ARTICLE IN PRESS

Journal of Quantitative Spectroscopy & Radiative Transfer ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt


Journal of
Quantitative
Spectroscopy &
Radiative
Transfer

# *Ab initio* and long-range studies of the electronic transition dipole moments among the low-lying states of $Rb_2$ and $Cs_2$ molecules[☆]

Elena A. Pazyuk, Elena I. Revina, Andrey V. Stolyarov[*]

*Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Leninskie gory 1/3, Russia*

ARTICLE INFO

*Article history:*
Received 24 November 2015
Received in revised form
30 December 2015
Accepted 1 January 2016

*Keywords:*
Electronic transition dipole moments
*Ab initio* calculations
Long-range perturbation theory
Alkali metal dimers

ABSTRACT

The spin allowed electronic transition dipole moments (ETDM) of rubidium and cesium dimers are calculated among the states converging to the lowest three dissociation limits. The ETDM functions are evaluated for a wide range of internuclear distances $R$ in the basis of the spin-averaged wavefunctions corresponding to pure Hund's coupling case (a) by using small (including the 8 subvalence $+1$ valence electrons) effective core pseudopotentials (ECP). The dynamic correlation is accounted for in a large scale multi-reference configuration interaction (MR-CI) method applied to only two valence electrons. The core-polarization potentials (CPP) are implemented to implicitly take the residual core–valence effect into account. The reliability of the present EDTM functions is discussed through comparison with preceding *ab initio* calculations and their long range perturbation theory counterparts. The achieved accuracy allowed us to quantitatively support the asymptotic behavior of the ETDM functions predicted in Marinescu and Dalgarno (1995 [4]). The long $R$-range transition moments could be useful to optimize stimulated Raman processes employed in ultracold molecule production.

## 1. Introduction

Comprehensive knowledge of the transition probabilities between the ground and excited diatomic states is important in studying the cold collision processes as well as laser cooling, assembling and trapping of atoms [1]. In particular, the radiative lifetimes, branching ratios, absorption and emission Einstein coefficients play a decisive role in optimization and control of laser synthesis of ultracold molecular ensembles [2]. Reliable electronic transition dipole moments (ETDM) possessing the correct long range behavior and the relevant accompanying potential energy curves (PECs) are certainly needed to design the photoassociation (PA) and stimulated Raman adiabatic passage (STIRAP) processes exploited in ultracold molecule production [3].

Considerable attention has been given to establishing the adiabatic PECs and ETDM functions of alkali metal dimers in a wide range of internuclear distances $R$. However, in contrast with PECs [4,5] the long range behavior of relevant $d_{ij}(R)$ functions is little known so far [6,7]. The most *ab initio* electronic structure calculations have been carried out for rubidium and cesium dimers within the framework of both (a) and (c) Hund's coupling cases using alternative effective core potential (ECP) methods. Indeed, both alkali metal dimers were considered in Refs. [8–10] as the two electron system in which the interaction between the valence electrons and each atomic ion is modeled by means of a non-empirical relativistic one electron ECP. The residual core–valence correlation effects were taken into

---

[☆] Electronic Supplementary Information (ESI) available: the resulting *ab initio* pointwise electronic transition dipole moments and potential energy curves are given for $Rb_2$ and $Cs_2$.

[*] Corresponding author. Tel.: +7 495 939 28 25; fax: +7 495 939 02 83.
*E-mail address:* avstol@phys.chem.msu.ru (A.V. Stolyarov).

http://dx.doi.org/10.1016/j.jqsrt.2016.01.004

Please cite this article as: Pazyuk EA, et al. *Ab initio* and long-range studies of the electronic transition dipole moments among the low-lying states of $Rb_2$ and $Cs_2$ molecules. J Quant Spectrosc Radiat Transfer (2016), http://dx.doi.org/10.1016/j.jqsrt.2016.01.004

account by the *l*-depended core polarization potential (CPP). Recently, the $Rb_2$ molecule was treated as a system of effectively 18 electrons [11,12]. Scalar relativistic effects were included by the small-core fully relativistic energy-consistent ECP from Ref. [13] while the electronic wavefunctions were obtained using the multi-reference configuration interaction (MRCI) method restricted to single and double excitations with a large active space.

In the present work we have performed independent *ab initio* calculations of the ETDM functions of $Rb_2$ and $Cs_2$ molecules in a wide range internuclear distances $R$ focusing on the asymptotic behavior of $d_{ij}(R)$ functions at $R\to\infty$. We have also assessed the accuracy of the present calculations by comparing them with preceding *ab initio* ETDM functions and their long-range perturbation theory (LRPT) analytical counterparts [4,14]. The LRPT functions deviate from the limiting atom value as $\beta_n/R^n$ with the degree $n=3,4$, where the coefficients $\beta_n$ may be calculated using the atomic wavefunctions and energies. The result could be applied for the correct long-range extrapolation of the point-wise *ab initio* functions and for probing their quality.

## 2. Computational *ab initio* approach

The singlet–singlet and triplet–triplet electronic transition dipole moment functions $d_{ij}(R)=\langle\Psi_i^{el}|\mathbf{d}|\Psi_j^{el}\rangle|_{\mathbf{r}}$ (where $\mathbf{d}=\sum_i e_i\mathbf{r}_i$ is the dipole momentum operator) of both rubidium and cesium dimers were evaluated on the basis of the zeroth-order (spin-averaged) MRCI wavefunctions $\Psi^{el}(\mathbf{r};R)$ corresponding to the pure Hund's coupling case (a). All electronic structure calculations were performed by means of the MOLPRO v.2010.1 program package [15]. The computational details can be found elsewhere [16,17].

Briefly, the inner core shell of the rubidium and cesium atoms was replaced by spin-orbit averaged non-empirical effective core potentials (ECPs), leaving 8 subvalence and 1 valence electrons for explicit treatment. Both shape [18,19] and energy [13] consistent ECP basis sets were used in the present quasi-relativistic calculations to monitor the sensitivity of the resulting matrix elements to the particular basis set. The relevant spin-averaged Gaussian basis sets used for each atom were borrowed from the above references. Shape-consistent ECPs were augmented by the diffuse part of the all-electron basis for electric property calculation [20] and were extended by additional diffuse and polarization functions [21]. The relativistic energy consistent basis sets (ECP28MDF and ECP46MDF for the Rb and Cs atoms, respectively) borrowed from MOLPRO basis library [15] and Ref. [13] were fully decontracted and augmented by the comprehensive set ($6s6p6d3f1g$) of bound functions [22] centered in the middle of internuclear separation.

