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Thermodynamic stable diatomic dications: the case of SrO^{2+}

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Abstract: The perspective that many diatomic dications XY^{2+} should exist as long-lived metastable, or even thermodynamically stable molecules in the gas phase, brings to evidence a class of chemical species with challenging problems to explored both experimentally and theoretically [1]. In the literature, it has been verified qualitatively that if the second ionization potential of X is smaller than the first ionization of Y, leading to the dissociation fragments X^{2+} + Y, then the system is expected to be thermodynamic stable; if it is greater than the first ionization of Y, it has been usually assumed that the channel is associated with a metastable system with the dissociation fragments X^{+} + Y^{+} species. However, it could also lead instead to a purely thermodynamic stable species due to a more delicate energetic balance involving the depth of the potential well and the excitation energies of the two ions.

In the present work, we constructed potential energy curves, dipole moment, and transition moment functions, and calculated the associated spectroscopic parameters corresponding to the first four dissociation channels of SrO^{2+}. Additionally, we also computed the double ionization potential of SrO. In our theoretical approach, we first carried out state-averaged complete active space self-consistent field (SA-CASSCF) calculations [2, 3] followed by the multireference configuration interaction MRCI [4, 5] method, both implemented in Molpro code [6]; the correlation consistent set cc-pV5Z-PP for strontium [8] and cc-pV6Z for oxygen [7] were used as basis functions.

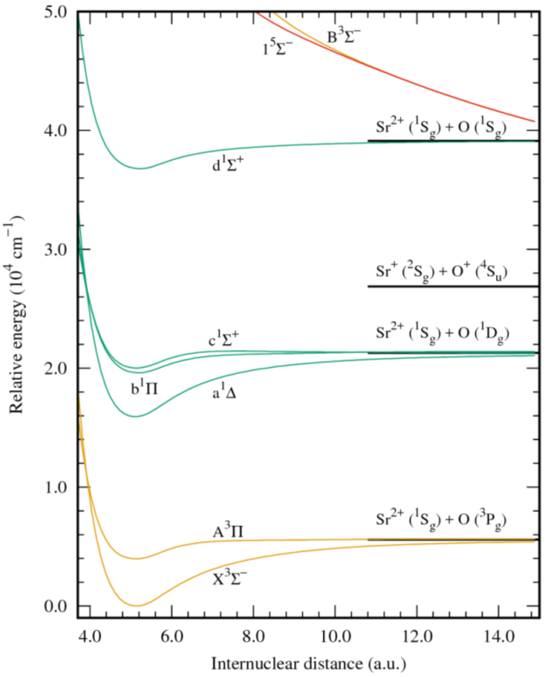

Fig. 1. PEC of the lowest-lying Λ + S states of SrO^{2+}

All singlet, triplet, and quinted states investigated are illustrated in Fig. 1, where the four dissociation channels limits are indicated. Correlating with the Sr^{2+} + O asymptote, the ground state (X $^3\Sigma^-$) has an equilibrium distance of 5.134 a_0, and a harmonic vibrational constant of 231.9 cm^{-1}; the dissociation energy of 5.91 kcal mol^{-1} indicates a much weaker bond than the one in SrO (X $^1\Sigma^+$), 137.93 kcal mol^{-1}, and SrO^+ (X $^2\Sigma^+$), 79.57 kcal mol^{-1}. The repulsive states $^{3,5}\Sigma^-$, partially shown in the upper right corner, correlate with the third channel in the asymptotic limit; all of the other states are thermodynamic stable. The first excited state, A $^3\Pi$, also correlating with the first channel lies higher by 3 968 cm^{-1}. Still higher in energy, in the approximate range between 16 000 and 20 000 cm^{-1}, we located the three singlet states correlating with the second dissociation channel, namely: $a^1\Delta$ (R_e = 5.104 a_0, T_e = 15 929 cm^{-1}, ω_e = 231.3 cm^{-1}), $b^1\Pi$ (R_e = 5.189 a_0, T_e = 19 611 cm^{-1}, ω_e = 186.6 cm^{-1}), and $c^1\Sigma^+$(R_e = 5.134 a_0, T_e = 20 019 cm^{-1}, ω_e = 181.0 cm^{-1}). The fourth state, $d^1\Sigma^+$ (R_e = 5.229 a_0, T_e = 36 778 cm^{-1}, ω_e = 186.3 cm^{-1}) is bound by 6.67 kcal mol^{-1}. As an indirect assessment of the quality of the results presented above, we note that our estimates of the energy differences at the asymptotic limit between the atomic fragments is quite concordant with the ones obtained experimentally [9].

This work reports for the first time reliable theoretical data characterizing singlet, triplet and quintet states of the species SrO^{2+} which are expected to be a useful guide to experimentalists to properly identify the states and assign the allowed transitions.

Key-words: spectroscopy, SrO^{2+}, dications, electronic states, CASSCF/MRCI.

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