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Ab Initio Study of the Interaction Potentials of CF_4, CH_4, SiF_4 and SiH_4 Molecules with the Rb Atom in the Ground and Electronically Excited States

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The potentials of the electronic states of $RbXY_4$ molecules, $XY_4 = CF_4$, CH_4, SiF_4 and SiH_4, correlating with the ground $5s\ ^2S_{1/2}$ and excited $5p\ ^2P_{1/2,3/2}$ states of the Rb atom are studied using the methods of ab initio quantum chemistry. The calculations are performed by the SCF method of the full active space of orbitals, taking into account dynamic electronic correlations and spin-orbital interaction. It is established that the character of the interaction in the A and A' states, correlating respectively with the lower and upper states of the Rb $(5p\ ^2P_{1/2,3/2})$ doublet and corresponding to the perpendicular orientation of the Rb p-orbital relative to the Rb−X axis, differ significantly (attraction or repulsion) for different XY_4 molecules, which is explained by the difference in the charge distribution in the XY_4 molecules. In order to evaluate the accuracy of the calculation results for $RbXY_4$ molecules, similar calculations are performed for the diatomic RbAr molecule using different basis sets. It is found that, as compared with the A and A' states, the potential of the repulsive B state, which correlates with the upper state of the doublet and corresponds to the orientation of the Rb p-orbital along the Rb−X axis, is significantly more sensitive to the size of the basis set which is due to the accuracy of accounting for the configuration interaction with states that correlate with the Rb $(6s\ ^2S_{1/2})$ and Rb $(4d\ ^2D_{3/2,5/2})$ states and other states of the Rb atom lying above Rb $(5p\ ^2P_{1/2,3/2})$.

Keywords: alkali metals, excited states, carbon tetrafluoride, quantum chemistry, ab initio calculations.

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Introduction

In recent year, active research has been carried out on lasers based on transitions of alkali metal atoms with optical pumping by radiation from diode lasers [1]. The generation occurs at the transition from the lower state of the main resonant doublet A $(np^2P_{1/2} \rightarrow ns^2S_{1/2})$, where A = Na, K, Rb, Cs and $n = 3$, 4, 5, 6, respectively, upon optical excitation of the upper doublet state at the transition frequency A $(np^2P_{3/2} \leftarrow ns^2S_{1/2})$. The population transfer A $(np^2P_{3/2}) \leftarrow \mathrm{A}(ns^2P_{1/2})$ occurs as a result of collisions with gas mixture atoms and molecules. As a rule, the working mixture of these lasers consists of a light buffer gas (He, Ar) with CH_4 added; the total mixture pressure is several atmospheres. The role of CH_4 is to ensure rapid transfer of the population from the pumped state to the laser state — compared to inert gas atoms, the rate constant of this process for collisions with CH_4 is several orders of magnitude higher. However, as noted in [2], over time, the plaque forms on the windows of the laser cell, that indicates a chemical interaction between the alkali metal and CH_4.

As was established in recent studies [3,4], the mixtures of alkali metal vapors with CF_4 are chemically stable in the temperature range up to 250°C. In this case, compared to CH_4, collisions with CF_4 are characterized by a higher efficiency of population transfer between doublet states. Thus, according to the data for Rb [5], the rate constant of this process for CF_4 is more than twice as high. As noted in [3], CF_4 may be of interest as an alternative to CH_4 in the working mixtures of these lasers.

Initially, the purpose of this study was to calculate the potentials of the $RbCF_4$ states, which correlate with the ground Rb $(5s\ ^2S_{1/2})$ and electronically excited states of the Rb doublet $(5p\ ,^2P_{1/2,3/2})$. The stimulus was the previous experimental studies of the absorption spectra of mixtures CF_4 with vapors Rb and other alkali metals [3,4]. Then, for comparative analysis, similar calculations were performed for other „molecules−pyramids", including CH_4, SiH_4, and SiF_4. With the same geometry these molecules are characterized by very different electron density distributions, and a comparison of the results can provide valuable information about the contribution of the electrostatic interaction to the interaction potential of the Rb atom and the XY_4 molecule. Note that the $RbCH_4$ molecule has already been studied using quantum chemistry [2]. As far as we know, similar studies have not been carried out for $RbSiF_4$ and $RbSiH_4$ molecules.

This article also discusses the results of calculations for the diatomic RbAr molecule. The electronic structure of RbAr and other RbRg molecules (Rg — an atom of an inert gas) has been repeatedly studied earlier using quantum chemistry methods [6–10]. Compared to $RbXY_4$, RbAr calculations are much less time consuming. In the present study the RbAr molecule was used as a model system for studying the influence of the basis size on the calculation accuracy. Based on these results, the calculation accuracy of $RbXY_4$ was estimated.