The optimized molecular orbitals (MOs) were obtained from the solutions of the state-averaged complete active space self-consistent field (SA-CASSCF) problem for all 18 electrons and the lowest $(1-5)^{1,3}\Sigma^+_{u/g}, (1-3)^{1,3}\Pi_{u/g}$ and $(1)^{1,3}\Delta_{u/g}$ electronic states taken with equal weights [23]. The dynamical correlation effects were introduced through the internally contracted MRCI method [24] which was applied only for two valence electrons keeping the rest frozen.

**Table 1**
The dipole static polarizability of the cation ($\alpha_c$) and the cut-off radius ($r_c$) used to build the core-polarization potentials (CPPs) of the Rb and Cs atoms. All parameters in *a.u.*

| Atom | $\alpha_c$ [27] | $r_c$ [PW] |
|---|---|---|
| Rb | 9.096 | 0.39 |
| Cs | 15.687 | 0.275 |

**Table 2**
The transition dipole moments $d_{S-P}$ and energies $E_{S-P}$ between the ground and first excited states of Rb and Cs atoms as well as the relevant ionization potentials *IP* and the dipole static polarizabilities $\alpha_S$ of the ground state.

| Method | $d_{S-P}$ *a.u.* | $E_{S-P}$ $cm^{-1}$ | *IP* $cm^{-1}$ | $\alpha_S$ *a.u.* |
|---|---|---|---|---|
| | | Rb | | |
| ECP | 3.408 | 10,759 | 33,437 | 319 |
| ECP+CPP | 3.160 | 12,702 | 35,041 | 271 |
| Expt. | 2.992[a] | 12,737.36[a] | 33,690.80[a] | 319[b] |
| | | Cs | | |
| ECP | 3.694 | 9596 | 31,296 | 405 |
| ECP+CPP | 3.413 | 11,509 | 32,821 | 333 |
| Expt. | 3.182[a] | 11,547.65[a] | 31,406.47[a] | 401[b] |

[a] Refs. [25,26].
[b] Ref. [27].

The *l*-independent CPPs of both atoms were introduced to implicitly take the residual core-polarization effects into account. The corresponding CPP cut-off radius (see Table 1) were adjusted to reproduce experimental energies of the lowest $^2$P atomic states [25,26]. The transition dipole moments, lowest energies, ionization potentials and the dipole static polarizabilities obtained within the framework of "test" atomic calculations are presented in Table 2.

The present ETDM calculations were complimented with the relevant potential energy curves (PECs). The original electronic energies are suffered by the pronounced *R*-dependent systematic error. First of all these are basis set superposition error as well as dispersion and repulsive correction to large core potential estimates. Since the systematic error of the electronic energies weakly depends on the vertical energy excitation the main part of the error could be compensated for the excited states through the semi-empirical relation [28]:

$$U_i^*(R)=[U_i^{ab}(R)-U_X^{ab}(R)]+U_X^{emp}(R) \quad (1)$$

where $U_X^{emp}(R)$ is the highly accurate empirical PECs available for the ground $X^1\Sigma_g^+$ state of the $Rb_2$ [29] and $Cs_2$ [30] in a wide *R*-range.

## 3. Asymptotic long-range behavior

The spin-allowed molecular $\Lambda''-\Lambda'=0;\pm1$ transition moments $d_{ij}(R)$ are known [6,7] to converge at large

Please cite this article as: Pazyuk EA, et al. *Ab initio* and long-range studies of the electronic transition dipole moments among the low-lying states of $Rb_2$ and $Cs_2$ molecules. J Quant Spectrosc Radiat Transfer (2016), http://dx.doi.org/10.1016/j.jqsrt.2016.01.004

internuclear distances to the asymptotic form [4,14]:

$$d_{ij}(R \to \infty) = d^{at}_{\Lambda'\Lambda''} + \frac{\beta_{\Lambda'\Lambda''}}{R^n} \tag{2}$$

where $n \geq 3$ is an integer while $d^{at}$ and $\beta$ are the $R$-independent coefficients being functions of atomic energies and wavefunctions [4,14]. The degree $n = 3, 4$ and the ratio $\beta_{\Sigma\Sigma}/\beta_{\Sigma\Pi} = -2, -\sqrt{3}$ were predicted in Ref. [4] for the $S-P$ and $S-D$ transitions, respectively. In a case of the dipole allowed $l'' - l' = 0; \pm 1$ atomic transitions the corresponding non-zero $d^{at}_{\Lambda'\Lambda''}$ values can be estimated as [31]:

$$d^{at}_{\Lambda'\Lambda''} = S^{l'l''}_{\Lambda'\Lambda''} \times \langle \nu' l' | r | \nu'' l'' \rangle \tag{3}$$

where

$$S^{l'l''}_{\Lambda'\Lambda''} = (-1)^{\Lambda'} \sqrt{(2l'+1)(2l''+1)} \times \begin{pmatrix} l' & 1 & l'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & 1 & l'' \\ \Lambda' & q & \Lambda'' \end{pmatrix} \tag{4}$$

is the angular matrix element with the $q = \Lambda'' - \Lambda'$ while $\langle \nu' l' | r | \nu'' l'' \rangle$ is the appropriate atomic dipole matrix element [32].

The long range perturbation theory (LRPT) representation (2) is valid only for $R \geq R_{LR-m}$, where $R_{LR-m}$ is the modified Le Roy radius [33]:

$$R_{LR-m} = 2\sqrt{3}\left[\sqrt{\rho^{l'}_{\Lambda'}} + \sqrt{\rho^{l''}_{\Lambda''}}\right] \tag{5}$$

with

$$\rho^{l}_{\Lambda} = \left[\frac{1}{3} - \frac{2}{3}\frac{3\Lambda^2 - l(l+1)}{(2l+3)(2l-1)}\right] \times \langle \nu l | r^2 | \nu l \rangle \tag{6}$$

In the framework of the simplest single-channel quantum-defect theory (QDT) approximation [34], the radial matrix elements involved in Eqs. (3) and (6) are defined as

$$\langle \nu' l' | r^k | \nu'' l'' \rangle = \int_{r_c}^{\infty} P^{l'}_{\nu'}(r) P^{l''}_{\nu''}(r) [r(1-\kappa(r))]^k \, dr \tag{7}$$

where $k = 1, 2$ and $P^{l}_{\nu}(r)$ are the radial wavefunctions of the Rydberg electron available in the analytical form [34]. Aside from the numerical integration of Eq. (7) the quadruple $\langle \nu l | r^2 | \nu l \rangle$ matrix elements involved in Eq. (5) may be estimated analytically [33]:

$$\langle \nu l | r^2 | \nu l \rangle = \nu^4 \times \left[1 + \frac{3}{2}\left(1 - \frac{l(l+1) - 1/3}{\nu^2}\right)\right] \tag{8}$$

where the required effective quantum numbers $\nu$ of the states studied are readily calculated using the Rydberg formula

$$\nu = \frac{1}{\sqrt{2(IP - E^l_{\nu})}} \tag{9}$$

with the experimental atomic energies $E^l_{\nu}$ and relevant ionization potential $IP$.

