Multireference configuration interaction study of the 21 low-lying states of the OF radical

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ABSTRACT

This paper calculated the potential energy curves of 21 Λ-S and 42 Ω states of the OF radical. The 21 Λ-S states were the $X^2\Pi$, $A^2\Sigma^-$, $B^2\Sigma^-$, $C^2\Delta$, $D^2\Sigma^+$, $E^2\Sigma^+$, $2^2\Pi$, $a^4\Sigma^-$, $b^4\Delta$, $2^4\Sigma^-$, $1^4\Sigma^+$, $1^4\Pi$, $2^4\Pi$, $3^2\Sigma^+$, $3^2\Sigma^-$, $3^2\Pi$, $4^2\Pi$, $5^2\Pi$, $2^2\Delta$, $3^2\Delta$, and $1^2\Phi$, which arose from the first two dissociation limits. The 42 Ω states were generated from these Λ-S states. All the potential energy curves were calculated with the CASSCF method, which was followed by the icMRCI+Q approach. The $1^4\Pi$, $2^4\Pi$, $2^2\Pi$, $4^2\Pi$, $5^2\Pi$, $3^2\Sigma^+$, and $3^2\Delta$ states were repulsive whether the spin-orbit coupling effect included or not, but the $A^2\Sigma^-$, $D^2\Sigma^+$, $3^2\Sigma^-$, $2^2\Delta$, and $1^2\Phi$ states became repulsive with the spin-orbit coupling effect included. Only the 16 Ω states were bound. With the spin-orbit coupling effect accounted for, the $X^2\Pi$ state was inverted among the bound states; the $X^2\Pi$, $a^4\Sigma^-$, and $E^2\Sigma^+$ states were strongly bound; and the $3^2\Pi$, $b^4\Delta$, $B^2\Sigma^-$, $C^2\Delta$, $2^4\Sigma^-$, and $1^4\Sigma^+$ states were very weakly bound. The spectroscopic and vibrational properties were determined. Franck–Condon factors of some transitions were evaluated. The spin-orbit coupling effect on the spectroscopic parameters and vibrational properties was discussed. It is very difficult to explore the $X^2\Pi$, $a^4\Sigma^-$, and $E^2\Sigma^+$ states by observing the electronic transitions between them because all these strong transitions originating only from the highly-vibrational states of the $X^2\Pi$ or $a^4\Sigma^-$ state. It is also very hard to detect the $3^2\Pi$, $b^4\Delta$, $B^2\Sigma^-$, $C^2\Delta$, $2^4\Sigma^-$, and $1^4\Sigma^+$ states by observing the transitions originating from these states, because these states are very weakly bound and unstable, though some transitions originating from them are very strong. These results can well explain why the OF radical is very difficult to detect in a spectroscopic experiment by observing the electronic transitions between different states.

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1. Introduction

The Fluorine monoxide (OF) radical has received considerable attention due to its participation in atmospheric ozone depletion chemistry [1–3]. OF radicals are formed in the stratosphere from the reaction of F with ozone, resulting in the destruction of ozone. To observe the destruction of ozone, it is necessary to know some spectroscopic information of this radical. For this reason, many groups of spectroscopic experimental [1–17] and theoretical [18–36] work were done in the past several decades. However, almost all the experimental and theoretical studies were focused on the ground state [1–36].

Experimentally, Arkell et al. [4] in 1965 reported the first direct and conclusive evidence for the existence of OF radical. Subsequently, Spratley et al. [5] in 1966 made the matrix photolysis

of O_2 and F_2 mixtures. However, no OF radicals were produced. In the similar work, Ogden and Turner [6] in 1967 did not find this radical. Arkell [7] in 1969 did not confirm the existence of this radical by the infrared detection. Andrews and Raymond [8] in 1971 detected the matrix infrared spectrum of this radical. Andrews [9] in 1972 observed argon matrix Raman spectra of this radical. McKellar [10] in 1979 studied this radical using CO_2 laser magnetic resonance. Several spectroscopic parameters and molecular constants were evaluated. In 1979, Huber and Herzberg [37] summarized some accurate spectroscopic parameters of this radical as of that time.

Since 1979, there were many experimental investigations [1,2,11–17], in which the spectroscopic and molecular properties were evaluated. In these experiments, this radical was studied by many experimental approaches such as laser magnetic resonance [11,16,17], infrared absorption [12,13], infrared emission [15], and millimeter-wave spectroscopy [2]. Some spectroscopic parameters and spin-orbit coupling (SOC) constants were also determined. As

noted above, all these measurements [1–17] were restricted to the ground state of the OF radical.

