] and Zel'dovich [15]. Hänsch and Shawlow [16] and Wineland and Dehlmet [17] developed this idea in 1975 to propose practical schemes for the laser cooling of ions in traps and free neutral atoms. In the case of neutral atoms, these methods proved to be the most efficient for atoms from the first and second groups of the periodic table (and also some rare-earth atoms). The first experiment on the laser cooling of Na atoms was performed in Letokhov's group at the Institute of Spectroscopy, Russian Academy of Sciences, in 1981 [18] (see also review [19]). In this experiment, velocity compression was achieved only for a small part of the sodium atoms in the atomic beam. However, methods for considerably increasing the fraction of slowed atoms were also developed by the research group at the Institute of Spectroscopy [20]. Later, a number of researchers performed three-dimensional cooling and trapping of atoms in atomic traps.

In 1997, Steven Chu, Claude Cohen-Tannoudji, and William Phillips were awarded with the Nobel Prize in Physics for developing methods to cool and trap atoms with laser light [21-23]. The general principles of one type of laser cooling, namely, Doppler cooling, are presented in Section 4. We note, however, that the laser cooling of atoms was later used by researchers from the Joint Institute for Laboratory Astrophysics (JILA), USA and the Massachusetts Institute of Technology (MIT), USA to obtain the Bose-Einstein condensate of Rb (JILA) and Na (MIT) atoms (the Nobel Prize in Physics was awarded in 2001 to Eric Cornell, Carl Wieman, and Wolfgang Ketterle [24, 25]). In 2005, Theodore Hänsch, one of the authors of the method of laser cooling of neutral atoms, was also awarded the Nobel Prize in Physics "for contribution to the development of laser-based precision spectroscopy, including the optical frequency comb technique" [26]. Another author of the method for laser cooling of ions, David Wineland, was awarded the 2012 Nobel Prize in Physics "for ground-breaking experimental methods that enable measuring and manipulation of individual quantum systems" [27]. Finally, Arthur Ashkin, one of the laureates of the 2018 Nobel Prize in Physics, is also known for his studies on trapping and manipulation of neutral atoms, which resulted in the development of the optical tweezers widely used in biological systems.

The complete control of all the degrees of freedom of cold atoms resulted in the creation of ultraprecision atomic clocks [28, 29] and initiated the study of exotic phases of matter [30], transition regimes between Bose–Einstein and Fermi condensates in cold gases [31–33], the ultraprecision measurements of physical constants [34, 35], and many other investigations. We can expect rapid progress in the development of a quantum computer based on ultracold Rydberg atoms [36] and high-precision atomic clocks based on atoms of f-transition elements [37, 38].

It would seem that the use of laser methods to cool molecules offers great hopes for considerable progress in numerous fundamental and applied regions; however, the application of such cooling methods to molecules seemed impossible until recently, first of all because of the much more complicated structure of molecular levels compared with atomic levels. Nevertheless, considerable recent progress was achieved in the laser cooling of molecules due to improvements in laser equipment and the better understanding of the molecular electronic structure.

3. Methods for obtaining cold molecules

All the methods for obtaining cold molecules can be divided into two large classes: direct and indirect. As follows from the name, indirect methods use molecules synthesized from preliminarily cooled fragments, whereas in direct methods the molecules are first obtained chemically² and then cooled.

3.1 Indirect methods

In the field of indirect methods, the greatest progress has been achieved in the combined method of stimulated Raman population transfer (STIRAP) from the Feshbach bound state [39] (recent progress in this area is described in [40, 41]). This method provided record-breaking densities of cold molecules (about 10^8 cm⁻³) and the lowest temperatures (tens of nanokelvins). The STIRAP/Feshbach method is in fact a variant of the traditional photoassociation method (which is also used to synthesize cold molecules), the difference being that the weakly bound state of two atoms is produced at the initial stage. In this case, the intersection of the bound electronic level in a magnetic field with the states of the continuous spectrum, the so-called Feshbach resonance, is used. Then the weakly bound state can be efficiently transferred to the ground rovibronic state of the ground electronic level of the associated molecule using coherent population transfer.

Despite the considerable successes of this method, there are some fundamental limitations inherent in the method and other indirect methods. One of them is the use of already preliminarily cooled atoms (or other fragments) to assemble cold molecules, which considerably restricts the chemical composition of such molecules; these are mainly quite exotic compounds of alkali and alkali-earth metals (KRb type). Proposals to synthesize molecules from atoms of f-elements appeared only recently (Er₂ in [42]). In addition, it is rather difficult to synthesize molecules consisting of more than two atoms (although this is possible in principle). The assembled molecules are often chemically unstable, i.e., a barrierless chemical reaction occurs during their contact with each other (for example, the reaction KRb + KRb \rightarrow K₂ + Rb₂ for KRb is barrierless).

Among specific problems with the STIRAP/Feshbach method and photoassociation as a whole is the difficulty of finding a combination of suitable states used to convert unbound atoms to a molecular bound state. Here, theoretical calculations of the probability of corresponding transitions in combination with experimental data can be very useful (see review [43]). Nevertheless, despite their considerable history, indirect methods of obtaining cold molecules can still be applied only to a quite narrow class of molecules.

3.2 Direct methods

As regards direct methods, they also have disadvantages limiting their applications.

3.2.1 Stark methods. The family of Stark slowing methods, as follows from the name, is based on the molecular Stark effect in which a force acting on a molecule appears due to interaction of the molecular dipole moment with the gradient of an external electric field. The typical scheme of a Stark decelerator is presented in Fig. 1.

A molecular beam, typically obtained upon expansion of a carrier gas (He, Ar or Kr) mixed with the molecules to be slowed, enters a region with an electric field gradient changing in both space and time. For slowing, molecules in both the socalled low-field-seeking states and high-field-seeking states can be used. In the first case, the potential energy of molecules decreases with decreasing the electric field strength, which allows using a sufficiently simple quadrupole/hexapole scheme for the slowing [44]. For the high-fieldseeking states, in which the energy of a molecule decreases with increasing the electric field strength, the variable gradient method is used, which is in hard 'the hard focusing' method widely used in particle accelerators [44]. The deceleration works efficiently for a rather narrow range of molecular velocities, i.e., the velocity filtration of molecules occurs along with slowing. As a result, in a coordinate system comoving with the center of masses of the decelerating molecules, the molecular gas temperature can be of the order of tens of millikelvin.

However, in any case, for the efficient application of Stark methods, a considerable molecular dipole moment is required along with a small enough molecular mass. As a rule, the ratio of the dipole moment to the molecular mass should not exceed 0.04 D a.e.m.⁻¹. The list of molecules slowed down



Figure 1. Principal scheme of a Stark decelerator. A molecule loses its energy in the electric field gradient. At the moment it pass through the potential energy maximum, the voltage is switched to the next pair of electrons, and so on. A constant gradient of the electric field is produced. The molecule interacting with this gradient can in principle be slowed down to the capture velocity in a molecular trap.

 $^{^2}$ Besides conventional chemical reactions, other methods, e.g., laser-induced reactions can be used.