The correction term $\kappa(r)$ and the mean radius of the core $r_c$ in the integral (7) can be taken in the modified form [35]

$$\kappa(r) = \frac{\alpha_c}{r^3}(1 - \exp[-(r/r_c)]^3); \quad r_c = \alpha_c^{1/3} \tag{10}$$

where $\alpha_c$ is the static dipole polarizability of the core (cation) [27]. The dipole operator defined by Eq. (10) accounts for the core-polarization effect [36] leading to systematic diminishing of the $d^{at}_{\Lambda'\Lambda''}$ estimates (3) by about a few percents compared with the standard dipole operator with $\kappa(r) \equiv 0$.

**Table 3**
The angular factor $S^{l'l''}_{\Lambda'\Lambda''}$ of the homonuclear transition moments calculated by Eq. (4) for the dipole allowed S–P and P–D atomic transitions.

| Transition | $\Sigma-\Sigma$ | $\Sigma-\Pi$ | $\Pi-\Pi$ | $\Pi-\Sigma$ | $\Pi-\Delta$ |
|---|---|---|---|---|---|
| S-P[a] | $\sqrt{\frac{2}{3}}$ | $-\sqrt{\frac{2}{3}}$ | | | |
| P-D | $\frac{2}{\sqrt{15}}$ | $-\frac{1}{\sqrt{5}}$ | $\frac{1}{\sqrt{5}}$ | $-\frac{1}{\sqrt{15}}$ | $-\sqrt{\frac{2}{5}}$ |

[a] For heteronuclear molecules the data should be divided by $\sqrt{2}$.

**Table 4**
The limiting atom values of molecular dipole moment $d^{at}_{\Lambda'\Lambda''}$ (in *a.u.*) obtained by Eqs. (3), (4) and (7) within the framework of the quantum-defect theory approximation.

| Transition | $\Sigma-\Sigma$ | $\Sigma-\Pi$ | $\Pi-\Pi$ | $\Pi-\Sigma$ | $\Pi-\Delta$ |
|---|---|---|---|---|---|
| | | Rb–Rb | | | |
| S–P | 4.23 | −4.23 | | | |
| P–D | 3.76 | −3.26 | 3.26 | −1.88 | −4.61 |
| | | Cs–Cs | | | |
| S–P | 4.51 | −4.51 | | | |
| P–D | 3.19 | −2.76 | 2.76 | −1.59 | −3.90 |

**Table 5**
The modified Le Roy radius $R_{LR-m}$ (in Å) obtained by Eqs. (5), (6) and (8).

| Transition | $\Sigma-\Sigma$ | $\Sigma-\Pi$ | $\Pi-\Sigma$ | $\Pi-\Pi$ | $\Pi-\Delta$ |
|---|---|---|---|---|---|
| | | Rb–Rb | | | |
| S–P | 16.2(2) | 11.7(2) | | | |
| S–D | 17.0(6) | 12.0(2) | | | |
| P–D | 22.1(3) | 21.2(4) | 17.8(4) | 16.7(4) | 12.2(2) |
| | | Cs–Cs | | | |
| S–P | 17.2(3) | 12.4(3) | | | |
| S–D | 15.0(6) | 12.7(3) | | | |
| P–D | 20.2(5) | 19.4(4) | 15.5(4) | 14.7(3) | 11.2(2) |

## 4. Results and discussion

The angular factors $S^{l'l''}_{\Lambda'\Lambda''}$, limiting atom values $d^{at}_{\Lambda'\Lambda''}$ and modified Le Roy radius $R_{LR-m}$ evaluated for the molecular transitions under consideration are presented on Tables 3, 4 and 5, respectively. The alternative ETDM functions calculated using the shape-consistent and energy-consistent pseudopotentials coincided within a margin of error of 1–2%. To elucidate the core-polarization effect the atomic and molecular ETDM functions were calculated with and without CPP but with the same shape-consistent ECP basis set. The machine-readable tables of the resulting pointwise ETDM and PEC functions corresponding to the ECP+CPP calculations are given in the Supplementary

Please cite this article as: Pazyuk EA, et al. *Ab initio* and long-range studies of the electronic transition dipole moments among the low-lying states of Rb$_2$ and Cs$_2$ molecules. J Quant Spectrosc Radiat Transfer (2016), http://dx.doi.org/10.1016/j.jqsrt.2016.01.004

