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Multireference configuration interaction study of the 27 low-lying states of the PF^+ cation

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Abstract:

This paper studied the spectroscopic parameters and vibrational properties of 27 Λ -S and 60 Ω states of PF^+ cation. The 27 Λ -S states were the $X^2\Pi$, $A^2\Sigma^+$, $B^2\Pi$, $C^2\Sigma^-$, $D^2\Delta$, $a^4\Sigma^-$, $b^4\Pi$, $c^4\Sigma^+$, $d^4\Delta$, $2^2\Sigma^+$, $3^2\Sigma^+$, $4^2\Sigma^+$, $2^2\Sigma^-$, $3^2\Sigma^-$, $3^2\Pi$, $4^2\Pi$, $5^2\Pi$, $6^2\Pi$, $2^2\Delta$, $3^2\Delta$, $1^2\Phi$, $2^4\Sigma^-$, $3^4\Sigma^-$, $2^4\Pi$, $3^4\Pi$, $1^6\Sigma^-$, and $1^6\Pi$, which were generated from the first four dissociation limits. The 60 Ω states were produced from the 27 Λ -S states. All the potential energy curves were calculated with the CASSCF method, which was followed by the icMRCI+Q approach. The $a^4\Sigma^-$, $b^4\Pi$, and $D^2\Delta$ states were inverted with the spin-orbit coupling effect accounted for. The $2^4\Pi$, $2^4\Sigma^-$, $2^2\Delta$, $3^2\Delta$, $3^2\Sigma^+$, $4^2\Sigma^+$, $1^2\Phi$, and $2^2\Sigma^-$ states were repulsive whether the spin-orbit coupling effect was included or not, but the $5^2\Pi$ and $D^2\Delta$ states became repulsive only with the spin-orbit coupling effect included. The $C^2\Sigma^-$ state was very weakly bound. The $a^4\Sigma^-$ state had one barrier. The avoided crossings existed between the $a^4\Sigma^-$ and $2^4\Sigma^-$ states, the $2^2\Sigma^+$ and $3^2\Sigma^+$ states as well as the $D^2\Delta$ and $2^2\Delta$ states. Core-valence correlation and scalar relativistic corrections were taken into account. The extrapolation to the complete basis set limit was done. The spectroscopic parameters and vibrational properties were determined. The transition dipole moments were calculated and the Franck-Condon factors of some electric dipole transitions were evaluated. The spin-orbit coupling effect on the spectroscopic and vibrational properties was discussed.

Keywords: potential energy curve; spectroscopic parameter; transition dipole moment; electric dipole transition; vibrational state; spin-orbit coupling.

1. Introduction

The PF radical and PF^+ cation can form stable complexes with transition metal fragments [1], which have received continuing interest for a long time due to their potential as an electronic energy storage system or a candidate for a chemically pumped laser system. In addition, the PF radical was important in fluorination reactions of various phosphorus-containing compounds [2]. For this reason, the spectroscopic and vibrational properties of PF radical [1-16] were widely investigated in the past several decades, both experimentally and theoretically. To our surprise, only few experimental [16-18] and theoretical studies [1, 18-20] addressed the spectroscopic and vibrational properties of PF^+ cation till now, though the PF^+ cation has the equivalent importance when compared with the PF radical.

Experimentally, Douglas and Frackowiak [16] in 1962 observed the $X^2\Pi$ - $A^2\Sigma^+$ transitions of PF^+ cation for the first time. With the spectra results obtained, they evaluated the spectroscopic parameters of $X^2\Pi$ and $A^2\Sigma^+$ states and determined the spin-orbit coupling (SOC) splitting energy of $X^2\Pi$ state to be approximately 323.9 cm^{-1} . Using photoionization mass spectrometry, Berkowitz et al. [17] in 1984

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