Figure 2. (Color online.) Diagrams of the Sisyphus cooling of the fluoromethane molecule [53]. The population of working rotational levels with the total momentum projections M = 4 and M = 3 (J = 4) and M = 3 and M = 2 (J = 3) occurs by pumping these levels with an IR laser at the $v = 0 \rightarrow v = 1$ transition between the rotational levels (red arrow 1). Green arrow 2 shows the microwave transition decreasing the population of the excited rotational level with J = 4. Cooling occurs when fluoromethane molecules in the states with M = 4 (J = 4) and M = 3 (J = 3) having a high polarizability enter the region with a high electric field strength. After reaching the region with the potential energy maximum and hence the minimum of kinetic energy, the molecule is transferred to the state with M = 3 (J = 4) and M = 2 (J = 3) with a considerably lower polarizability (blue arrows 3) and is then extracted from the region with the high electric field strength. Here, J, M, and K are the quantum numbers of a symmetric top, J is the total angular momentum of the total angular momentum on the external field direction, K is the projection of the total angular momentum on the molecular third-order symmetry axis, and v labels vibrational states.

by the Stark method, NH₃, CO, OH, NH, SO₂, C₇H₅N, H₂CO, and YbF, is presented in review [45].³ For all molecules from this list, except YbF, the ratio of the dipole moment to the mass does not exceed a few hundredths of a D a.e.m.⁻¹. As regards YbF, we note that the attempt to slow down these molecules was not entirely successful: for the length of the operation part of the setup greater than 30 cm, the slowing rate was only 7% [46], while a noticeable increase in the setup length is problematic because of the molecular beam divergence.

A group at the Imperial College (London, Great Britain), who have been working with YbF, changed to the more efficient Stark deceleration by the traveling wave method [47]. This method can also be efficiently applied to heavy molecules in the high-field-seeking states. In this case, molecules are slowed down in a moving potential well formed by a special configuration of electric fields. Such an approach solves the problem of molecular beam divergence and allows constructing decelerators up to a few meters in length. However, for example, to slow down the SrF molecule from 290 m s⁻¹ to 120 m s⁻¹, the setup length should be 4 m [48], which makes it rather complex and costly.

3.2.2 Cooling by a buffer gas. The *method of cooling by a buffer gas* proposed and mainly developed by Doyle's group at Harvard University (USA) is quite universal [49, 50]. In this method, a molecular beam is injected into a cell with a buffer gas (as a rule, helium) at low temperature, which is followed by thermalization of the beam molecules with the buffer gas. The thermalized molecules can then be extracted from the cell in the intermediate gas outflow regime. The success of the method depends on the ratio of probabilities of the elastic and

inelastic scattering of buffer-gas atoms by cooled molecules. If the inelastic scattering cross section is high, buffer-gas atoms attach to molecules so as to form clusters. Nevertheless, the elastic scattering cross section for a broad class of molecules is high enough for thermalization to occur before the extraction of molecules from the cell. However, the method of cooling by a buffer gas is accompanied by difficulties in cooling molecules to temperatures noticeably lower than 1 K and is mainly used to obtain slow molecular beams and for preliminary cooling before the subsequent deeper cooling stages. In addition, only a very small proportion of thermalized molecules directly enters the extracted molecular beam, which means that a great amount of the working substance is required. Nevertheless, this is one of the few methods that in principle provide the cooling of polyatomic nonpolar molecules, which is its great advantage.

There are also some other methods of molecular cooling and slowing, but they either require rather exotic molecules (for example, molecules in Rydberg states [51]) or are rather complicated to realize (like cooling of molecules in an optical cavity [52]). We see that the molecular cooling methods discussed above cannot be efficiently applied to many diatomic molecules and cannot be used for polyatomic molecules (except one). This circumstance stimulated the further search for molecular cooling methods that should be both quite universal (applicable to diatomic and polyatomic molecules) and sufficiently efficient, robust, and not very complicated. One of the candidates for this role is electrooptical cooling, demonstrated in [53, 54].

3.2.3 Electro-optical method. The idea of the method is to take away the translational energy of a polyatomic molecule (in the ideal case) during only one Sisyphus cooling cycle [55]. We can see from Fig. 2 that if the Stark interaction of a molecule in an excited vibrational state noticeably exceeds this

³ A number of isotopic homologs of these molecules of the DH type, etc. not included on the list were also slowed down.

interaction in the ground vibrational state, then by appropriately selecting the interaction time of the molecule with an external field, the kinetic energy of the molecule can be almost completely transferred to the potential energy, which can then be completely removed from the molecule–trap system. As a result, the molecule is cooled.

Using this scheme, Zeppenfeld's group managed to cool formaldehyde molecules to 400 μ K, which is at present the lowest temperature obtained for polyatomic molecule gases. Nevertheless, despite the obvious successes of this method and good prospects, we note that (1) working molecules should already be captured in a trap before cooling, (2) the method requires rather expensive and nonstandard equipment, and, finally, (3) this method can be used, like the Stark methods, most efficiently for sufficiently light polar molecules.

Another candidate for the role of the 'gold standard' of molecular cooling is at present a family of laser molecular cooling methods.

4. Methods for laser cooling of molecules

It was long assumed that laser cooling methods used in atomic spectroscopy cannot be applied to molecules. As mentioned above, this opinion was motivated by the complexity of molecular spectra, in which transitions between electron levels do not follow any selection rules in the general case. We consider this in more detail with the example of direct laser cooling by the Doppler method.

In the Doppler cooling method, as in other direct cooling methods, the principal feature is the possibility of reemission of a large number of photons: from 10^3 (for a simple manipulation/deflection of atomic/molecular beams) to 10^7 (for cooling heavy atoms from room temperature to submillikelvin temperatures) for a quite short time (about 10 ms). Dissipative forces appearing during Doppler cooling are considered in detail in book [4]. Here, we discuss only the principal features of this technique required for understanding this problem.

Figure 3 shows the scheme of Doppler cooling in the simplest model case of a two-level atom. The photon absorption probability drastically increases for an atom moving towards the radiation source due to the Doppler effect and, respectively, decreases (or remains invariable) for an atom moving in other directions. For example, if we con figure six laser beams to intersect at one point, an atom entering the beam intersection region experiences the counter light pressure when moving in any direction. The force producing pressure is dissipative because it explicitly depends on the atom velocity, and when the laser frequency is tuned to the red, the atom loses its energy, i.e., is cooled. The cooling is possible, in principle, down to the so-called Doppler limit [20] corresponding to the temperature $\hbar\Gamma/2k_{\rm B}$, where Γ is the natural width of the working level and $k_{\rm B}$ is the Boltzmann constant. The typical limit temperature for operation at the allowed dipole transition is hundreds of microkelvins (for example, the Doppler limit for the Cs atom is 120 μ K). In this case, the populations of the ground and excited levels periodically change, but their sum always remains the same (no 'population leakage' occurs), which is quite natural for a two-level system.