Theoretically, O'Hare and Wahl [18] in 1970 first calculated the potential energy curves (PECs) of this radical using the Roothaan expansion method. Langhoff et al. [19] in 1983 computed the PECs and dipole moment functions at the levels of CASSCF, internal contracted CI and MRCI(SD) theory. Zhao and Francisco [20] in 1990 as well as Tozer et al. [24] in 1993 studied the ground-state properties using Møller-Plesset theory. Jensen [21] in 1990 studied the spin contamination on the vibrational frequency. Haaland [22] in 1991 evaluated the ground-state structure using the QCISD(T) method. Koseki et al. [23] used the MCSCF/6–31G(d, p) approach to compute the ground-state SOC splitting energy and determined it to be 187.90 cm^{-1}. Laming et al. [25] in 1993 and Chong [27] in 1994 made the density functional theory calculations on many diatomic molecules including the OF radical. And Xie et al. [26] in 1993 employed the MRSDCI approach to compute the $X^2\Pi$ and $a^4\Sigma^-$ states. with these PECs, some spectroscopic parameters were evaluated. However, these spectroscopic parameters obtained were in poor agreement with available measurements.

Subsequently, Koseki et al. [28] in 1995 determined the ground-state SOC splitting energy using the MCSCF approach. Johnson [29] in 1995 calculated the ground-state PEC by the CCSD(T)/cc-pVTZ approach. Ventura and Kieninger [30] in 1995 evaluated the ground-state spectroscopic parameters using the B3LYP/6–311++g(3df, 3pd) approach. Visscher et al. [31] in 1996 used the relativistic open-shell CCSD(T) method to study the fine structure splitting of many molecules. The ground-state SOC splitting energy of this radical was determined to be approximately 194.6 cm^{-1}. Li and Paldus [32] in 1996 made the unitary group based open-shell coupled cluster study of the equilibrium position and vibrational frequency. McGrath and Rowland [33] in 1996 computted the ground-state spectroscopic parameters by the internal contracted MRCI (icMRCI) method. Leonard et al. [34] in 2000 used the all-electron QCISD and QCISD(T) approaches together with the 6–311+G(3df) basis set to determine the spectroscopic parameters of diatomic halogen oxides. Feller et al. [35,36] in 2008 and 2010 employed the CCSD(T) theory with higher order correlation combined with large Gaussian basis sets and various corrections to investigate the atomization energies and structures on some molecules including the OF radical. Till today, all the theoretical studies are almost focused on the ground state. Only one group of calculations [26] was involved in the $a^4\Sigma^-$ state.

Recently, we calculated the PECs of 21 Λ-S and 42 Ω states of the OF radical and evaluated their spectroscopic parameters and vibrational properties. The 21 Λ-S states were the $X^2\Pi$, $A^2\Sigma^-$, $B^2\Sigma^-$, $C^2\Delta$, $D^2\Sigma^+$, $E^2\Sigma^+$, $2^2\Pi$, $a^4\Sigma^-$, $b^4\Delta$, $2^4\Sigma^-$, $1^4\Sigma^+$, $1^4\Pi$, $2^4\Pi$, $3^2\Sigma^+$, $3^2\Sigma^-$, $3^2\Pi$, $4^2\Pi$, $5^2\Pi$, $2^2\Delta$, $3^2\Delta$, and $1^2\Phi$, which arose from the first two dissociation limits. The 42 Ω states were generated from the 21 Λ-S states. Our results had the following features. (1) Twelve states ($1^4\Pi$, $2^4\Pi$, $2^2\Pi$, $4^2\Pi$, $5^2\Pi$, $3^2\Sigma^+$, $3^2\Delta$, $A^2\Sigma^-$, $D^2\Sigma^+$, $3^2\Sigma^-$, $2^2\Delta$, and $1^2\Phi$) were repulsive with the SOC effect included. (2) Only the 16 Ω states were bound among all the 42 Ω states. (3) With the SOC effect accouted for, only the $X^2\Pi$ state was inverted among the nine bound states ($X^2\Pi$, $a^4\Sigma^-$, $E^2\Sigma^+$, $3^2\Pi$, $b^4\Delta$, $B^2\Sigma^-$, $C^2\Delta$, $2^4\Sigma^-$, and $1^4\Sigma^+$). (4) Of these 21 Λ-S states, only the $X^2\Pi$, $a^4\Sigma^-$, and $E^2\Sigma^+$ states were strongly bound; and all the states except for $X^2\Pi$, $a^4\Sigma^-$, and $E^2\Sigma^+$ were either very weakly bound or repulsive. In combination with these vibrational states, we can well explain why it was very difficult to detect this radical in a spectroscopic experiment [19]. These features make us believe that it deserves to report the spectroscopic parameters and vibrational properties of these states in this paper.