Calculation details

The calculations were carried out using the OPEN MOLCAS [11] software package. The energies of electronic states, taking into account the static component of the correlation energy of electrons, were calculated by the SCF method of the complete active space of orbitals CASSCF (complete active space self consistent field). Dynamic electron correlations were taken into account by the perturbation theory method CASPT2 (complete active space with second order perturbation theory correction) [12]. The energies and wave functions obtained by the CASSCF/CASPT2 method were further used by the RASSI (restricted active space state interaction) [13] program to calculate the energies taking into account the spin-orbital interaction. The method is based on the Douglas–Kroll transformation of the relativistic Hamiltonian. The RASSI program also calculates dipole moments and rates of radiative transitions between molecular states.

The calculations used ANO-RCC (atomic natural orbital relativistic correlation consistent) basis sets with different degrees of contraction — VQZP for Rb atom and VTZP for XY_4 molecular atoms (VQ(T)ZP – - valence quadruple (triple) zeta with polarization functions). The VTZP basis was also used for the Rb atom in calculations of the diatomic RbAr molecule. Besides, for RbAr we used ANO-RCC-type bases with the lowest degree of contraction (denoted LARGE in the text).

ANO-RCC type bases were developed and optimized primarily for calculations by the CASSCF/CASPT2 [14] method, that justifies their choice. Note that all three bases (VTZP, VQZP, and LARGE) reproduce with fairly good accuracy the energies of the states of the Rb $(5p\ ^2P_{1/2,3/2})$ doublet (deviation from experiment $\sim 100\,\mathrm{cm}^{-1}$). However, the accuracy of calculating the potentials of the states of the $RbXY_4$ molecule, which correlate with Rb $(5p\ ^2P_{1/2,3/2})$, also depends on the accuracy of taking into account the interaction with higher-lying states . The corresponding calculation would require a specialized extended basis for the Rb atom, including at least the states Rb $(4d\ ^2D_{3/2,5/2})$ and Rb which are the closest in energy, $(6s\ ^2S_{1/2})$. This issue is discussed in more detail at the end of the next section.

The calculations were carried out in C_{1V} symmetry (symmetry element — plane passing through the symmetry axis of the molecule and one of the three Y atoms forming a plane perpendicular to the symmetry axis) for the two most different geometries of the $RbXY_4$ molecule : a) geometry *Vertex* — atom Rb is on the axis of symmetry from the side of atom Y at the vertex of the pyramid and b) geometry *Base* – - the Rb atom is also on the axis of symmetry, but on the reverse side of the pyramid, i.e. on the side of the plane formed by three Y atoms. When calculating the $RbXY_4$ potentials, the Rb–X distance was varied, while the internuclear distances in the XY_4 molecule were fixed and corresponded to the equilibrium values in the free molecule.

Results and discussion

Figure 1 shows the potentials of the electronic states of the RbAr and $RbCF_4$ molecules. Let us first discuss the results for RbAr.

The states of RbAr which correlate with the excited states Rb $(5p\ ^2P_{1/2})$ and Rb $(5p\ ^2P_{3/2})$ differ orientation of the $5p$-orbital Rb with respect to Ar. The $B(^2\Sigma^+_{1/2})$ state correlates with Rb $(5p\ ^2P_{3/2})$ and corresponds to the orientation of the $5p$ orbital along the axis approach of atoms. In its turn the states $A(^2\Pi_{1/2})$ and $A'(^2\Pi_{3/2})$ correlate respectively with Rb$(5p\ ^2P_{1/2})$ and Rb$(5p\ ^2P_{3/2})$ and correspond to the perpendicular orientation of the $5p$-orbital. The potentials of the states A and A' differ very little, so later these states will be considered as a single state denoted by $A^{(\prime)}$.

The B state is repulsive, which is explained by the dominant role of the interaction which occurs when the electron orbital of the Rb atom overlaps with completely filled Ar orbitals (Pauli repulsion). In the $A^{(\prime)}$ state, the repulsion is weaker because the overlap is smaller. For this state the dominant interaction is the attraction of the Ar atom to the ionic core of the Rb atom. As a consequence, the potential of the state $A^{(\prime)}$ has a minimum.

Like the RbAr molecule, the dominant interaction in the B state of the $RbCF_4$ molecule is repulsion. This is true for any geometry of approach of an atom and a molecule. However, in the $A^{(\prime)}$ state the nature of the interaction is more sensitive to the geometry. As can be seen from Fig. 1, *b*, in the geometry *Vertex* the state $A^{(\prime)}$ has a minimum, while in the geometry *Base* this state is repulsive. Let us consider in more detail the issue of the influence of the geometry of $RbXY_4$ molecules on the interaction potential.