In general, in the presence of several decay channels of the excited state, for example, into an intermediate electronic state, the atom can transfer to this state, dropping out of resonance with radiation. The circular sequence of photon



Figure 3. (Color online.) Principle of Doppler cooling for a model twolevel atom with a broad atomic transition line (blue profile *I*) and a narrow laser line (orange profile 2). The laser radiation frequency in the laboratory reference frame (Fig. 3a) is detuned to the red with respect to the atomic transition frequency. In this case, the atom interacts with radiation nonresonantly, which is seen in the energy level diagram. However, if the atom has the velocity component opposite to the radiation direction, the radiation frequency in the atom reference frame (Fig. 3b) shifts to the blue due to the Doppler effect, i.e., the atom 'sees' radiation at a resonance frequency, which is absorbed much more strongly than nonresonance radiation. In this case, in each reemission event, the atom loses on average the energy $\Delta \epsilon = \hbar(\mathbf{kv}) = v/c (\hbar\omega)$ (emission is assumed isotropic). Here, **k** is the wave vector and **v** is the atom velocity.

absorption and emission events followed by the change in the population of electron levels and the cooling of an atom/ molecule can naturally be called a cooling cycle (or a 'cooling loop'), similarly to thermodynamic cycles. The organization of the efficient cooling cycle even for the simplest atoms from the first and second groups of the periodic table (respectively having one or two valence electrons above filled electron shells) is nontrivial. For example, the interaction of photons with a specified polarization with atomic states having a certain projection of the electron angular momentum/spin obeys certain selection rules (including those of the vector addition of angular momenta). In this case, the decay of the excited electron state of an atom can occur into states that do not interact with radiation due to some selection rules, the socalled *dark* states (states in which an atom does interact with radiation are called *light* states). In the case of atoms, the methods of suppressing the effect of dark states are well developed, for example, by mixing dark and light states in a magnetic field. Nevertheless, the total number of levels involved in the cooling cycle, is typically not greater than ten, and it is important that in most cases the cooling cycle can be efficiently realized with the help of one laser.

We consider the level structure of an arbitrary diatomic molecule 4 in Fig. 4. If the working transition occurs between

⁴ We use the known Born–Oppenheimer approximation in which the electron and nuclear dynamics are separated. In this case, the energy of a molecular level can be quite accurately written as the sum of the kinetic electron energy with the potential energy of interaction between electrons and nuclei, on the one hand, and the kinetic nuclear energy, on the other hand. In turn, the kinetic nuclear energy is separated into the vibrational part and the rotational energy of a molecule. This leads to a description of the given rovibronic level by approximate quantum numbers (T, v, J), where T is the quantum numbers of the electron term, v is the quantum number of the vibrational level for the given electronic term, and J is a set of quantum numbers of a rotational level of some vibrational level for the specified electronic term.

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Figure 4. Potential curves (terms) of the ground and first excited electron states of an arbitrary diatomic molecule. Horizontal lines indicate vibrational states. The solid arrow corresponds to the cooling laser frequency. Dotted arrows show spontaneous radiative transitions from the vibrational v = 0' level to vibrational levels with v = 0, 1, 2, 3, etc.

the zeroth vibrational level of the ground electron state (which is usually denoted as 0-0', where 0 is the vibrational quantum number v and the prime refers to the excited state), the 0' level also decays into levels with $v = 1, 2, 3, \dots$ The probability of such a decay is in the first approximation determined by the square of the overlap integral between vibrational wave functions of nuclei, the Franck-Condon factor. Obviously, already after a few reemission cycles, the excited vibrational levels are populated (and the zeroth level is depopulated accordingly) and, as a result, the molecule is removed from the cooling cycle. The idea of using a separate laser for each 0' - v, v = 0, 1, ... transition theoretically solves this problem, but the use of more than three lasers in experiments is rather problematic. It is also very difficult to use various chirping methods (selection of the laser pulse shape), which are similar to those used in [56] to 'sweep' the population of higher vibrational levels followed by pumping to the zeroth vibrational level.

Thus, direct laser cooling cannot be applied to molecules in the general case due to spontaneous transitions between vibrational levels. At the same time, there is no problem with transitions between rotational levels just because of the existence of selection rules for transitions between levels with a certain angular momentum. The example of the efficient cooling loop for levels with a certain angular momentum in the general case is presented in [58] (Fig. 5). We can see that upon the transition from the J = 1 level to the J' = 0 level, only the decay to the J = 1 level can occur, i.e., the number of spontaneous transition channels is considerably limited simply because of a special choice of working levels.

But the problem of nonselective spontaneous transitions to vibrational levels cannot be solved in the general case.

4.1 First proposal and first experiments

In 2004, Di Rosa [57] noticed the existence of molecules with a so-called quasidiagonal Franck–Condon matrix. In such molecules, spontaneous-emission rates A in the bands of the spectrum corresponding to the $0'-0(A_{0'0}), 0'-1(A_{0'1}), 0'-2$ $(A_{0'2}), \ldots$ transitions, the relation $A_{0'0} \ge A_{0'1} \ge A_{0'2} \ge \ldots$ is satisfied. As already mentioned, if the dependence of the matrix element of the electric dipole transition between electron molecular levels on the internuclear distance is

Figure 5. Transitions between states with angular momenta *J* and *J'*. If the working transition is $J = 1 \rightarrow J' = 0$, only the electric dipole transition back to the J = 1 level is possible. Transitions to the J = 2, 3, ... levels require a change in the angular momentum by more than 1, whereas the $0 \rightarrow 0$ transition is forbidden by the angular momentum and parity conservation laws.

disregarded,⁵ the strengths A are determined by the Franck– Condon factor, and vibrational transitions are often characterized by the corresponding (associated) Franck–Condon factors. In molecules proposed by Di Rosa, Franck–Condon factors for the 0'-0, 0'-1, and 0'-2 transitions were approximately in the ratio 0.99:009:0.0009. In other words, the probability of population of the first three vibrational levels of the ground electron states after spontaneous emission from the zeroth vibrational level of the excited electronic state is of the order of 0.9999. Di Rosa proposed arranging a molecular cooling cycle by adding lasers at the 1-0' and 2-0' transitions to the main cooling laser at the 0-0' transition for transferring the population back to the main cycle at the 0-0' transition.

Why is the transition probability written in the form 0.9999 instead of 'approximately 0.9' or 'almost unity?' The answer is obvious if we consider the probability of a molecule remaining in the initial state after N photon absorption and emission events. Assuming that each photon absorption followed by its spontaneous emission is an independent event after which the molecule returns to the initial state with a probability P, we have the probability P^N of the molecule remaining in the initial state after N photon absorption and emission events. Table 1 also presents such a probability after the rescattering of 1000 to 1,000,000 photons by a molecule. For example, the rescattering of at least 1000 photons is necessary for the optical manipulation (photode-

Table 1. Probability of a molecule remaining in the initial state after reemission of N photons as a function of the effective Franck–Condon factor P.