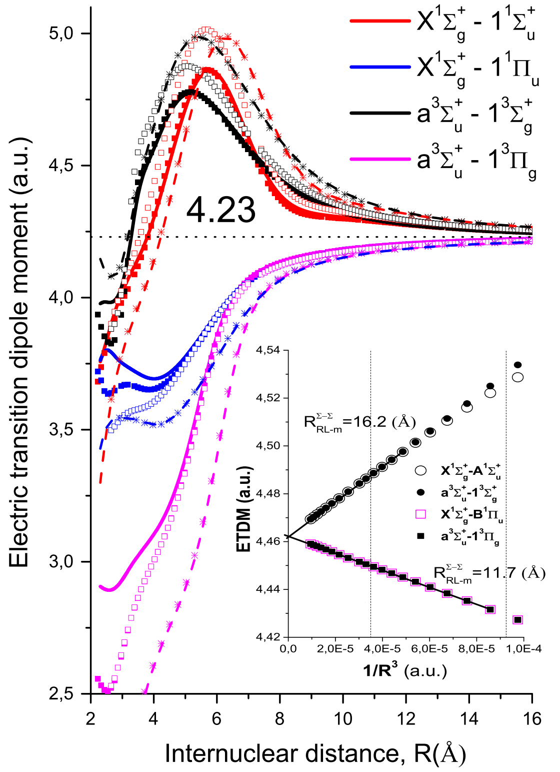

**Fig. 1.** Comparison of the dipole allowed ETDM functions of $Rb_2$ calculated between the ground $X^1\Sigma_g^+$, $a^3\Sigma_u^+$ and excited $1^1\Sigma_u^+$, $1^1\Pi_u$, $1^3\Sigma_g^+$, $1^3\Pi_g$ states converging to the second ($5^2S-5^2P$) dissociation threshold. The dash and solid lines denote the present ECP and ECP+CPP results, respectively. The solid, open and star symbols correspond to the *ab initio* data borrowed from Refs. [8,10–12]. The original *ab initio* functions were uniformly scaled to match at $R\to\infty$ the relevant "atomic" moment. The inset displays the long-range fragment of the present $d_{ij}(R)$ functions with respect to the $1/R^3$ coordinate.

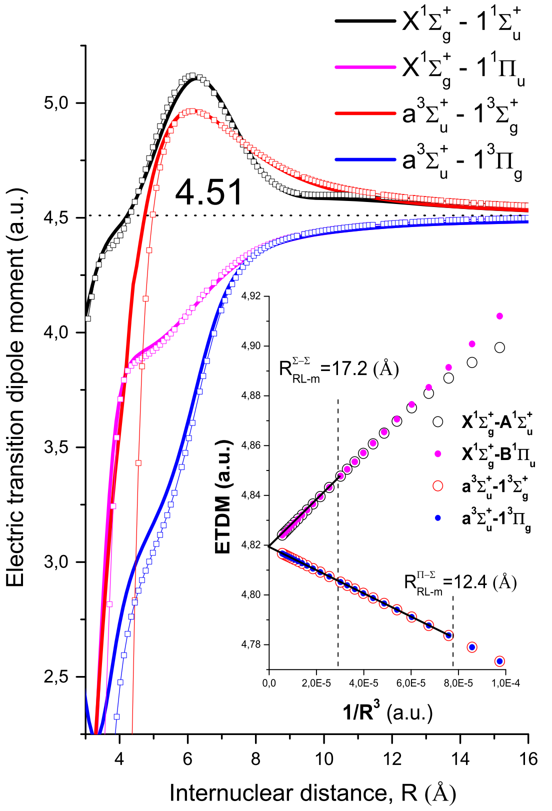

**Fig. 2.** The present (solid lines) and preceding (open symbols [10]) ETDM functions calculated between the ground $X^1\Sigma_g^+$, $a^3\Sigma_u^+$ and excited $1^1\Sigma_u^+$, $1^1\Pi_u$, $1^3\Sigma_g^+$, $1^3\Pi_g$ states of $Cs_2$ converging to the second ($6^2S-6^2P$) dissociation threshold. The original *ab initio* functions were uniformly scaled to match at $R\to\infty$ the relevant "atomic" moment. The inset displays the long-range fragment of the present $d_{ij}(R)$ functions with respect to the $1/R^3$ coordinate.

material for future modeling of the radiative properties of $Rb_2$ and $Cs_2$.

The ETDM functions corresponding to parallel $\Delta\Lambda=0$ and perpendicular $\Delta\Lambda=\pm1$ transitions of both dimers are presented in Figs. 1–8, where they are compared with their preceding *ab initio* counterparts [8–12]. It should be noted that, in contrast to the $Rb_2$, extensive ETDM data are available for $Cs_2$ only in Ref. [10] except for the $d_{AX}(R)$ function depicted for the $A^1\Sigma_u^+-X^1\Sigma_g^+$ transition in Fig. 1 of Ref. [9].

It is clearly seen that at intermediate and large internuclear distances the present ECP+CPP functions are in a good agreement to their *ab initio* counterparts calculated using the 1-electron *l*-depended ECPs [8–10]. The most pronounced deviations take place for triplet–triplet transitions at short internuclear distances. The largest systematic deviations reaching 15–20% are observed with the recent MRCI results on $Rb_2$ [11,12] based on 9-electron energy consistent ECPs [13]. It could be attributed to residual core-polarization effects which have been apparently accounted for large (1-electron) and small (9-electron) ECP basis sets though significance different ways. Indeed, the present ETDM functions calculated for $Rb_2$ without CPP contribution are found to be remarkably close to their MRCI counterparts [11,12] (see dash lines on Figs. 1, 3, 5, 7, and 8).

The resulting ETDM functions behave correctly at large *R*. All present figures and Table 6 demonstrate that at $R\to\infty$ the *ab initio* functions vanish or converge to the relevant limiting atom values $d^{at}_{\Lambda'\Lambda''}$ given in Table 4. The coincidence is slightly better for $Rb_2$ than $Cs_2$ as well as for the $P-D$ transitions than for the $S-P$ and $S-D$. According to correlation principle, the most pronounced molecular moments should correspond to the dipole allowed $S-P$ and $P-D$ atomic transitions. Indeed, for both dimers we observe strong (reaching 5 *a.u.*) parallel $A^1\Sigma_u^+-X^1\Sigma_g^+$ and $1^3\Sigma_g^+-a^3\Sigma_u^+$ transitions (see Fig. 1 for $Rb_2$ and Fig. 2 for $Cs_2$) from the ground to the excited states converging to the second dissociation limit. A similar situation takes place for the ETDM functions between the excited states converging to the second and third dissociation limits (see Figs. 3–7). There are also several spectroscopically important dipole forbidden transitions between the ground and excited states converging to the third dissociation limit which have rather strong moments in the intermediate *R*-region while vanishing at $R\to\infty$ (see, for example, Fig. 8).