The potentials of the B and $A^{(\prime)}$ states of the $RbXY_4$ molecules are compared in Fig. 2. As can be seen, in the geometry *Vertex* the depth of the potential well of the $A^{(\prime)}$ state of the $RbCF_4$ molecule (Fig. 2, *a*) is significantly greater than of the $RbCH_4$ molecule (Fig. 2, *c*), while for the geometry *Base* the opposite is true (Fig. 2, *b* and Fig. 2, *d* respectively). Qualitatively this result can be explained taking into account the difference in the electron density distribution in the CF_4 and CH_4 molecules. In the region of small distances in the geometry *Vertex*, the interaction with

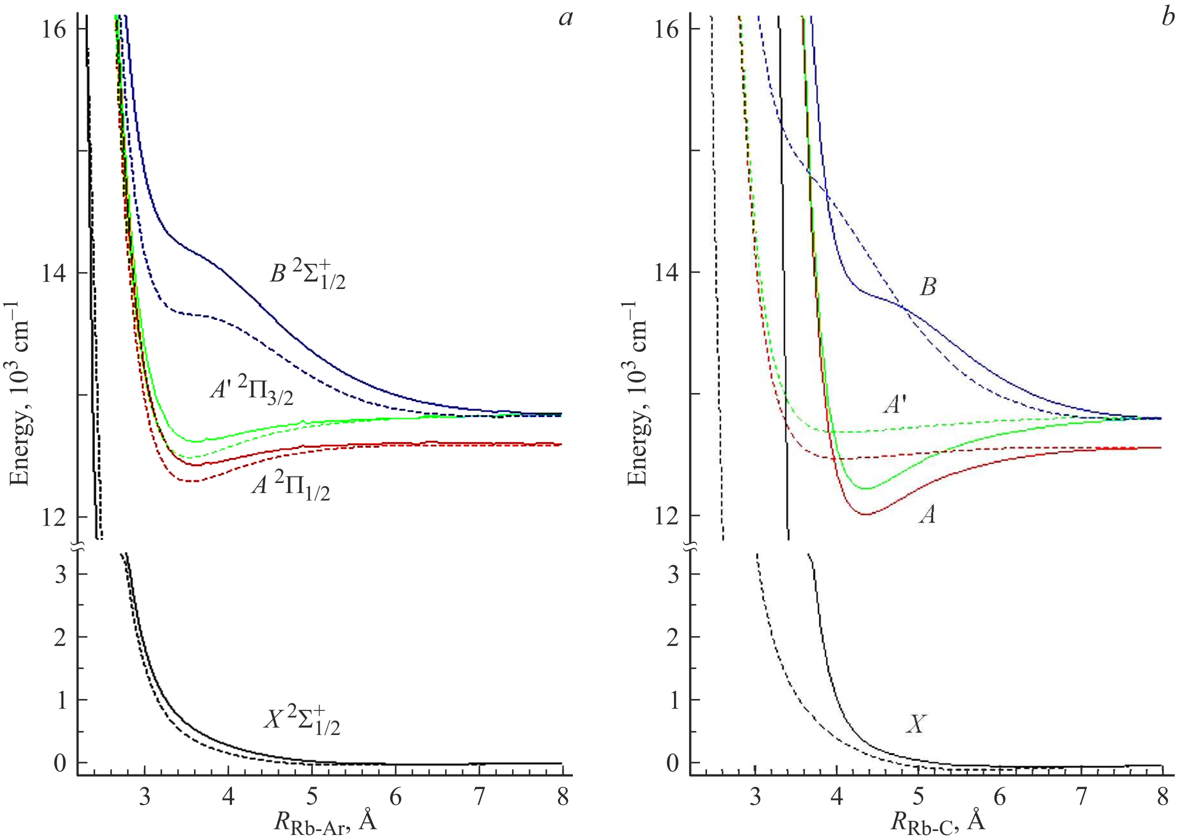

Figure 1. (*a*) Potential curves of electronic states of RbAr calculated using the following basis sets: (solid curves) VQZP for Rb and VTZP for Ar, (dashed curves) LARGE for Rb and Ar. (*b*) Potential curves of the electronic states of the $RbCF_4$ molecule in the (solid curves) *Vertex* and (dashed curves) *Base* geometry calculated with the VQZP basis for the atom Rb and VTZP basis for C and F atoms.

Effective charges on X and Y atoms in XY_4 molecules. Calculation using the LoProp subprogram in MOLCAS (see method description in [16]) and ANO-RCC-VTZP bases for X and Y atoms

	Charge Q per atom X/Y, unit electron charge	
	Q_X	$Q_Y{}^a$
CF_4	1.180	−0.295
CH_4	−0.412	0.103
SiH_4	0.532	−0.133
SiF_4	2.152	−0.538

[a] $Q_Y = -Q_X/4$.

the nearest atom at the vertex of the pyramid is dominant. In CF_4 and CH_4 molecules, the F and H atoms have a charge of a different sign (see table). In the $A^{(\prime)}$ state, the *p*-orbital Rb is perpendicular to the Rb−C axis. If we take into account the incomplete screening of the charge of the ionic core at such an orientation of the *p*-orbital, the difference in the nature of the interaction potential can be explained by the attraction of the ionic core to the negatively charged atom F in the case of CF_4 and, accordingly, its repulsion from the positively charged atom H in the case of CH_4. In the geometry *Base* the situation is reversed. If at the center „of the triangle“formed by atoms F (H) the field of a positively (negatively) charged atom C is not completely screened, then the interaction of the fields of a C atom and the ionic core Rb^+ will give a positive (repulsion) and negative (attraction) contribution to the interaction energy in the cases of CF_4 and CH_4, respectively.