P N	1000	10,000	100,000	1,000,000
0.90000	0.0000000	0.0000000	$\begin{array}{c} 0.0000000\\ 0.0000000\\ 0.0000000\\ 0.0000453\\ 0.3678780\end{array}$	0.0000000
0.99000	0.0000431	0.0000000		0.0000000
0.99900	0.3676950	0.0000451		0.0000000
0.99990	0.9048330	0.3678610		0.0000000
0.99999	0.9900500	0.9048370		0.0000453

⁵ Below, we always assume that the radiative transition is an electric dipole transition.



Figure 6. Probabilities of spontaneous transition of a TiO molecule from the zeroth vibrational level of the excited electron state to the first three vibrational levels of the ground electron state (the Franck–Condon factors are taken from [58]).

flection) or noticeable cooling of a molecule such as strontium monofluoride (SrF). Obviously, in this case the probabilities 0.99 and 0.999 belong to 'two different worlds': the difference between the numbers of molecules remaining in the initial state after the rescattering of 1000 photons reaches four orders of magnitude. This explains the meaning of the expressions 'diagonal Franck–Condon matrix' or 'large Franck–Condon factor': we are dealing with the (total) probability of a spontaneous transition for the given set of vibrational levels different from unity at most by 10^{-3} (or even better by 10^{-5}).

The existence of molecules with large Franck–Condon factors of the 0'-0 transition has been known for at least several decades. However, Di Rosa was the first to notice that the inclusion of only an additional pair of vibrational levels of the ground electron states into the cooling cycle is sufficient to make the total probability of a molecule to remain inside the cooling equal 0.999. For example, the associated Franck–Condon factor for the 0'-0 transition in the TiO molecule [58] (Fig. 6) is only 0.875, which at first glance rules out the possibility of laser cooling of this molecule. But when two additional vibrational levels of the ground state are included in the cooling cycle, the total probability of the TiO molecule to remain inside the cooling cycle is 0.9997, which is sufficient for the efficient rescattering of more than 10,000 photons.

Of course, there are reasons for the presence of so strongly closed cooling cycles in molecules, and we discuss them in more detail below. Here, we only note that despite the breakthrough character of paper [57], the author lists only 10 diatomic molecules for which optical spectra were measured with a high enough resolution. Although Di Rosa believes that other diatomic (and even triatomic) molecules suitable for laser cooling should exist, he has not indicated how these molecules can be found.

4.2 Successful development of the method for direct laser cooling of molecules

and creation of a molecular magneto-optical trap

The direct laser cooling of diatomic molecules was demonstrated for the first time by DeMille's group at Yale University (USA) [2, 59]. In this experiment, an SrF molecular beam was 'compressed' in the transverse direction from velocities corresponding to the 'transverse' temperature



Figure 7. Setup of the experiment on the 'transverse' cooling of an SrF molecular beam [2]. The SrF molecular beam was obtained by ablation of a pressed SrF_2 solid target in a helium cell containing helium at a temperature of 4 K. The beam was formed by two collimator holes and had an rms transverse-velocity spread 1.9 m s⁻¹ at the entrance to the cooling region.

of 50 mK to temperatures of 4 mK (in the Doppler cooling regime) or 300 μ K (in the Sisyphus regime). The setup of the experiments is presented in Fig. 7 and the energy level diagram in Fig. 8.

At the first stage, a very slow and cold molecular beam was obtained by the method of buffer gas cooling, providing a considerable population of the lower rovibronic levels of the aground electronic states in SrF. Then the laser beam was reflected many times in the cooling region from mirrors mounted along the setup axis, by intersecting the SrF molecular beam 75 times.



Figure 8. (Color online.) (a) Working levels of the SrF molecule with the hyperfine splitting caused by the magnetic moment of the fluorine nucleus for the 663.3 nm 0'-0 vibrational transition taken into account. Here, *N* is the rotational angular momentum, *J* is the total angular momentum without the nuclear spin, *F* is the total angular momentum, and *g* are magnetic *g*-factors of the corresponding states. Solid arrows correspond to transitions in the cooling cycle. (b) Dotted curves are the profiles of molecular spin-rotational levels (with normalized line intensities for better clarity), and solid red lines correspond to the cooling lasers frequencies. A single laser was actually used with the frequency splitting achieved with the help of an electro-optical modulator.

In this experiment, three lasers were used: one at the main 0-0' working transition, a repumping laser at the 1-0'transition, and a so-called cleaning laser at the 2-1'transition (as above, the prime refers to the vibrational level in the excited electron state). The cleaning laser was used to estimate the degree of the cooling cycle closeness, which proved to be high enough to rescatter 10,000 photons without a considerable loss of the molecular beam intensity. Having verified the viability of the method, in the course of the next four years, DeMille's group achieved the threedimensional cooling of SrF molecules and created the first molecular magneto-optical trap [60]. This last circumstance should be especially emphasized: magneto-optical traps are the specific 'work horses' for researchers in the field of atomic cooling. The technique of magneto-optical confinement of atoms is well studied, stable, and relatively cheap in operation. For example, magneto-optical trapping is typically performed before deeper sub-Doppler atomic cooling, which finally leads to the formation of a Bose-Einstein condensate. It is for this reason that the creation of a molecular magnetooptical trap attracted great interest, and after some time researchers from the Imperial College (Great Britain) demonstrated the trapping and cooling of CaF molecules below the Doppler limit [61].

Besides the Yale and Imperial College groups, researchers led by Jun Ye at JILA (USA) also achieved the threedimensional cooling and magneto-optical confinement of YO molecules [62]. This molecule was the first oxide molecule for which cooling to 4.1 ± 0.5 mK was achieved. Researchers from the Center for Ultracold Atoms at Harvard University (USA) demonstrated the slowing down of CaF molecules by a so-called 'white laser', which can slow (and hence provide capturing in traps) a much greater number of molecules (~ 10⁴) than in the case of simpler schemes [63]. Later, these researchers managed to cool 1300 CaF molecules to 20 μ K for a density of almost 10⁸ cm⁻³ by using the advanced technique of so-called 'grey' optical molasses [64].

One of the main problems encountered by researchers working with molecular magneto-optical traps is the noticeable decrease in the photon scattering rate in the case of socalled second-type traps, or traps involving the $F \rightarrow F - 1$ scheme, when the total angular momentum F is higher for the ground state than for the excited state. The photon scattering rate decreases for molecules because of the presence of numerous rotational and superfine levels in the ground electron state. The methods for working with second-type traps are developed much less than that for the first-type traps $(F \rightarrow F + 1)$ commonly used for atoms. Researchers from the Centre for Cold Matter at the Imperial College analyzed optical forces in second-type traps [65, 66] and showed that their trapping efficiency can be increased to the level of the first-type traps.

4.3 Laser cooling from the standpoint of the molecular electronic structure

4.3.1 General principles in the case of diatomic molecules. We consider the requirement for the Franck–Condon matrix to be quasidiagonal in the simplest case of a diatomic molecule with two electron states (Fig. 9).

