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AB INITIO STUDY ON SPECTROSCOPIC AND RADIATIVE PROPERTIES OF THE LOW-LYING STATES OF THE RaAt MOLECULE

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В рамках релятивистского метода связанных кластеров в пространстве Фока рассчитаны функции потенциальной энергии основного и нижних возбуждённых электронных состояний молекулы RaAt. Получены молекулярные спектроскопические параметры термов, энергии вибронных состояний, дипольные моменты переходов, факторы Франка – Кондона и другие радиационные характеристики. Предложена схема прямого лазерного охлаждения молекул RaAt.

During the last decades, the unique properties of ultracold diatomic molecules are considered to be used for manifold potential applications including controlling dipole–dipole interactions between two or more molecules, quantum information processing, control of collisions and chemical reactions, and some others. New promising applications of ultracold molecules also include research for parity-violation effects, namely, the possibility of observation of an electron's electric dipole moment (eEDM) [1]. In the latter case measured parameters critically depend on the atomic mass, and thus, for these goals it is preferable to use heavy atoms, which often do not have stable isotopes. The mentioned applications require ultralow temperatures of molecular gases, which can be reached using laser cooling methods, including direct laser cooling [1]. The principles of direct laser cooling of molecules are based on scattering (absorption and re-emission) of a large number of photons by a molecule. Among numerous promising candidates for the successful realization of the cooling scheme, the alkaline earth monohalides look most attractive due to their unique electronic structure of the ground and lower excited states, which is determined by excitation of the valence ns electron of the metal atom to the np or $(n-1)d$ state in the ionic M^+X^- structure (where M = Be, Mg, Ca, Sr, Ba, or Ra; X = F, Cl, Br, I, or At) [2]. As a result, excitation of valence electron almost does not influence the form of the low-lying potential energy curves (PECs). Among alkaline earth monohalides family the radium compounds are of the highest interest from the point of view of the possible determination of eEDM due to the largest mass of the radium atom compared to other alkaline earth metal atoms. However, due to the high degree of radioactivity of radium and the absence of its stable isotopes, the radium monohalides are the least experimentally studied. Recently, we used the FC-RCC (Fock-space relativistic coupled cluster) level of theory to obtain spectroscopic properties of the ground and five low-lying excited states of the RaF [3], RaBr [4], and RaI [5] radicals. Our calculations for the RaF molecule [3] demonstrate an excellent agreement with the experimental data [6]. The main spectroscopic parameters of the ground and low-lying ionic excited terms as well as the parameters of parity-violation effects of the RaCl molecule were also recently calculated [7]. There are no cooling parameters for RaAt at all. To fill in this blank here we use the same level of theory to calculate PECs and other spectroscopic and radiative characteristics of the RaAt radical and clarify the advantages of the various radium monohalides compounds from the point of view of their effective direct laser cooling.

We used the Stuttgart ECPDS78MDFSO and ECPDS60MDFSO fully relativistic effective core potentials and Gaussian cc-pwCVTZ-PP basis sets. *Ab initio* relativistic calculations were performed using Kramers unrestricted FS-RCCSD method. Firstly, pseudospinors were generated at the HF-SCF level of theory for the closed-shell ground state of RaAt$^+$ ion. Then, the FS-RCCSD calculations in the (0,1) Fock sector (0 holes, 1 electron) were performed for the RaAt$^+$ ion for six low-lying states. All calculations were performed using the DIRAC quantum chemical package [8].

The calculated PECs are shown in Fig. 1. Systems of the lowest ionic terms of all radium monohalides are similar in the minima region. The equilibrium internuclear distances in the series RaF → RaCl → RaBr → RaI → RaAt monotonously increase (2.269–2.287 Å for RaF [3], 2.813–