On the whole, the above conclusions are confirmed by the results of calculations for the $RbSiF_4$ and $RbSiH_4$ molecules. Like the CF_4 molecule, the SiF_4 molecule has strongly polar bonds, and the effective charges on the Si and F atoms are almost two times higher than the charges on the C and F atoms (see table). The potentials of states $A^{(\prime)}$ and B states of the $RbSiF_4$ and $RbCF_4$ molecules are compared in Fig. 2, *a* (the geometry *Vertex*) and Fig. 2, *b* (geometry *Base*). As can be seen, the difference in potentials is quantitative. In particular, the depth of the potential well of the $A^{(\prime)}$ state of the $RbSiF_4$ molecule in the geometry *Vertex* is somewhat larger, that can be explained by the large negative charge on the F atoms in the SiF_4 molecule (see table) and, accordingly, a stronger attraction to the nearest atom F of the ion core Rb^+. Inits turn, in the geometry *Base* the situation is reversed. As noted above, in this geometry the potential of the $A^{(\prime)}$ state is significantly affected by the interaction of the Rb^+ ionic core with the central atom of

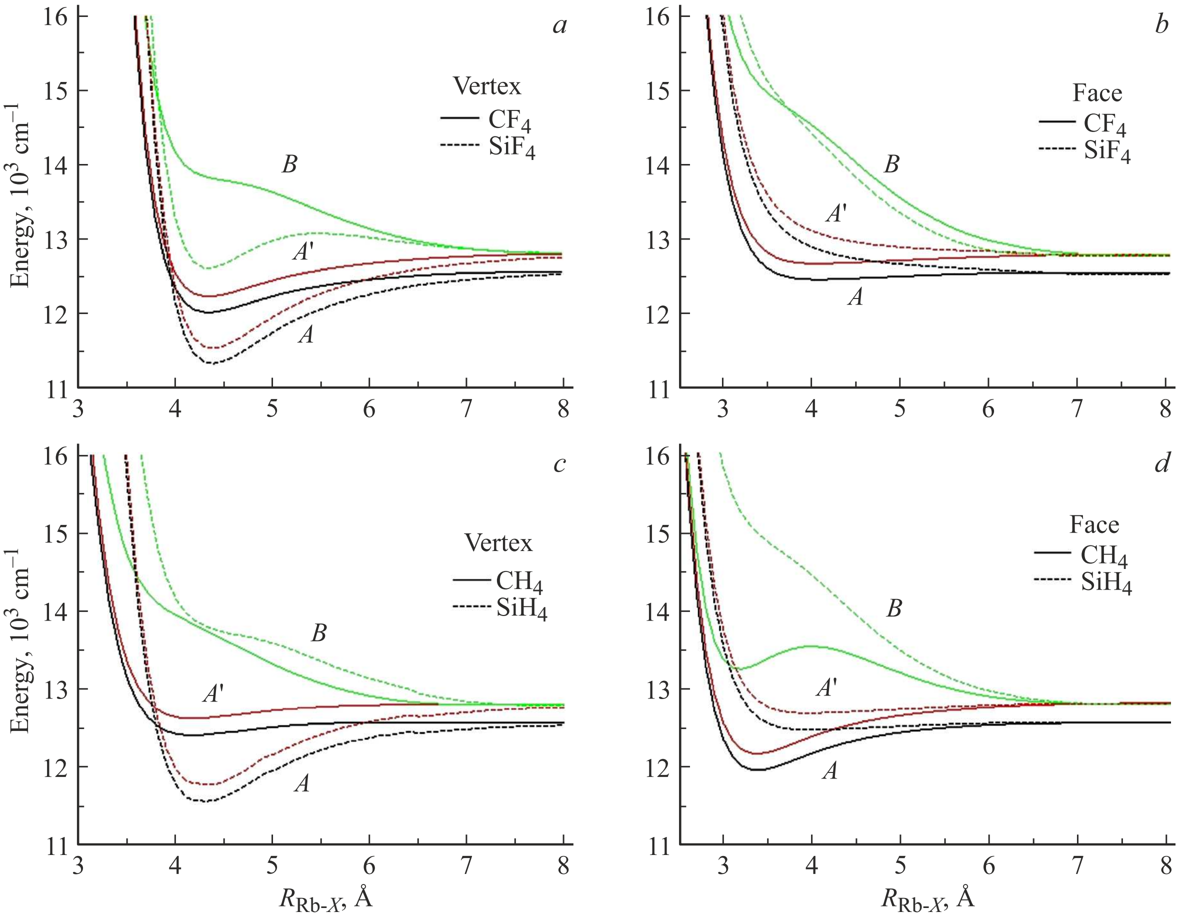

Figure 2. Potential curves of electronic states A, A' and B of $RbXY_4$ molecules calculated using the VQZP basis for the Rb atom and the VTZP basis for the C, Si, F and H atoms: (*a*) $RbCF_4$ (solid curves) and $RbSiF_4$ (dashed curves), geometry *Vertex* (Vertex), (*b*) same molecules, geometry *Base* (Face); (*c*) $RbCH_4$ (solid curves) and $RbSiH_4$ (dashed curves) geometry Vertex, (*d*) same molecules , geometry *Base*.

the XY_4 molecule. Since the C and Si atoms have a positive charge, the interaction will be repulsive and, other things being equal (the same distance to the Rb atom), stronger in the case of the Si atom, since its charge is greater.