The long-range behavior of the present *ab initio* $d_{ij}(R)$ functions corresponding to the $S-P$, $P-D$ and $S-D$ atomic

Please cite this article as: Pazyuk EA, et al. *Ab initio* and long-range studies of the electronic transition dipole moments among the low-lying states of $Rb_2$ and $Cs_2$ molecules. J Quant Spectrosc Radiat Transfer (2016), http://dx.doi.org/10.1016/j.jqsrt.2016.01.004

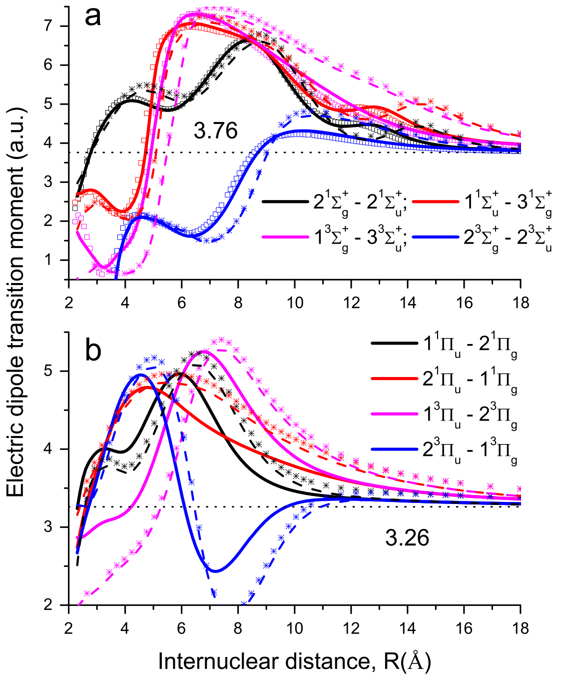

**Fig. 3.** The dipole allowed $^{1,3}\Sigma^+_{u,g}-{}^{1,3}\Sigma^+_{g,u}$ (a) and $^{1,3}\Pi_{u,g}-{}^{1,3}\Pi_{g,u}$ (b) transition dipole moments of $Rb_2$ between the states converging to the second and third ($5^2P-4^2D$) dissociation thresholds. The solid and dash lines correspond to the present work, open symbols to [10] and stars to [11,12].

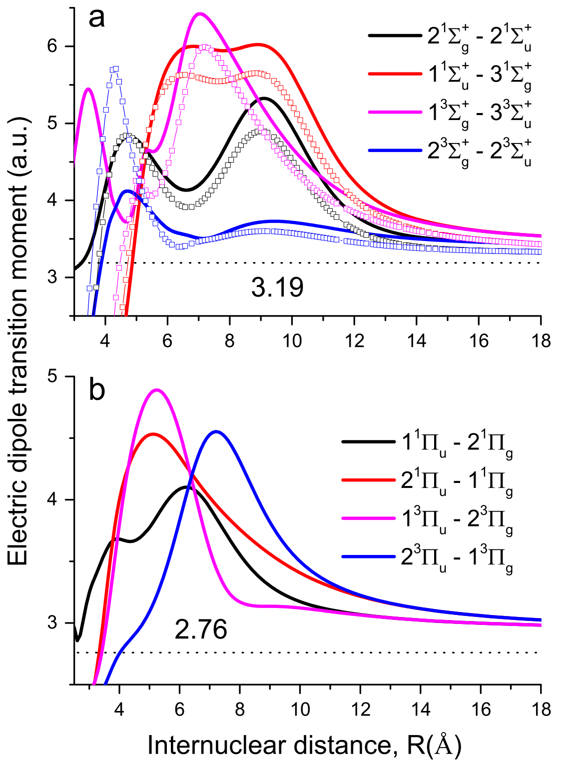

**Fig. 4.** The dipole allowed $^{1,3}\Sigma^+_{u,g}-{}^{1,3}\Sigma^+_{g,u}$ (a) and $^{1,3}\Pi_{u,g}-{}^{1,3}\Pi_{g,u}$ (b) transition dipole moments of $Cs_2$ between the states converging to the second and third ($6^2P-5^2D$) dissociation thresholds. The solid lines correspond to the present work while open symbols to [10].

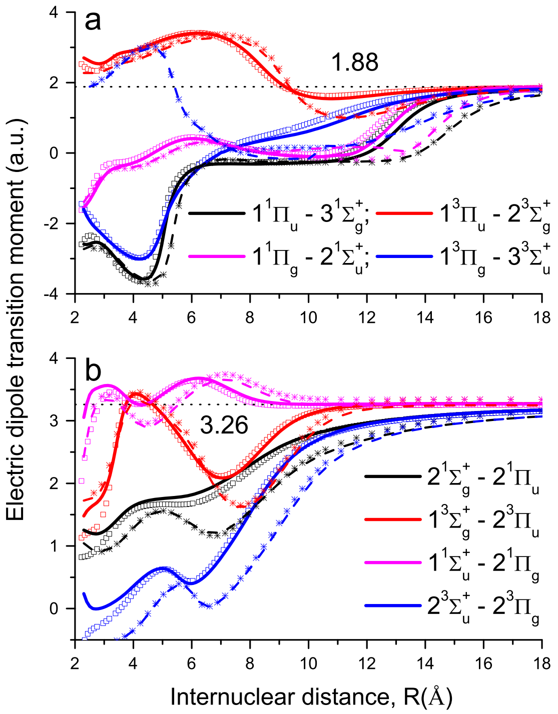

**Fig. 5.** The dipole allowed $^{1,3}\Pi_{g,u}-{}^{1,3}\Sigma^+_{u,g}$ (a) and $^{1,3}\Sigma^+_{u,g}-{}^{1,3}\Pi_{g,u}$ (b) transition dipole moments of $Rb_2$ between the states converging to the second and third dissociation thresholds. The solid and dash lines correspond to the present work while open symbols to [10] and stars to [11,12].

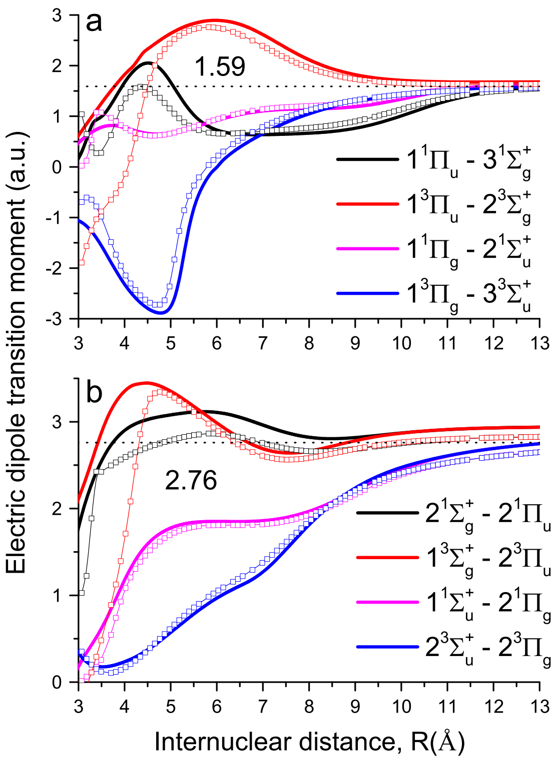

**Fig. 6.** The dipole allowed $^{1,3}\Pi_{g,u}-{}^{1,3}\Sigma^+_{u,g}$ (a) and $^{1,3}\Sigma^+_{u,g}-{}^{1,3}\Pi_{g,u}$(b) transition dipole moments of $Cs_2$ between the states converging to the second and third dissociation thresholds. The solid lines correspond to the present work while open symbols to Ref. [10].