2.828 Å for RaCl [7], 2.986–3.001 Å for RaBr [4], 3.214–3.230 Å for RaI [5], and 3.307–3.325 Å for RaAt); the energies of all excited terms monotonously decrease. The sequence of the lowest PECs is the same ($X^2\Sigma^+$, $A^2\Pi_{1/2}$, $B^2\Delta_{3/2}$, $B^2\Delta_{5/2}$, $A^2\Pi_{3/2}$, and $C^2\Sigma^+$) for all radium monohalides, excluding the RaF radical, for which according to our calculations [39] the $A^2\Pi_{3/2}$ term lies lower than the $B^2\Delta_{5/2}$ one.
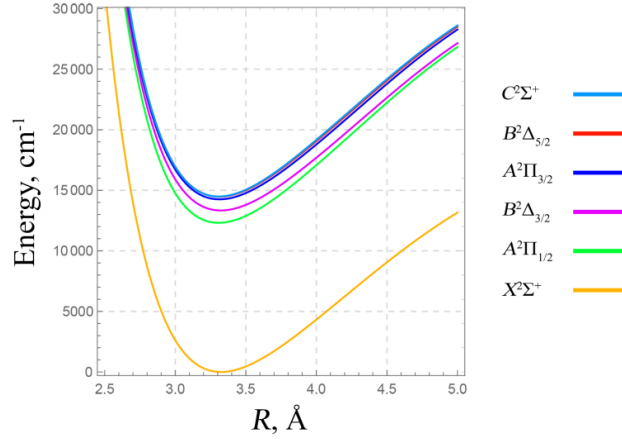

Figure 1 – The calculated PECs for low-lying states of the RaAt molecule.

Radium and astatine have no stable isotopes; the longest-lived isotopes of radium and astatine are ^{226}Ra with a half-life of about 1600 years and ^{210}At with a half-life of about 8 hours. We calculated the vibrational energies for the ^{226}Ra^{210}At radical for six low-lying PECs and then obtained the harmonic vibrational frequencies ω_e and other molecular spectroscopic parameters for these electronic states. Based on the calculated PECs and vibrational energies, we predicted Franck–Condon factors (FCFs) and vibrational branching ratios (VBRs), which, in contrast to FCFs, can be directly measured in a spectroscopic experiment. The FCFs and VBRs were calculated for the $A^2\Pi_{1/2} \rightarrow X^2\Sigma^+$, $A^2\Pi_{3/2} \rightarrow X^2\Sigma^+$, and $C^2\Sigma^+ \rightarrow X^2\Sigma^+$ allowed vibronic transitions. Since the $A^2\Pi_{1/2}$ state is a lower excited one, the $A^2\Pi_{1/2} \leftrightarrow X^2\Sigma^+$ channel satisfies at least two Di Rosa's criteria [9] and is considered as the most advantageous for direct laser cooling. The FCFs distribution for the transitions between the lowest vibrational states of the $A^2\Pi_{1/2}$ and $X^2\Sigma^+$ terms are shown in Fig. 2.
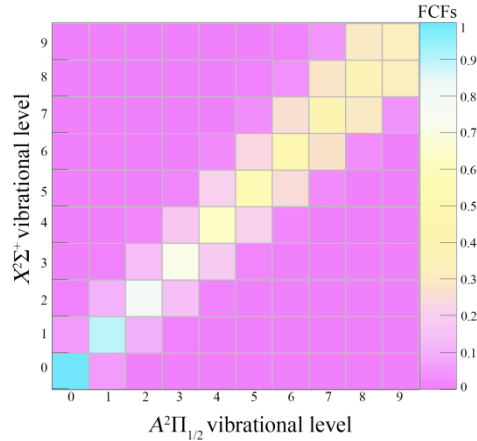

Figure 2 – The calculated FCFs for the $A^2\Pi_{1/2}(v'= 0\ldots9) \rightarrow X^2\Sigma^+(v''= 0\ldots9)$ vibronic transitions of the RaAt molecule.

Diagonal FCFs for the $A^2\Pi_{1/2} \rightarrow X^2\Sigma^+$ transitions demonstrate the trend to decreasing in a series of the RaF, RaCl, RaBr, RaI, and RaAt molecules. E.g., the $0' \rightarrow 0''$ FCF is equal to 0.999998 (RaF, [3]), 0.998516(RaCl [7]), 0.990752 (RaBr [4]), 0.954439 (RaI [5]), and 0.949196 (RaAt). Generally, the FCFs distribution for the radium monohalides exhibits more and more diffuse character as shown in Fig. 2.