In the case of $RbCH_4$ and $RbSiH_4$, the situation differs significantly from that considered in the previous paragraph — in these molecules, the central C and Si atoms have charges of different signs (see table), which is correspondingly true for hydrogen atoms in tetrahedron vertices. Note that this difference in the charge distributions in the SiH_4 and CH_4 molecules is known from the literature (see, for example, the results of ab initio calculations for these molecules in the database [15]).

The potentials of the $A^{(\prime)}$ and B states of the $RbSiH_4$ and $RbCH_4$ molecules are compared in Fig. 2, *c* and 2, *d*. As can be seen, the behavior of the $A^{(\prime)}$ state potentials of these molecules is very different — in the geometry *Vertex* (Fig. 2, *c*) the $A^{(\prime)}$ state of the $RbSiH_4$ molecule has a relatively deep minimum, while this state of the $RbCH_4$ molecule is repulsive. In its turn, in the geometry Base the opposite is true. These results convincingly confirm the conclusion about the decisive influence of the electrostatic interaction on the nature (attraction or repulsion) of the interaction potential.

The issue on the accuracy of the results obtained is of interest. Calculations of polyatomic $RbXY_4$ molecules are very time consuming, which makes it difficult to use bases with a large number of basis functions. To estimate the accuracy, we used an indirect method. For comparative analysis, calculations of the RbAr molecule were performed using different basis sets, including the same pair of basis sets (VQZP for Rb and VTZP for Ar) that was used for $RbXY_4$ molecules. Let us discuss these results (Fig. 1, *a* and Fig. 3, *a*) in more detail.

Figure 1, *a* shows the results of calculations of the potentials of the RbAr molecule with the basis sets with the least compression (LARGE). As can be seen from Fig. 1, *a*, the potential curves obtained with these bases are somewhat lower than the curves calculated with VQZP/VTZP.

It is interesting to compare the results with the LARGE basis with those available in the literature. For the state X the calculation with this basis gives

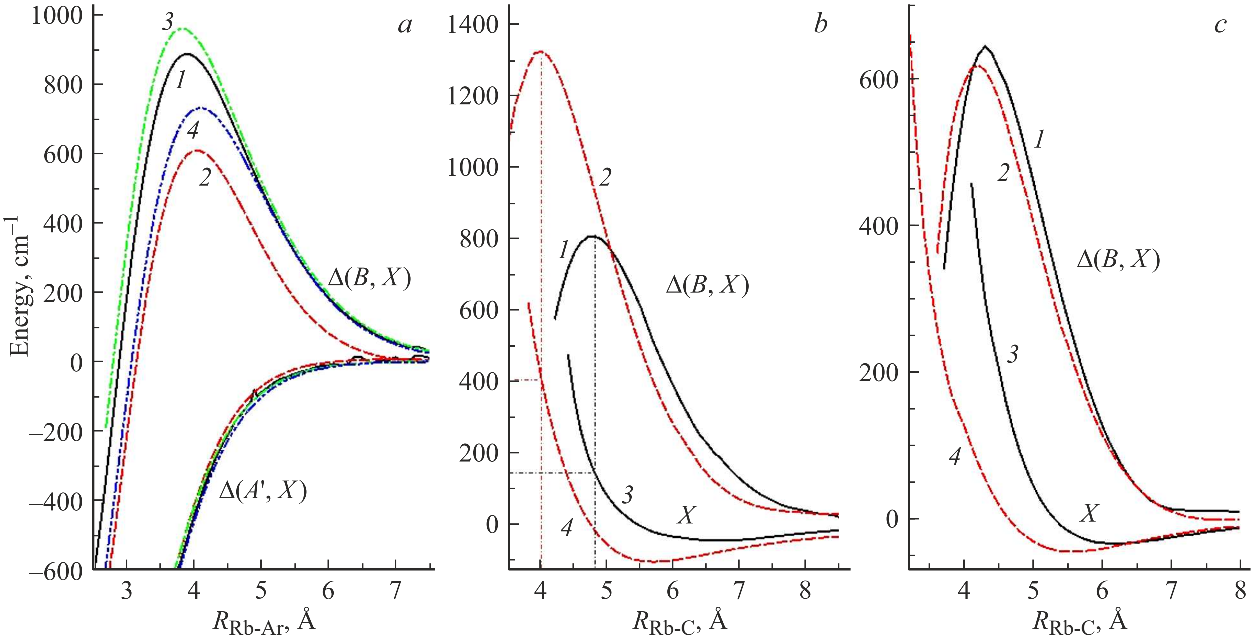

Figure 3. (*a*) Difference potentials $\Delta(B,X)$ and $\Delta(A',X)$ of the RbAr molecule calculated using the following bases: (*1*) VQZP for Rb and VTZP for Ar; (*2*) LARGE for Rb and Ar, (*3*) VTZP for Rb and Ar; (*4*) results from the work [6]; on the scale of the figure, the results of the calculation (*1*–*4*) for $\Delta(A',X)$ are almost indistinguishable. (*b*) (*1, 2*) Difference potential $\Delta(B,X)$ and (*3, 4*) potential of the ground state of the $RbCF_4$ molecule in the geometry (*1, 3*) *Vertex* and (*2, 4*) *Base*; (*c*) the same for the $RbCH_4$ molecule.