It is clear that if the shape and position of the potential energy curve of the excited electron state *exactly* repeat the shape and position of the potential energy curve of the ground electron state, then the vibrational functions of nuclei in such



Figure 9. (Color online.) Nuclear vibrational functions in a harmonic potential for an arbitrary diatomic molecule in the ground and first excited electronic terms. Blue curve *1* shows the ground vibrational function (v = 0), red curve *2* corresponds to the first vibrational function (v = 1), and green curve *3* corresponds to the second vibrational function (v = 2). For internuclear potentials of the same shape, we can assume without loss of generality that the functions differ only by phase, which does not affect their orthogonality properties. In the case of insignificant differences in potentials, the Franck–Condon matrix $Q_{vv'} = |\langle v|v' \rangle|^2$ is quasidiagonal with the largest elements on the diagonal and decreasing nondiagonal elements.

a potentials can differ only by the phase factor, and in this case, the Franck–Condon matrix is *strictly* diagonal. This consideration can be generalized to the case of a multidimensional potential surface: if the potential surfaces are 'parallel' in this sense, the multidimensional Franck–Condon matrix is diagonal. However, such a situation looks rather strange from the physical standpoint, for example, in the simplest case of single-electron excitation, which can be approximately described as the transition of a valence electron between single-electron orbitals. In the general case, the ground state of such an electron can be quite accurately described as a superposition of atomic orbitals localized on atomic nuclei (we ignore the spin part for simplicity),

$$\phi_{\rm g} = c_{1,\,\rm g}\,\chi_1 + c_{2,\,\rm g}\,\chi_2\,,\tag{1}$$

where χ_1 and χ_2 are atomic orbitals localized on nuclei 1 and 2, $c_{1,g}$ and $c_{2,g}$ are some coefficients, typically chosen from the condition of minimizing the total energy of a molecule, and ϕ_g is the molecular orbital describing the state of the valence electron in the molecule. For example, in the case of the simplest molecule H₂⁺, χ_1 and χ_2 are the 1s orbitals of the first and second hydrogen atoms, and $c_{1,g} = c_{2,g} = 1/\sqrt{2(1+S)}$, with $S = \langle 1s_1 | 1s_2 \rangle$. Similarly, the orbital of the valence electron for the excited electronic state is written as

$$\phi_{\rm e} = c_{1,\rm e}\chi_1 + c_{2,\rm e}\chi_2 , \qquad (2)$$

where the subscript e refers to the excited electron state. In the case of H₂⁺, χ_1 and χ_2 are again the 1s orbitals of hydrogen atoms and $c_{1,g} = -c_{2,g} = 1/\sqrt{2(1-S)}$.

It is important that the chemical bond in the H_2^+ molecule drastically changes in the excited state. In the ground state, the electron density has a maximum between the positions of protons and the potential curve has a distinct minimum at the equilibrium distance point, but in the excited state the potential curve has no minimum at all, i.e., the molecule dissociates upon electronic excitation. If we assume that the potential curves of the ground and excited electron states are 'parallel', that would mean that the internuclear potential remains invariable upon electronic excitation. How can the internuclear interaction potential remain invariable (or change insignificantly) after the input of a few electronvolts of energy into the molecule?

Such a situation is encountered in molecular spectroscopy upon excitation of the so-called *nonbonding* electrons — those that are not involved in the formation of a chemical bond.⁶ Such a behavior of valence electrons seems strange at first glance, and we therefore consider the formation mechanism of nonbonding orbitals in more detail in the simplest case of molecular radicals with one valence electron above filled electron shells.

Symmetry. We consider the valence electron structure in the molecular cation HI⁺. The ground electron state (term) of HI⁺ is ${}^{2}\Pi_{3/2}$, where Π is the state with the ± 1 projection of the spatial orbital angular momentum of the electron on the molecular axis, 2 is the spin multiplicity, and 3/2 is the projection of the total (orbital plus spin) angular momentum of the electron on the molecular axis, which we take with the positive sign for definiteness. We assume for simplicity that the only valence electron on the highest filled orbital produces all the electron angular momentum in the ground electron state, while the rest of the electrons occupy low-lying molecular orbitals and make no contributions to the electron angular momentum.⁷ Of course, the real situation is more complicated, but this simplification does not qualitatively affect our consideration below. The orbital of a valence electron can be represented in the same form as the electron orbital in H₂⁺: $\phi_g = c_{I,g}\chi_I + c_{H,g}\chi_H$. The state with the projection of the total angular momentum 3/2 can be naturally obtained by taking the $5p_{3/2}$ valence atomic orbital of iodine as χ_I .

As regards $\chi_{\rm H}$, it would seem that the low-lying atomic orbital 1s should be taken as $\chi_{\rm H}$; but the only possible projection of the electron angular momentum for the 1s orbital is 1/2. Of course, a molecular orbital with a certain projection of the angular momentum cannot be composed of atomic orbitals with different projections of angular momenta; therefore, the lowest-energy atomic orbital with the angular momentum projection 3/2, $2p_{3/2}$, should be used as $\chi_{\rm H}$. However, the 2p atomic orbital in hydrogen lies almost

⁷ Such an approximation is used, for example, by solving the manyelectron problem in the so-called restricted Hartree–Fock method.



Figure 10. (Color online.) Isosurface for the real part of the highest occupied π -orbital of the HI⁺ cation (the imaginary part of the orbital has the same shape, but is turned with respect to the real part through 90° around the internuclear axis) in the ground electronic state. Blue color *I* corresponds to negative values of the one-electron wave function, red color *2* to positive values.

10 eV above 1s! Because the coefficients c_1 and c_2 are determined from the condition of the minimal total energy of the molecule (which is in the first approximation the sum of energies of molecular orbitals), it is difficult to imagine that the addition of an atomic orbital with the energy exceeding the dissociation energy of HI⁺ to the molecular orbital would be energetically advantageous.

The direct molecular calculation confirms this qualitative consideration (Fig. 10). It follows that the highest singly occupied orbital in HI^+ is quite nearly the atomic p orbital centered on the iodine atom. We can say that the valence electron 'does not know' that it is located in the molecule, and its sharing (i.e., participation in chemical bonding) is forbidden due to a certain symmetry of the electron wave function.

Destructive interference. There is a different type of formation of a nonbonding electron orbital when the valence electron, on the contrary, very well 'feels' chemical bonding but does not take part in it because of destructive hybridization. Such a situation occurs, for example, in compounds of the second group of the periodic table with halogens (MgF, CaF, SrF, BaF, and RaF molecules). The calculation of the molecular electron structure shows that the electron density for the valence electron is mainly concentrated outside the molecular-bond region (Fig. 11). In this case, excitation of the valence electron does not affect the internuclear potential if the electron in the excited state is still located on the nonbonding orbital (which is not sp- but pd-hybridized). Such a qualitative consideration is confirmed by spectroscopic experimental data, for example, for the CaF molecule (presented in Table 2).

We also note also that the more distant the valence electron is from the valence-bond region, the lower its chances are to excite molecular vibrations upon transition to (from) the excited state. Such diffusion states of the valence electron appear, for example, in compounds of heavy elements. One of the examples is the YbF molecule, where the description of the valence electron with an acceptable accuracy of molecular calculations requires Gaussian basis functions localized at a greater distance from Yb than the F nucleus.