In the next section, we will briefly introduce the methodology used. In Section 3, the PECs are reported for the 21 Λ-S and 42 Ω states. The spectroscopic parameters and vibrational prop-

erties were predicted. Franck-Condon (FC) factors of some transitions were determined. The SOC effect on the spectroscopic parameters and vibrational levels was evaluated. In Section 4, some conclusions are drawn. The spectroscopic parameters and vibrational properties obtained here can be expected to be reliably predicted ones.

2. Theory and method

The first two dissociation limits of OF radical are the $O(^3P_g) + F(^2P_u)$ and $O(^1D_g) + F(^2P_u)$. Using the molecular group theory, we deduced the 21 Λ-S states, which arose from the two dissociation limits. These Λ-S states together with the two dissociation limits are collected in Table 1. For reason of comparison, we also tabulate the experimental energy separation [38,39] between the $O(^3P_g) + F(^2P_u)$ and $O(^1D_g) + F(^2P_u)$ dissociation limits in Table 1.

To obtain more accurate PECs, we put altogether 30 states into the calculations. The additional 9 states were the $4^2\Sigma^+$, $4^2\Sigma^-$, $6^2\Pi$, $4^2\Delta$, $2^2\Phi$, $2^4\Delta$, $3^4\Sigma^-$, $2^4\Sigma^+$, and $3^4\Pi$. This paper deals with only the 21 states arising from the first two dissociation limits. All the PECs were calculated with the CASSCF method, which was followed by the icMRCI approach for internuclear separations from approximately 0.11 to 0.9 nm. The calculations were done with the MOLPRO 2010.1 program package [40] in the C_{2v} point group. Here, the CASSCF was used as the reference wavefunction for the icMRCI calculations. The basis sets used here were the aug-cc-pV5Z [41] and aug-cc-pV6Z [42].

The point spacing interval employed here was 0.04 nm for each state. To accurately determine the PECs, the point spacing interval was 0.005 nm for internuclear separations from approximately 0.13 to 0.33 nm. The molecular orbitals (MOs) used for the icMRCI calculations came from the CASSCF results. The state-averaged technique was used in the CASSCF calculations. Each state had the same weight factor of 0.33333. The eight outermost MOs ($4a_1$, $2b_1$ and $2b_2$) were put into the active space, corresponding to the 3 - 6σ, 1π and 2π MOs in the radical. The thirteen valence electrons were distributed into the eight valence MOs. Therefore, this active space was referred to as CAS (13, 8). The rest four inner electrons were put into the two lowest a_1 MOs. For the aug-cc-pV6Z basis set, the number of external MOs ($44a_1$, $26b_1$, $26b_2$, and $12a_2$) was 108. In summary, altogether 10 MOs ($6a_1$, $2b_1$, and $2b_2$) were used to calculate the PECs.

Davidson correction [43,44] was taken into account when we determined the PECs using the aug-cc-pV5Z and aug-cc-pV6Z basis sets. Core-valence correlation correction was calculated with the cc-pCVQZ basis set [45]. Its contribution to the total energy was denoted as CV. Scalar relativistic correction was computed with the cc-pVQZ-DK basis set [46] by the third-order Douglas-Kroll-Hess (DKH) Hamiltonian approximation. Its contribution to the total energy was denoted as DK. The basis set extrapolation [47] to the complete basis set (CBS) limit was performed with the aug-cc-pV5Z and aug-cc-pV6Z basis sets. The energy obtained by the basis set extrapolation was denoted as 56. We in detail described the approach to calculate the extrapolation to the CBS limit, core-valence correlation and scalar relativistic corrections in our earlier papers [48,49].

With these PECs determined by the icMRCI + Q/56 + CV + DK calculations, we fitted the spectroscopic parameters, T_e, R_e, ω_e, $\omega_e x_e$, $\omega_e y_e$, α_e, B_e, and D_e. The meanings of these spectroscopic notations were explained in our earlier paper [48]. All the PECs were fitted to an analytical form by cubic splines so that the rovibrational Schrödinger equation was solved. That is, the rovibrational constants were first determined from the analytic potential by solving the rovibrational Schrödinger equation, and then the spectroscopic parameters were evaluated by fitting the vibrational