$R_e = 5.60$ Å and $D_e = 30\,\text{cm}^{-1}$, according to the literature $R_e = 5.82$ Å and $D_e = 49\,\text{cm}^{-1}$ [6]. We also present the results for the states A and A': $R_e(A, A') = 3.55$ Å, $D_e(A) = 310\,\text{cm}^{-1}$ and $D_e(A') = 350\,\text{cm}^{-1}$; according to the results [6] $R_e(A, A') = 3.81$ Å, $D_e(A) = 255.2$ and $D_e(A') = 315.7\,\text{cm}^{-1}$. Considering that the considered states are weakly coupled, the agreement can be characterized as satisfactory.

The shape of the molecular absorption band on the short-wavelength wing of the D_2 line is determined by the difference potentials $\Delta(B,X) = E(B){-}E(X)$; in its turn the long-wavelength wings of the D_2 and D_1 lines are determined by the difference potentials $\Delta(A',X) = E(A'){-}E(X)$ and $\Delta(A,X) = E(A){-}E(X)$ respectively. Note that the difference between $\Delta(A',X)$ and $\Delta(A,X)$ is very small.

The dependences of $\Delta(B,X)$ and $\Delta(A',X)$ on the internuclear distance are shown in Fig. 3, *a, b* (for convenience comparison, from the energies $\Delta(B,X)$ and $\Delta(A',X)$ the asymptotic energy of the states B and A' is subtracted, equal to the energy $\text{Rb}(5p\ ^2P_{3/2})$). As can be seen, in the region $R > 3$ Å the difference potential $\Delta(A',X)$ weakly depends on the chosen pair of bases. This is due to the random „compensation effect" — the closeness of the values of the change in the energy of the upper and lower states when the basis is changed.

Unlike $\Delta(A',X)$, the difference potential $\Delta(B,X)$ is more sensitive to the chosen basis. According to the results in Fig. 3, *a* the maximum values of the difference potential are $\Delta(B,X)_{\max} = 605$, 885 and $955\,\text{cm}^{-1}$ for LARGE/LARGE, VQZP/VTZP and VTZP/VTZP respectively. In this case, for bases with a smaller contraction the value of $\Delta(B,X)_{\max}$ is smaller than for the bases with a larger contraction. Note that the calculations of the RbHe molecule using basis sets of various sizes revealed similar tendencies [10].

The value $\Delta(B,X)_{\max}$ determines the position of the short-wavelength maximum of the absorption band of RbAr molecules on the blue wing of the D_2 line. In the spectrum, this feature is located at a wavelength of 755 nm, which corresponds to $\Delta(B,X)_{\max} \sim 425\,\text{cm}^{-1}$. Thus, the deviation of the above calculated value $\Delta(B,X)_{\max}^{\text{VQZP/VTZP}}$ from the experimental value is $885-425 = 460\,\text{cm}^{-1}$. This value can be used to estimate the accuracy of the difference potentials of the $RbCF_4$ molecule calculated using the same pair of bases VQZP/VTZP.

According to the calculation results, in the geometry *Vertex* the maximum of the difference potential $\Delta(B,X)$ of the $RbCF_4$ molecule is in the region $R_{\max} \sim 4.8$ Å and in the geometry *Base* — $R_{\max} \sim 4.0$ Å (Fig. 3, *b*). The energy of colliding particles, which is necessary to reach $R_{\max}$, corresponds to the energy at the point of intersection of the ground state potential with the vertical line passing through $R_{\max}$. As can be seen from Fig. 3, *b*, for two collision geometries, these energies differ by several fold: $\sim 140\,\text{cm}^{-1}$ (*Vertex*) and $\sim 400\,\text{cm}^{-1}$ (*Base*). For comparison, the average thermal energy of a particle at $T = 250°\text{C}$ (the temperature at which the absorption spectra of the Rb/CF_4 mixture were measured in [3]) is $360\,\text{cm}^{-1}$; the total kinetic energy of two particles in a collision is twice as high. Thus, to achieve $R_{\max}$ in the geometry *Vertex* it is enough to convert $\sim 20\%$ of the total kinetic energy into potential energy, while in the geometry *Base* — more than half. The latter is possible only for small values of the impact parameter, so such collisions are relatively unlikely.

It follows from the above that, in the first approximation, the absorption spectrum of $RbCF_4$ on the blue wing of the resonant doublet can be considered as a superposition of two bands, one of which has a short-wave boundary (geometry *Vertex*), and the other (*geometry it Base*) extends into the shorter wavelength region. At an experimental temperature of [3], the last component may not have a clear boundary, since the fraction of collisions corresponding to reaching the region $R \leq R_{\max}$ is relatively small (in other words, as one moves away from resonance line, the absorption intensity gradually decreases to zero). A more detailed discussion of this issue requires mathematical modeling of the spectra.