Please cite this article as: Pazyuk EA, et al. *Ab initio* and long-range studies of the electronic transition dipole moments among the low-lying states of $Rb_2$ and $Cs_2$ molecules. J Quant Spectrosc Radiat Transfer (2016), http://dx.doi.org/10.1016/j.jqsrt.2016.01.004

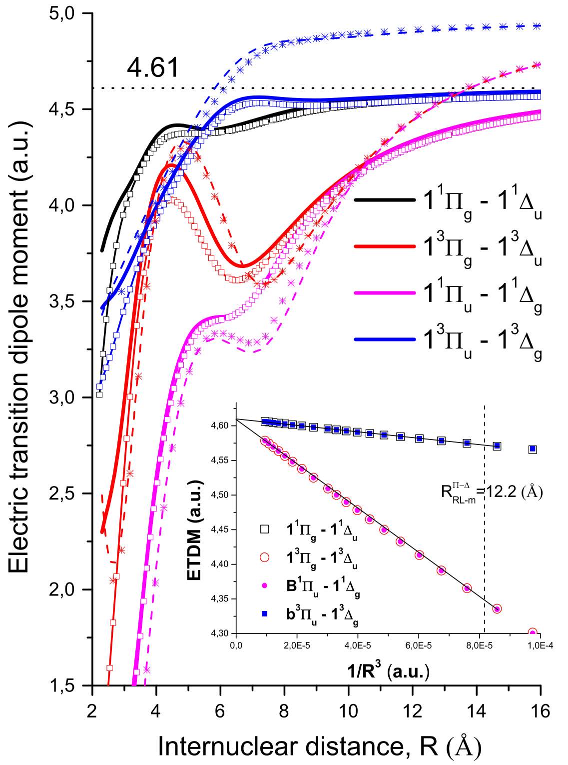

**Fig. 7.** The present (solid and dash lines) and preceding (open symbols [10] and stars [11,12]) dipole allowed ETDM functions of $Rb_2$ between the $^{1,3}\Pi_{u,g}$ and $^{1,3}\Delta_{u,g}$ states converging to the second and third dissociation limits, respectively. The originally calculated functions were multiplied by $\sqrt{2}$. The inset displays the long-range fragment of the present $d_{ij}(R)$ functions with respect to the $1/R^3$ coordinate. The resulting fitting parameters (in *a.u.*) are $d^{Rb}_{\Pi-\Delta} = 4.605$, $\beta_{\Pi_{u,g}-\Delta_{g,u}} = -425$ and $\beta_{\Pi_{g,u}-\Delta_{u,g}} = -3080$.

transitions is represented as a function of the $1/R^n$ coordinate on the insets of Figs. 1, 2, 7 and 8. As it should be expected, the ETDM functions of the singlet-singlet transitions coincide with their triplet–triplet counterparts at internuclear distances beyond the modified Le Roy radius estimated in Table 5. Table 6 shows that the slope coefficients $\beta_{\Lambda'\Lambda''}$ of the long range expansion (2) extracted from the *ab initio* $d_{ij}(R)$ functions for both dimers are remarkably close to their $S-P$ atomic analogues evaluated in the framework of the long range perturbation theory [4]. The most significant deviation is observed for the dipole forbidden $S-D$ transitions of the $Cs_2$ molecule. It should be noted that for the $P-D$ transitions the corresponding LRPT estimates are not available.

The asymptotic values $d_{ij}(R\to\infty)$ extracted by a linear extrapolation of the *ab initio* ETDM functions overestimate their experimental and QDT counterparts corresponding to the $S-P$ transitions of Rb and Cs atoms (see Tables 4 and 6 by about 5% and 7%, respectively). This is partly attributed to the shortcut of the MOLPRO package [15] where the operator dipole moment does not take into account the polarization of the atomic cores. The values obtained by the modified dipole operator (10) tell us that the negligence of the core-polarization effect could lead to the systematic increase of the ECP+CPP results by about 4% for Rb and 5% for Cs, respectively. Indeed, the uniformly scaled original *ab initio* ETDM functions become remarkably close to each other at least at large and intermediate internuclear distances.

For the most excited states of $Rb_2$ and $Cs_2$ the PECs obtained by Eq. (1) from original *ab initio* data coincide with their theoretical [8,10–12] and empirical counterparts within 50–150 cm$^{-1}$ at least in vicinity of the

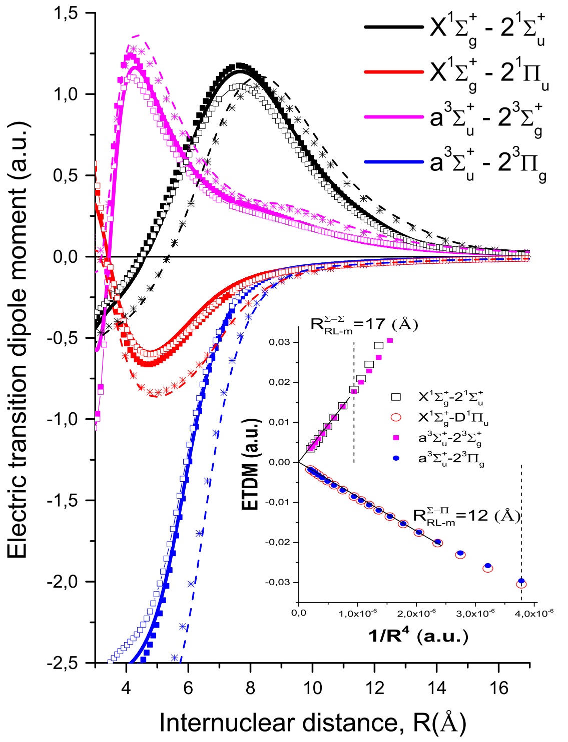

**Fig. 8.** The present (solid and dash lines) and preceding (open symbols – [8], solid symbols [10] and stars [11,12]) dipole forbidden ETDM functions of $Rb_2$ calculated between the ground $X^1\Sigma^+_g$, $a^3\Sigma^+_u$ and excited $2^1\Sigma^+_u$, $2^1\Pi_u$, $2^3\Sigma^+_g$, $2^3\Pi_g$ states converging to the third dissociation limit. The inset displays the long-range fragment of the present $d_{ij}(R)$ functions with respect to the $1/R^4$ coordinate.