Compounds of transition element atoms. The division into valence and core electrons in the d- and f-element compounds is rather conventional, even for the simplified picture of

⁶ We note that the concept of a nonbonding electron can vary in different fields of chemistry and physics. In theoretical chemistry, nonbonding electrons normally mean unshared electrons that are not involved in chemical bond formation. This does not mean, however, that a change in the states of such electrons do not lead to considerable changes in the molecular geometry. A detailed consideration of this question is outside the scope of this review. However, we note here that we call electrons nonbonding if a *change in their state* barely affects the chemical bond, which additionally restricts the theoretical chemical definition.



Figure 11. (Color online.) Isosurface of the highest occupied sp-hybridized σ orbital of the CaF molecule in the ground electron state. Blue color *1* corresponds to the negative values of the one-electron wave function, red color 2 to positive values.

Table 2. Experimental spectroscopic parameters of the CaF molecule for the ground ${}^{2}\Sigma_{1/2}$ and the first excited ${}^{2}\Pi_{1/2}$ electron states. The equilibrium states and vibrational constants for these states are very close (within 1%), confirming the nonbonding type of the valence-electron states. Here, $R_{\rm e}$ is the equilibrium distance, ω is the vibrational constant, and $T_{\rm e}$ is the transition energy between equilibrium configurations.

State	$R_{\rm e}, \ {\rm \AA}$	ω, cm^{-1}	$T_{\rm e},{\rm cm^{-1}}$
${}^{2}\Sigma_{1/2} \ {}^{2}\Pi_{1/2}$	1.967 1.952	581.1 586.8	16,489.8

independent electrons, and strongly depends on the criterion for assigning electron orbitals to one class or the other. As a rule, chemical activity is shown by the most weakly bound electrons located in the chemical-bond region. At the same time, electrons on inner atomic orbitals of a transitionelement atom can be optically active. For example, the inner f-electrons of the Yb atom in the YbF molecule are not in fact involved in chemical bonding; however, their energy is close to that of valence s-electrons. This leads to the appearance of a number of low-lying electron states related to excitation of f-electrons to σ -orbitals [67]. The equilibrium parameters for such states can be expected to be close to the ground-state parameters. Nevertheless, the electron structure of transitionelement compounds is typically so complicated that possible candidates for laser cooling cannot even be approximately determined from simple qualitative considerations.

4.3.2 Prediction of a promising candidate for laser cooling and search for \mathcal{P} - and \mathcal{T} -odd effects based on molecular calculations. We consider the RaF molecule proposed in [68] as a promising candidate for experiments on searching for the effects of breaking spatial parity (so-called \mathcal{P} -odd effects) and time invariance (\mathcal{T} -odd effects) in laser-cooled molecules. The RaF molecule has all the features of a promising candidate for laser cooling: a nonbonding valence electron is located on the diffuse sp-hybridized orbital (pd-hybridized orbital in the excited state) of a heavy Ra nucleus. On the other hand, due to the same heavy nucleus, a considerable enhancement of the \mathcal{P} - and \mathcal{T} -odd effects can be expected in this molecule [69]. Table 3 presents molecular parameters calculated for the ground and excited electron states of the RaF molecule (the calculation method is described in detail in [69]). Table 4 presents a comparison of the sensitivity of experiments on searching for the electric dipole moment of the electron for the ThO molecule used by the ACME collaboration, the RaF molecule, and the hypothetical CnH molecule (copernicium monohydride, an isoelectronic analog of the HgH molecule).

Table 3. Molecular spectroscopic parameters for the ground ${}^{2}\Sigma_{1/2}$ electron state and excited states from calculations by the coupled-cluster method in the Fock space with one- and two-particle cluster amplitudes for 226 RaF. The equilibrium distance $R_{\rm e}$ is presented in atomic units; the vibrational constant $\tilde{\omega}_{\rm e}$, the transition energy $\tilde{T}_{\rm e}$, and the dissociation energy $\tilde{D}_{\rm e}$ are given in inverse centimeters. The correlation calculation involves 17 valence electrons. The results are presented for calculations with the RCC-ANO basis set [89] for the Ra atom. Franck–Condon factors are presented for the ${}^{2}\Pi_{1/2} \rightarrow {}^{2}\Sigma_{1/2}$ electron transition.

	$R_{\rm e}, a_0$	$\tilde{\omega}_{\rm e},{\rm cm}^{-1}$	$\tilde{T}_{\mathrm{e}}, 10^4 \mathrm{~cm^{-1}}$	$\tilde{D}_{\mathrm{e}}, 10^4 \mathrm{~cm^{-1}}$	
	RaF				
${}^{2}\Sigma_{1/2}$	4.29	431		4.26*	
${}^{2}\Pi_{1/2}$	4.29	428	1.33		
$^{2}\Pi_{3/2} + ^{2}\varDelta_{3/2}$	4.31	415	1.50		
$^{2}\varDelta_{3/2} + ^{2}\Pi_{3/2}$	4.28	431	1.54		
$^{2}\Delta_{5/2}$	4.30	423	1.58		
${}^{2}\Sigma_{1/2}$	4.32	419	1.67		
Franck–Condon factor for the $0'-0$ transition is > 0.999. Experimental data from [71].					
${}^{2}\Sigma_{1/2}$	_	441.8(1)			
${}^{2}\Pi_{1/2}^{1/2}$	_	435.5(1)	1.32878(1)		
$^{2}\Pi_{3/2} + ^{2}\varDelta_{3/2}$	-	419.1(2)	1.53554(3)		
$^{2}\varDelta_{3/2} + ^{2}\Pi_{3/2}$	_	431.9(2)	1.51477(2)		
$^{2}\Delta_{5/2}$	-	_	_		
${}^{2}\Sigma_{1/2}$	-	430.9(2)	1.61806(1)		
* Reference [86].					

Table 4. Estimate of the statistical uncertainty δd_e in measuring the electric dipole moment of the electron for different molecules. In all cases, the statistics collection time τ is assumed to be one day. Molecular flows *F* are taken from corresponding papers (see footnotes) for ThO and RaF molecules, whereas for CnH, the detection of only one molecule during the whole experiment is assumed. The coherent interaction time *T* for ThO is assumed to be equal to the time of flight of the molecule in the working region of the ACME setup, whereas for RaF and CnH, some reasonable assumptions are made.

Molecule	ThO	RaF	CnH
$F, \text{ moll } \text{s}^{-1}$ $T, \text{ s}$ $\delta d_{\text{e}}, e \text{ cm}$	$\begin{array}{c} 8.2\times 10^{3}\ *\\ 1.5\times 10^{-3}\\ 3.6\times 10^{-29} \end{array}$	1^{**} 1 2.5 × 10 ⁻²⁹	${1/\tau \atop 1} \\ {10.7 \times 10^{-29}}$

* Number of detected molecules in one cycle.

^{**} Estimate is based on data from [88], where the RaF + ion flow was estimated as 10^7 mol s^{-1} . The efficiency of the ion-neutralization scheme was assumed to be 10%. Similarly to the detection of ThO molecules in [87], the loss of six orders of magnitude in the number of detected molecules is assumed.