According to the results of calculations of the potentials of the $RbCF_4$ molecule using the VQZP/VTZP basis sets, the maximum value of the difference potential is $\Delta(B,X)_{\max} \sim 805$ and $1320\,\mathrm{cm}^{-1}$ in the geometry *Vertex* and *Base* respectively. As shown above, in the case of the RbAr molecule, the value of $\Delta(B,X)_{\max}$ calculated using the same pair of bases is overestimated by $460\,\mathrm{cm}^{-1}$. Taking into account this correction, $\Delta(B,X)_{\max} \sim 335$ and $860\,\mathrm{cm}^{-1}$ in the geometry *Vertex* and *Base*, respectively. Let us now turn to the experimental spectrum.

The maximum in the absorption spectrum of $RbCF_4$ molecules on the blue wing of the D_2 line is in the region of $500\,\mathrm{cm}^{-1}$, and, compared to the spectrum of RbAr, the maximum is less pronounced (in the sense of the ratio of the intensities of the maximum and of the „pedestal") and its half-width is much larger [3]. This is quite expected, since we consider only the two most distinct geometries, and the experimental spectrum contains contributions from various intermediate geometries. Note further that in the spectrum of RbAr there is practically no absorption in the energy region above the short-wavelength maximum, while in the spectrum of $RbCF_4$ absorption is observed up to the energies $\sim 1000\,\mathrm{cm}^{-1}$ from the resonance line D_2. In general, absorption in this region is expected and can be attributed to geometries close to the geometry *Base* (see above). We note that in this region it is difficult to unambiguously assign absorption due to the overlap with the band corresponding to the process of pair excitation [3]

$$\mathrm{Rb}(^2S_{1/2}) + \mathrm{CF}_4(v_3 = 0) + h\nu \rightarrow \mathrm{Rb}(^2P_{1/2}) + \mathrm{CF}_4(v_3 = 1),$$

the maximum of this band is located near $1050\,\mathrm{cm}^{-1}$.

For comparison with $RbCF_4$ (Fig. 3, *b*), Fig. 3, *c* shows the results of calculating $\Delta(B,X)$ and ground state potential $RbCH_4$. This molecule was studied earlier using the *ab initio* [2] methods. As can be seen from Fig. 3, *c*, in contrast to $RbCF_4$ (Fig. 3, *b*), the values of $\Delta(B,X)_{\max}$ in the geometries *Vertex* and *Base* are approximately the same. A similar result was obtained in [2]. We also give the absolute values of $\Delta(B,X)_{\max}$: $839\,\mathrm{cm}^{-1}$ [2], 640 and $615\,\mathrm{cm}^{-1}$ for geometries *Vertex* and *Base* respectively (present study) and $388\,\mathrm{cm}^{-1}$ (experiment [17]). To achieve better agreement with the experiment, calculations are required using an extended basis for the Rb atom, which includes states lying above $\mathrm{Rb}(5p\ ^2P_{1/2,3/2})$. In this connection, we note the following.

As can be seen from Figs 1 and 2, the B state potential has a singularity in the form of an inflection or even a local minimum located approximately in the same region of the internuclear distance where the maximum of the difference potential $\Delta(B,X)$ is located. This feature has been discussed many times before [6–10]. The deviation from a smooth increase in the repulsion energy with decreasing internuclear distance is based on the configurational interaction of the B state with higher-lying states of the same symmetry ($^2\Sigma^+$ in the case of a diatomic RbAr molecule). In particular, one of the states correlating with $\mathrm{Rb}(4d\ ^2D_{3/2,5/2})$ and the state correlating with $\mathrm{Rb}(6s\ ,\ ^2S_{1/2})$. The energy gap between $\mathrm{Rb}(5p\ ^2P_{3/2})$ and these states is 6540 and $7318\,\mathrm{cm}^{-1}$, respectively. To consider the configurational interaction, the basis for the Rb atom should include these states and correctly describe their energies. However, this is partially satisfied only for the LARGE basis: when using this basis, the position of $\mathrm{Rb}(6s\ ^2S_{1/2})$ with respect to $\mathrm{Rb}(5p\ ^2P_{3/2})$ is reproduced with an error of $\sim 40\,\mathrm{cm}^{-1}$, while with the VQZP and VTZP bases the calculated values exceed the experimental values by 4470 and $7980\,\mathrm{cm}^{-1}$ respectively. In fact, the observed dependence of $\Delta(B,X)$ on the basis (Fig. 3, *a*) is largely a consequence of the difference in the value of the energy gap between the interacting states.