**Table 6**
The leading long-range coefficients in the ETDM function expansion of the ground S and excited P and D states of the interacting atoms.

| Transition | $d^{At}$ | $\beta_{\Sigma-\Sigma}$ | $\beta_{\Sigma-\Pi}$ | Source |
|---|---|---|---|---|
| Rb–Rb | | | | |
| 5S–5P | 4.462/<br>4.470[a] | 716 | −361 | *Ab initio* [PW] |
| | 4.290 | 697 | −348 | LRPT [4] |
| | 4.231 | | | Expt. [25] |
| 5S–4D | | $1.8\times10^4$ | $-9.2\times10^3$ | *Ab initio* [PW] |
| | | $1.66\times10^4$ | $-9.55\times10^3$ | LRPT [4] |
| Cs–Cs | | | | |
| 6S–6P | 4.819/<br>4.827[a] | 944 | −466 | *Ab initio* [PW] |
| | 4.577 | 932 | −466 | LRPT [4] |
| | 4.500 | | | Expt. [26] |
| 6S–5D | | $3.3\times10^4$ | $-1.6\times10^4$ | *Ab initio* [PW] |
| | | $4.69\times10^4$ | $-2.71\times10^4$ | LRPT [4] |

[a] is the present “atomic” calculation.

Please cite this article as: Pazyuk EA, et al. *Ab initio* and long-range studies of the electronic transition dipole moments among the low-lying states of $Rb_2$ and $Cs_2$ molecules. J Quant Spectrosc Radiat Transfer (2016), http://dx.doi.org/10.1016/j.jqsrt.2016.01.004

equilibrium distances $R_e$. However, the observed deviation of the electronic energies $T_e$ still exceeds a few vibrational quants. This circumstance does not allow ones to use the current PECs for unambiguous vibrational assignment of the experimental spectra. It should also be noticed that a direct comparison of the theoretical and experimental PECs does not actually reveals a quality of the ETDM calculation since the latter mainly depends on the reliability of the electronic wave functions involved.

## 5. Concluding remarks

The spin-allowed electric transition dipole moments $d_{ij}(R)$ between all states of rubidium and cesium dimers belonging to both singlet and triplet state manifolds of the $g/u$ symmetry and converging to the lowest three dissociation limits have been calculated for a wide range of internuclear distances.

The small ($\sim$5–7%) systematic errors of the present ETDM functions of $Rb_2$ and $Cs_2$ dimers are assessed by a comparison with preceding *ab initio* calculations and their long range theory counterparts. The accuracy could be even further improved (reducing error to about $\sim$2–3%) by the uniform scaling of the original $d_{ij}(R)$ functions to smoothly match the limiting atom value of the molecular dipole moment.

A good agreement of the present and preceding *ab initio* calculations strongly supports overall reliability of the ETDM functions derived through alternative computational methods. Furthermore, their asymptotic behavior (2) is found to be very close to theoretical estimates obtained within the framework of long range perturbation theory [4,14].

We believe that the *ab initio* ETDM functions, combined with the relevant adiabatic PECs and recently calculated spin–orbit coupling matrix elements [17] will be a good starting point for understanding complex decay of mutually perturbed states. The radiative properties could be particularly useful for designing efficient laser synthesis of stable ultracold molecular ensembles.

## Acknowledgments

We thank M. Tomza and R. Moszynski for providing their *ab initio* data in numerical ASCII format. The work was supported by the Russian Foundation of Basic Research (RFBR) Grant no. 16-03-00529-a.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jqsrt.2016.01.004.

## References

[1] Krems R, Friedrich B, Stwalley W. Cold molecules: theory, experiment, applications. Boca Raton, London, New York: CRC Press, Taylor & Francis Group; 2009.

[2] Pazyuk EA, Zaitsevskii AV, Stolyarov AV, Tamanis M, Ferber R. Laser synthesis of ultracold alkali metal dimers: optimization and control. Russ Chem Rev 2015;84(10):1001–20. http://dx.doi.org/10.1070/RCR4534.

[3] Bergmann K, Vitanov NV, Shore BW. Perspective: stimulated Raman adiabatic passage: the status after 25 years. J Chem Phys 2015;142 (17):170901–20. http://dx.doi.org/10.1063/1.4916903.

[4] Marinescu M, Dalgarno A. Dispersion forces and long-range electronic transition dipole moments of alkali-metal dimer excited states. Phys Rev A 1995;52(1):311–28.

[5] Marinescu M, Sadeghpour HR. Long-range potentials for two-species alkali-metal atoms. Phys Rev A 1999;59:390–403.

[6] Konowalow DD, Rosenkranz ME, Hochhauser DS. Electronic transition dipole moment functions and difference potentials for transitions among low-lying states of $Li_2$ and $Na_2$. J Mol Spectr osc 1983;99:321–38.

[7] Ratcliff LB, Fish JL, Konowalow DD. Electronic transition dipole moment functions for transitions among the twenty-six lowest-lying states of $Li_2$. J Mol Spectr osc 1987;122:293–312.

[8] Beuc R, Movre M, Horvatic V, Vadla C, Dulieu O, Aymar M. Absorption spectroscopy of the rubidium dimer in an overheated vapor: an accurate check of molecular structure and dynamics. Phys Rev A 2007;75:
032512–610. http://dx.doi.org/10.1103/PhysRevA.75.032512.

[9] Vexiau R, Bouloufa N, Aymar M, Danzl JG, Mark MJ, Nägerl HC, et al. Optimal trapping wavelengths of $Cs_2$ molecules in an optical lattice. Eur Phys J D 2011;65(1):243–50.