First of all, the aim of molecular calculations should be explained. The calculation reliably predicting the suitability of a molecule for laser cooling, as is clear from the data in Table 1, should reliably reproduce the probabilities of radiative transitions in molecules with an accuracy to the third digit and better. Such calculations are possible in principle, but are very time-consuming. In practice, the aim of calculations is in fact to narrow the scope of possible candidates for the choice of suitable molecules. The accuracy of calculations of spectroscopic parameters depends on a particular molecule and the properties to be calculated, on the other had, for diatomic molecules with heavy atoms, the accuracy of calculation of the sum of the three largest Franck-Condon factors for transitions between electron levels (the sum being used to estimate the closeness of the cooling loop) at a level of 5-10% is achieved by using quite

reasonable computer power with software packages for quantum chemical calculations available (for example, the popular DIRAC (Direct Iterative Relativistic All-electron Calculations) freely distributed package for fully relativistic calculations of electron structures).

Table 3 shows that potential curves for the ${}^{2}\Sigma_{1/2}$ and ${}^{2}\Pi_{1/2}$ states have the same equilibrium internuclear distances $R_{\rm e}$ and almost identical vibrational constants $\tilde{\omega}_{\rm e}$. In addition, all the molecular terms generated by the $7{\rm s}^{1} \rightarrow 6{\rm d}^{1}$ electron excitation of the Ra atom have sufficiently close values of $R_{\rm e}$ and $\tilde{\omega}_{\rm e}$. This convincingly demonstrates the nonbonding type of the valence-electron states, which is also confirmed by the calculation of the Franck–Condon factor for the 0-0' (${}^{2}\Sigma_{1/2} \rightarrow {}^{2}\Pi_{1/2}$) transition.⁸ We note that even in the case of a noticeable change in the basis set and the active space in the correlation calculation (see details in [69]), the Franck–Condon factor remains close to unity and the arrangement of excited electron levels also remains unchanged despite their close energies.

The accuracy of RaF calculations was verified by the ANO-RCC calculations of the BaF molecule, which correctly reproduced the experimental arrangement of electron levels and gave other spectroscopic parameters, such as transition energies, equilibrium distances, and vibrational constants, with good accuracy. The calculations of both molecules clearly demonstrate the necessity of the accurate quantum chemical calculation of the electron structure, because qualitative considerations cannot predict the order of electron terms or their spectroscopic parameters with an acceptable accuracy. In the case of BaF, the $^2\varDelta$ level is located between the ${}^{2}\Sigma$ and ${}^{2}\Pi$ levels. The problem is that the $\Sigma \to \Delta$ transition is strongly suppressed, which in fact rules out the organization of the cooling cycle at these levels, while working at the $\Sigma \to \Pi$ transition results in pumping the \varDelta level due to the allowed $\Pi \rightarrow \varDelta$ transition. For RaF, such a problem is absent, which alleviates the organization of the cooling cycle. In addition, it follows from Table 4 that the statistical sensitivity of experiments on searching for the electric dipole moment of RaF even exceeds that of ThO. At the end of 2018, the CRIS (Collinear Resonance Ionization Spectroscopy) collaboration at CERN performed measurements of the spectroscopic parameters of the ground and the first five excited electron states of the RaF molecule to verify theoretical predictions of the possibility of laser cooling this molecule. The experimental results (for a low resolution) were published in arXiv in November 2019 [71] and are presented in Table 3. We can see that the transition energy of all the excited states except ${}^{2}\Sigma_{1/2}$ was calculated with an error of less than 400 cm⁻¹. This quite accurate calculation of molecular levels allowed measuring the parameters of molecular states with the required accuracy in an acceptable time. In addition, spectroscopic data in [71] confirmed the assumption [68] about the possibility of creating an efficient laser cooling cycle in the RaF molecule.

4.4 Laser cooling of polyatomic molecules

It is already clear from the view of the nonbonding orbital in Fig. 11 that instead of a halogen atom, such compounds can in principle contain any group of atoms with combined



Figure 12. (Color online.) Isosurfaces of the wave functions of the valence electron in the CaCH₃ molecule. The singly occupied valence orbital for the leading electron configuration of the ground electron state is shown by light blue color *1* for positive values and by dark blue color *2* for negative values of the wave function. The singly occupied valence orbital for the leading electron configuration of the first excited state is shown by light yellow semi-transparent color *3* for positive values and by darker tint *4* for negative values of the wave function.

chemical properties, in particular, electron affinity resembling the properties of halogens (Fig. 12). Such groups are known in chemistry as functional groups, including, in particular, pseudohalogens. Examples are functional groups OH, CN, CH₃, and many others. Of course, because the valence electron is localized on the side of a metal atom, quasidiagonal Franck-Condon matrices can also be expected for compounds like CaOH, CaCN, CaCH₃, and many others. We proposed such compounds for laser cooling at the conference Cold and Controlled Molecules in Ions in Monte Verita in 2014. The corresponding paper with a theoretical justification was published in Phys. Rev. Let in 2016 [72]. The sum of Franck-Condon factors in these calculations for three vibronic transitions with the highest values of individual Franck-Condon factors for CaCN and CaOH molecules proved to be higher than 0.9, and for nonlinear molecules like CaCH₃, higher than 0.8. Thus, the chances of finding a nearly closed cooling loop in the spectra of proposed molecules were fairly high. Indeed, within only a year after the theoretical proposal, the Doyle group at Harvard for the first time cooled the triatomic SrOH molecule to 750 mK (Sr belongs to the same group of the periodic table as Ca [3]). In these experiments, so-called Sisyphus laser cooling (mentioned above) was used, which also requires the presence of a quasi-closed cycle, but uses a smaller number of scattered photons.

Almost immediately after the success of Doyle's group, proposals were published for using laser-cooled triatomic molecules to search for the \mathcal{P} - and \mathcal{T} -odd effects, in particular, the electric dipole moment of the electron. Here, we do not consider the features of different enhancement mechanisms of the \mathcal{P} - and \mathcal{T} -odd effects in molecules as a whole or the possibility itself of measuring extremely small energy shifts in molecular spectra (see reviews [73, 74] and the references therein). However, we note that (1) the statistical uncertainty δd of a molecular experiment on searching for the electric dipole moment of the electron (proton or neutron) is inversely proportional to the time τ of the coherent (continuous) interaction of molecules with external fields and only to *the*

⁸ Presenting the Franck–Condon factor to the third decimal place concerns the *numerical* accuracy of calculations; the calculation accuracy is estimated to be 10% compared to experiments for a given Franck–Condon factor.

square root of the total number N (flow) of working molecules, $\delta d \sim 1/(\tau \sqrt{N})$. Naturally, great efforts in experiments are expended to increase τ ; (2) the most important factors limiting the accuracy of ultraprecision measurements are systematic errors of different types. The possibility of suppressing such errors depends on the degree of control over the external fields and the internal and external degrees of freedom of a free working molecule. The use of cold molecules in traps allows one to achieve both a long interaction time (about 1 s) of molecules with external fields and the highest degree of controlling the molecular degrees of freedom.