Conclusion

In this study we present the results of calculations of the interaction potentials of XY_4 molecules (CF_4, CH_4, SiF_4, and SiH_4) with a Rb atom in the ground and electronically excited states. The calculations were carried out for two geometries of approach of an atom and a molecule — *Base* and *Vertex*. It is established that the $B(^2\Sigma^+_{1/2})$ state correlating with $\mathrm{Rb}\,(5p\ ^2P_{3/2})$ is repulsive for any geometry of atom and a molecule approach. In its turn the states $A(^2\Pi_{1/2})$ and $A'(^2\Pi_{3/2})$, which correlate respectively with the lower and upper states of the doublet $\mathrm{Rb}\,(\ 5p\ ^2P_{1/2,3/2})$, can be both related and repulsive. For the CF_4, SiF_4, and SiH_4 molecules the potential curves have a minimum in the geometry *Vertex*, while in the case of CH_4 the geometry *Base* corresponds to the bound state. This difference is explained by the difference in the charge distribution: in the CF_4, SiF_4, and SiH_4 molecules the central atom has a positive charge, while the atoms at the vertices of the pyramid have an excess negative charge; for CH_4 the opposite is true — the excess negative charge is concentrated on the central atom.

In order to assess the accuracy of calculations of $RbXY_4$ molecules, in this study we calculated the potentials of the electronic states of the diatomic RbAr molecule using various basis functions. It was found that the size of the basis has little effect on the difference potential $\Delta(A^{(\prime)}, X) = E(A^{(\prime)}) - E(X)$, which is determined by the shape of the red wing of the $D_{1(2)}$ line, while the difference potential $\Delta(B, X) = E(B) - E(X)$, on which the spectrum on the blue wing of the line D_2 depends, on the contrary, is very sensitive to the basis. An analysis of the results showed that this is due to the configurational interaction of the B state with the molecular states of the same symmetry, which correlate with the overlying states of Rb and, above all, Rb $(6s\ {}^2S_{1/2})$ and Rb $(4d\ {}^2D_{3/2,5/2})$, which are the closest in energy.

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Conflict of interest

The author declares that he has no conflict of interest.

References

[1] G.A. Pitz, M.D. Anderson. Appl. Phys. Rev., **4** (4), 041101 (2017). DOI: 10.1063/1.5006913

[2] M.C. Heaven. Proc. SPIE, **8238**, 823808 (2012). DOI: 10.1117/12.912930

[3] V.A. Alekseev, A.A. Pastor, A.S. Pazgalev, P.A. Petrov, P.Yu. Serdobintsev, T.A. Vartanyan. JQSRT, **258**, 107339 (2021). DOI: 10.1016/j.jqsrt.2020.107339

[4] V.A. Alekseev, A.A. Pastor, P.Yu. Serdobintsev, T.A. Vartanyan. JETP Lett., **114** (2), 65 (2021). DOI: 10.1134/S0021364021140034.

[5] M.D. Rotondaro, G.P. Perram. Phys. Rev., A **57** (4), 4045(1998). DOI: 10.1103/PhysRevA.57.4045

[6] L. Blank, D.E. Weeks, G.S. Kedziora. J. Chem. Phys., **136** (12), 124315 (2012). DOI: 10.1063/1.3696377

[7] J. Dhiflaoui, H. Berriche, M.C. Heaven. J. Phys. B: At. Mol. Opt. Phys., **49** (20), (2016) 205101. DOI: 10.1088/0953-4075/49/20/205101

[8] J. Dhiflaoui, M. Bejaoui, H. Berriche. Eur. Phys. J. D, **71**, 331 (2017). DOI: 10.1140/epjd/e2017-70576-1

[9] A.R. Sharma, D.E. Weeks. Phys. Chem. Chem. Phys., **20** (46), 29274 (2018). DOI: 10.1039/C8CP05550E

[10] L.A. Blank, A.R. Sharma, D.E. Weeks. Phys. Rev. A, **97** (3), 032705 (2018). DOI: 10.1103/PhysRevA.97.032705

[11] I.F. Galván *et al.* J. Chem. Theory Comput., **15** (11), 5925 (2019). DOI: 10.1021/acs.jctc.9b00532

[12] J. Finley, P.-A. Malmqvist, B.O. Roos, L. Serrano-Andres. Chem. Phys. Lett., **288** (2–4), 299306 (1998). DOI: 10.1016/S0009-2614(98)00252-8

[13] P.-Å. Malmqvist, B.O. Roos, B. Schimmelpfennig. Chem. Phys. Lett., **357** (3–4), 230 (2002). DOI: 10.1016/S0009-2614(02)00498-0

[14] B.O. Roos, R. Lindh, P.-A.Malmqvist, V. Veryazov, P.-O. Widmark. J. Phys. Chem. A, **108** (15), 2851(2004). DOI: 10.1021/jp031064

[15] *NIST Computational Chemistry Comparison and Benchmark Database,* [Electronic source]. URL: http://cccbdb.nist.gov/

[16] L. Gagliardi, R. Lindh, G. Karlström. J. Chem. Phys., **121** (10), 4494 (2004). DOI: 10.1063/1.1778131

[17] S.-Y. Ch'en, J. Jefimenko. J. Chem. Phys., **26** (2), 256 (1957). DOI: 10.1063/1.1743281