The generalized vibrational cooling scheme, including three-color lasers is shown in Fig. 3. The main laser with the wavelength $\lambda_{00} = 811.9$ nm drives the $A^2\Pi_{1/2}(v' = 0) \leftarrow X^2\Sigma^+(v'' = 0)$ transi-

tion. This pumping channel can provide only 20 scatterings. Therefore, the first additional repump laser with the wavelength $\lambda_{10} = 818.8$ nm (RaAt) returns the population directly from the $X^2\Sigma^+(v'' = 1)$ state to the $A^2\Pi_{1/2}(v' = 0)$ state. The second additional repump laser with the wavelength $\lambda_{21} = 818.6$ nm (RaAt) returns the population indirectly to the main cycle by driving the $A^2\Pi_{1/2}(v' = 1) \leftarrow X^2\Sigma^+(v'' = 2)$ transition. For the RaAt radicals the number of scattered photons per molecule increases up to 30 000, which is three times more than the lower limit. So, the cooling scheme for the RaAt molecule is assumed to use one pump and two repump lasers.
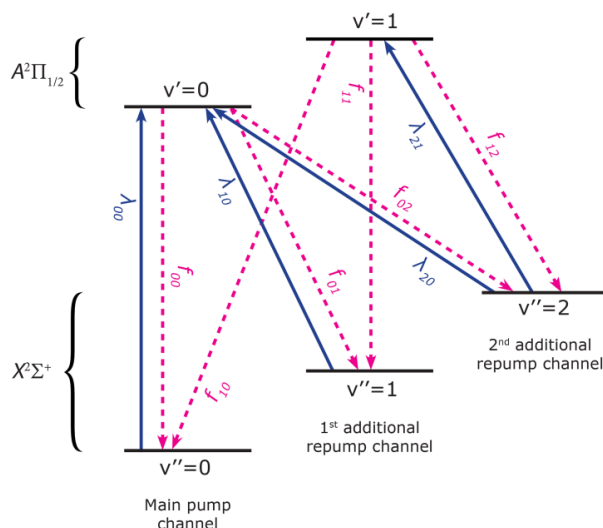

Figure 3 – Vibrational laser cooling scheme for the radium monohalides molecules using the $A^2\Pi_{1/2}(v') \leftarrow X^2\Sigma^+(v'')$ pump transitions (solid lines) and spontaneous decay (dashed lines).

Reference

1. Fitch, N.J. Laser-cooled molecules / N.J. Fitch, M.R. Tarbutt// Advances in Atomic, Molecular, and Optical Physics. – 2021. Vol. 70. – P. 157–262.

2. Törring, T. Energies and electric dipole moments of the low lying electronic states of thealkaline earth monohalides from an electrostatic polarization model / T. Törring, W.E. Ernst, J. Kändler // J.Chem. Phys. – 1989. Vol. 90. – P. 4927–4932.

3. Osika, Y. Fock-space relativistic coupled cluster study on the RaF molecule promising for the laser cooling / Y. Osika, M. Shundalau //Spectrochim. Acta A. – 2022. – Vol. 264. – P. 120274.

4. Osika, Y. Fock-space relativistic coupled cluster study on the spectroscopic properties of the low-lying states of the radium monobromide RaBr molecule / Y. Osika, M. Shundalau // J. Quant. Spectrosc. Radiat. Transfer. – 2021. – Vol. 276. – P. 107947.

5. Osika, Y. *Ab initio* study on the spectroscopic and radiative properties of the low-lying states of the radium monoiodideRaI molecule / Y. Osika, M. Shundalau, Y.-C. Han // J. Quant. Spectrosc. Radiat. Transfer. – 2022. – Vol. 285. – P. 108144.

6. Garcia Ruiz, R.F. Spectroscopy of short-lived radioactive molecules / R.F. Garcia Ruiz et al. // Nature. – 2020. Vol. 581. – P. 396–400.

7. Isaev, T.A.*Ab initio* study and assignment of electronic states in molecular RaCl / T.A. Isaev et al. // J. Quant. Spectrosc. Radiat. Transfer. – 2021. – Vol. 269. – P. 107649.

8. Saue, T. The DIRAC code for relativistic molecular calculations / T. Saue et al. // J. Chem. Phys. – 2020. Vol. 152. – P. 204104.

9. Di Rosa, M.D. Laser-cooling molecules. Concept, candidates, and supporting hyperfine-resolved measurements of rotational lines in the A–X(0,0) band of CaH / M.D. Di Rosa // Eur. Phys. J. D. – 2004. – Vol. 31. – P. 395–402.