[10] Allouche A-R, Aubert-Frecon M. Transition dipole moments between the low-lying $\Omega_{g,u}$ $(+/-)$ states of the $Rb_2$ and $Cs_2$ molecules. J Chem Phys 2012;136:114302–15. http://dx.doi.org/10.1063/1.3694014.

[11] Tomza M, Goerz MH, Musia M, Moszynski R, Koch CP. Optimized production of ultracold ground-state molecules: stabilization employing potentials with ion-pair character and strong spin-orbit coupling. Phys Rev A 2012;86:043424–513. http://dx.doi.org/10.1103/PhysRevA.86.043424.

[12] Tomza M, Skomorowski W, Musia M, Gonzalez-Ferez R, Koch CP, Moszynski R. Interatomic potentials, electric properties and spectroscopy of the ground and excited states of the $Rb_2$ molecule: ab initio calculations and effect of a non-resonant field. Mol Phys 2013;111(12–13):
1781–97. http://dx.doi.org/10.1080/00268976.2013.793835.

[13] Lim IS, Schwerdtfeger P, Metz B, Stoll. H. All-electron and relativistic pseudopotential studies for the group 1 element polarizabilities from K to element 119. J Chem Phys 2005;122:104103–12.

[14] Chu X, Dalgarno A. Molecular transition moments at large internuclear distances. Phys Rev A 2002;66:024701–3. http://dx.doi.org/10.1103/PhysRevA.66.024701.

[15] Werner HJ, Knowles PJ, Lindh R, Manby FR, Schutz M, Celani P, et al. MOLPRO, version 2010.1, a package of *ab initio* programs; http://www.molpro.net/.

[16] Kim JT, Lee Y, Stolyarov AV. Quasi-relativistic treatment of the low-lying KCs states. J Mol Spectrosc 2009;256:57–67.

[17] Pazyuk EA, Revina EI, Stolyarov AV. Theoretical study of spin–orbit and Coriolis coupling among the low-lying states of $Rb_2$ and $Cs_2$. Chem Phys 2015;462:51–6. http://dx.doi.org/10.1016/j.chemphys.2015.07.018.

[18] Hurley MM, Pacios LF, Christiansen PA, Ross RB, Ermler WC. *Ab initio* relativistic effective potentials with spin–orbit operators. II. K through Kr. J Chem Phys 1986;84:6840–53.

[19] Ross RB, Powers JM, Atashroo T, Ermler WC, John LA, Christiansen PA. Ab initio relativistic effective potentials with spin–orbit operators. IV. Cs through Rn. J Chem Phys 1990;93:6654–70.

[20] Sadlej AJ, Urban M. Medium-size polarized basis sets for high-level-correlated calculations of molecular electric properties III. Alkali (Li, Na, K, Rb) and alkaline-earth (Be, Mg, Ca, Sr) atoms. J Mol Struct 1991;234:147–71.

[21] Zaitsevskii A, Pazyuk EA, Stolyarov AV, Docenko O, Klincare I, Nikolyaeva O, et al. Permanent electric dipoles and $\Lambda$-doubling constants in the lowest $^1\Pi$ states of RbCs. Phys Rev A 2005;71: 012510–6.

[22] Partridge H, Bauschlicher Jr CW. The dissociation energies of $He_2$, HeH and ArH: a bond function study. Mol Phys 1999;96:705–10.

[23] Werner HJ, Knowles PJ. A second order multiconfiguration SCF procedure with optimum convergence. J Chem Phys 1985;82: 5053–63.

[24] Knowles PJ, Werner H-J. Internally contracted multi-reference configuration interaction calculations for excited states. Theor Chim Acta 1992;84:95–103.

[25] Steck Daniel A. Rubidium 85 D line data. Available online at http://steck.us/alkalidata [revision 2.1.6, 20 September 2013].

[26] Steck Daniel A. Cesium D line data. Available online at http://steck.us/alkalidata [revision 2.1.4, 23 December 2010].

Please cite this article as: Pazyuk EA, et al. *Ab initio* and long-range studies of the electronic transition dipole moments among the low-lying states of $Rb_2$ and $Cs_2$ molecules. J Quant Spectrosc Radiat Transfer (2016), http://dx.doi.org/10.1016/j.jqsrt.2016.01.004

[27] Mitroy J, Safronova MS, Clark CW. Theory and applications of atomic and ionic polarizabilities. J Phys B: At Mol Opt Phys 2010;43: 202001–38. http://dx.doi.org/10.1088/0953-4075/43/20/202001.

[28] Zaitsevskii A, Adamson SO, Pazyuk EA, Stolyarov AV, Nikolayeva O, Docenko O, et al. Energy and radiative properties of the low-lying NaRb states. Phys Rev A 2001;63:052504–10.

[29] Seto JY, Le Roy RJ, Vergès J, Amiot C. Direct potential fit analysis of the $X^1\Sigma_g^+$ state of $Rb_2$: nothing else will do!. J Chem Phys 2000;113: 3067.

[30] Coxon JA, Hajigeorgiou. PG. The ground $X^1\Sigma_g^+$ electronic state of the cesium dimer: application of a direct potential fitting procedure. J Chem Phys 2010;132:094105–17.

[31] Stolyarov AV, Child MS. Radiative properties of diatomic Rydberg states in quantum-defect theory. Application to the hydrogen molecule. J Phys B 1999;32:527–35.

[32] Chichkov BN, Shevelko VP. Dipole transitions in atoms and ions with one valence electron. Phys Scr 1981;23(6):1055–65.

[33] Ji B, Tsai CC, Stwalley WC. Proposed modification of the criterion for the region of validity of the inverse-power expansion in diatomic long-range potentials. Chem Phys Lett 1995;236: 242–6. http://dx.doi.org/10.1016/0009-2614(95)00216-Q.

[34] Seaton MJ. Quantum defect theory. Rep Prog Phys 1983;46(2): 167–257.

[35] Theodosiou CE. Lifetimes of alkali-metal-atom Rydberg states. Phys Rev A 1984;30:2881–909.

[36] Migdaleky J, Kim Y-K. Core polarization and oscillator strength ratio anomaly in potassium, rubidium and cesium. J Phys B 1998;31: 1947–60.

Please cite this article as: Pazyuk EA, et al. *Ab initio* and long-range studies of the electronic transition dipole moments among the low-lying states of $Rb_2$ and $Cs_2$ molecules. J Quant Spectrosc Radiat Transfer (2016), http://dx.doi.org/10.1016/j.jqsrt.2016.01.004