Returning to three-atomic laser-cooled molecules, RaOH [75] and YbOH [76] molecules were considered candidates for such experiments. It was found that linear triatomic molecules (with the symmetric top symmetry in a more general case) offer a number of considerable advantages over diatomic molecules in experiments on ultraprecision molecular spectroscopy. Among them are a lower radiative transition frequency than in diatomic analogs. For example, the ${}^{2}\Sigma_{1/2} - {}^{2}\Pi_{1/2}$ transition frequency in the RaF molecule is slightly above 13,000 cm⁻¹ (visible red light), whereas the corresponding transition frequency for its three-dimensional analog RaOH is 12,600 cm⁻¹ (near-IR range). In this case, the frequency difference is not very considerable, but it could be decisive, for example, if the transition was in the UV region, where it is still difficult to find lasers with a sufficiently narrow and stable line. We note that enhancement factors of the \mathcal{P} and \mathcal{T} -odd effects in RaOH are slightly different from these factors in RaF because of the properties of the valence electron orbital mentioned above.

An important feature of linear triatomic molecules is the presence of the so-called *l*-doubling in the excited vibrational states of the deformation (bending) mode [77]. This doubling is analogous to the known Ω -doubling in states with $\Omega \ge 1/2$ for diatomic molecules, in which, as is known, the degeneracy of states with different signs of the projections Ω of the electron angular orbital momentum on the molecular axis is lifted, when rotation is taken into account. In the case of the Π state (for example, the ground state in the PbF molecule is ${}^{2}\Pi_{1/2}$), two levels with opposite parities are formed with a typical energy difference about 2B, where B is the rotation constant. The Ω -doubling for low-lying spin-rotational levels of the PbF molecule is about 4 GHz, disregarding the hyperfine interaction. In the case of *l*-doubling for a triatomic linear molecule, the interval between the opposite-parity levels is of the order of B^2/ω , where ω is the vibrational quantum of the deformation mode . For example, the *l*-doubling for the YbOH molecule in the ground ${}^{2}\Sigma_{1/2}$ state is of the order of 10 MHz, which gives the distance between opposite-parity levels almost 400 times smaller that in PbF.

This circumstance can have dramatic consequences in experiments requiring the creation of polarization/alignment of molecules: while the electric field required for the total polarization of PbF is a few kV cm⁻¹, a field of the order of a few dozen V cm⁻¹ is required for YbOH. Leak currents decrease proportionally to the applied field, weak electric fields can be switched quite rapidly with respect to the magnetic field direction, etc., and hence the possibility of overcoming false effects in precision experiments drastically increases. Also, it is very important that such molecules contain so-called *internal comagnetometers*—a set of spinrotational states in which a signal from the electric dipole moment of the electron has the opposite sign in invariable laboratory fields. Internal comagnetometers also drastically

decrease the influence of external parasitic fields on the accuracy of experiments (see, e.g., the technical report by the ACME collaboration [78] as an example of the efficient use of this technique).

5. Some promising applications of cold molecules

Of course, the number of laser-cooled molecules is not restricted to molecules containing no more than five atoms [72]. Based on the same general principles, we can propose molecules for laser cooling with an intermediate oxygen atom between a metal and a pseudohalogen (molecules like SrOCH₃, etc., molecules with an extended halogen group (SrOCH₂CH₃), etc. [79]). Such compounds can have advantages over simple compounds of the SrCH₃ type due to the long distance between the metal atom and the pseudohalogen group, leading to a greater closeness of the cooling loop. Also of interest are 'semisandwich' metalorganic compounds, such as metal–pentadien (for example, CaC₅H₅ [80, 81]) proposed for laser cooling by the Harvard group.

All the examples presented above concern molecular radicals with one electron above the filled shells. At the same time, diatomic molecules with closed shells exist (in the ground electronic state), in particular, such is the best known TIF molecule, for which the Franck-Condon factor for the $0'-0 X({}^{1}\Sigma_{0}) \rightarrow B({}^{3}\Pi_{1})$ electron transition is about 0.989 [82]. The advantages of working with molecules with closed shells are rather obvious. They are chemically stable compounds, which can often be obtained more simply in the gas phase than can molecular radicals. In addition, such molecules have simpler spin-rotational spectra in the ground electron state, which makes the analysis of spectroscopic data more reliable. Of course, it would be interesting to analyze the electron structure of polyatomic molecules with closed electron shells from the standpoint of existing closed cooling loops. Such studies are being performed and, although they are now at the earliest stage, there are reasons to assume that very large polyatomic molecules (containing more than 10 atoms) of this class exist that are suitable for direct laser cooling.

Recently, based on general principles formulated in [72], different research groups have been proposing an increasing number of possible molecules for laser cooling. In some proposals, the cooling of molecules is only the intermediate stage for further obtaining cold atoms by the dissociation of molecules [83]. This method can be efficiently used to obtain a number of ultracold light atoms, including hydrogen. The high efficiency of cold-molecule dissociation methods for obtaining light ultracold atoms can be explained as follows. If the dissociation is performed such that the heating of dissociation products is negligible, the *velocity* distribution of final products coincides with the velocity distribution of initial molecules. However, the kinetic energy and therefore temperature are also proportional to the mass of atoms produced after dissociation. It is clear, for example, that upon dissociation of the BaH molecule to Ba and H, the temperature of the hydrogen atoms is $m_{\rm H}/m_{\rm Ba} \approx 100$ times lower than that of BaH for the same velocity distributions [84]. Because BaH can be cooled to temperatures of about a few hundred microkelvins, the temperature of hydrogen atoms produced after photodissociation is a single microkelvin already. The further cooling of hydrogen is possible by nonlaser methods, for example, by the evaporation method [85].

Finally, considerable progress was recently achieved in the creation of quantum simulators based on cold atoms [36]. These simulators are constructed in Rydberg atoms with the outer electron in the states with the principal quantum number of about 100 and higher. Such atoms have very high polarizability and can therefore interact with each other at large atomic distances of about 1 μ m. Polar molecules have an intrinsic dipole moment, which allows creating an ensemble of cold interacting molecules at easily achievable densities. For example, it is possible to use the states of molecules oriented differently along the direction of an external electric field as qubits [9].

6. Conclusions

Cold molecules offer unique possibilities for high-precision spectroscopy, the search for effects of new physics, quantum computation, and many other fields. Recently, numerous methods for cooling and trapping molecules have been supplemented by reliable, stable, and relatively low-cost methods of direct laser cooling. Laser cooling methods can be applied to numerous molecules, including polyatomic molecules with open and closed electron shells. The number of proposed polyatomic molecules is very large, which opens up prospects of studying various ultracold samples with different chemical and physical properties. The primary choice of candidates for laser cooling can be made based on rather simple and intuitively clear physical principles. Further quantum chemical calculations are used to refine the list of suitable molecules with high reliability. At present, methods of molecular laser cooling are at the initial development stage, but undoubtedly they will be developed in the nearest future.

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