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The Density Functional Theory Research on The Raman Spectra of SF_6 Decomposition Gas Products

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When partial discharge and overheating occurred inside SF_6 insulated electrical equipment, the status of SF_6 electrical equipment can be monitored and the development trend of insulation defect inside equipment can be expected through inspecting dissolved products. Raman spectra have more advantages compare with traditional SF_6 decomposition products inspection technique. Optimization of geometrical configuration of gas products and calculation of Raman spectra frequency are conducted in this research on the level of 6-31G (2df, p) basis set by utilizing The Density Functional Theory (DFT) and B3LYP method; and calculated shift is compared with actually measured shift of NIST. In addition, the relativity of calculated value and actually measured value of National Institute of Standards and Technology (NIST) is researched by utilizing correlation coefficient R^2 through linear regression. The result proves reliability of calculating Raman spectra of SF_6 decomposition gas product by DFT method and feasibility of using Raman spectra to qualitatively identify SF_6 decomposition gas products.

1. Introduction

Under the partial discharge and overheating condition of SF_6 insulated electrical equipment, SF_6 will dissolve and it will occur a series of complicated chemical reactions with micro-water and micro-oxygen inside the equipment (Belmadani et. al., 1991; Baldyga et al., 2017), which will finally generate SOF_4, SOF_2, SO_2F_2, S_2OF_{10} and HF, SO_2 and other acid gases; if discharge is occurred around internal solid insulation, CF_4, SiF_4, CO, CO_2 may be generated (Shengchang et al., 2015). Therefore, operation status of SF_6 electrical equipment can be monitored and diagnostic identification can be expected through inspecting SF_6 decomposition gas products (Tang et al., 2012). Currently, gas chromatography method, gas sensor method, detector tube method, infrared spectroscopy method, photo acoustic spectrometry method and other empirical methods on SF_6 decomposition gas product are mainly adopted in China, but the performances are varied (Tang et. al., 2012).

Density functional theory (hereinafter referred to as DFT) has been frequently used to calculate characteristics, structures and energies of conformation theoretically (Wu et. al., 2016), and many literatures have reported analysis of structural information and mechanism of action by utilizing DFT (Liu et al., 2014, Gao et al., 2013, Jia et al., 2016, Sun et al., 2014, Li et al., 2016), and they can much more accurately expect geometry, chemical bond properties, vibration level, various spectra and other information of molecule.

Raman spectra has been widely applied in industrial production monitoring and control, petrochemical, environmental protection, food identification, geological analysis, gemstone identification, commodity inspection, medical science and other areas (Shuhuan et. al., 2015; Chen et al., 2016; Tregrossi et al., 2017). Compare with traditional inspection technique of SF6 decomposition gas product, Raman spectra is advantageous in following aspects (Zhao, 2014).

In 2008, Li et al., from Shanghai Jiaotong University established a set of Raman inspection system of dissolved gas in transformer oil based on cavity enhancement method. In 2013, Somekawa et al., from Japanese Institute of Laser Technology put forward a type of in-situ inspection method of dissolved gas in transformer oil based on Raman spectra which is unnecessary to separate oil and gas. In 2014, Chen et al., from Chongqing University established Raman spectra inspection platform of silver plated quartz glass tube to

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inspect 7 mixed gases dissolved in transformer oil. However, the research report on optimizing geometrical configuration and expecting Raman spectra of SF_6 decomposition gas product by applying DFT is rare.

2. Calculation Method

Gaussian 09 program package is adopted for theoretical calculation of this research, molecular model is constructed by Gauss View. Geometrical configuration optimization of many gas products, namely SO_2F_2, SOF_2, SO_2, and CF_4 molecule, is conducted respectively on the level of 6-31G (2df,p) basis set by utilizing DFT and B3LYP method. There no imaginary frequency in the calculation result, demonstrating that optimized structure is the minimum energy and the most stable structure of molecule. Calculate Raman frequency on the basis of optimized geometrical configuration (Jiangyan et. al., 2009) and compare calculated Raman shift with Raman shift actually measured by NIST.

3. Result and Discussion

3.1 Geometrical Configuration of SO_2F_2 and Analysis of Simulation Result of Raman Spectra

SO_2F_2 is the cone type of molecule. There is no imaginary frequency after optimization, the bond length is r(1,2)=r(1,3)=141.5 pm, r(1,4)=r(1,5)=155.4 pm and bond angle is θ(2,1,3)=125.1°, θ(2,1,4)=θ(2,1,5)=θ(3,1,4)=θ(3,1,5)=108.1° and θ(4,1,5)=95.3°. Refer to Figure 1 for its structure after optimization and its calculated Raman spectra.

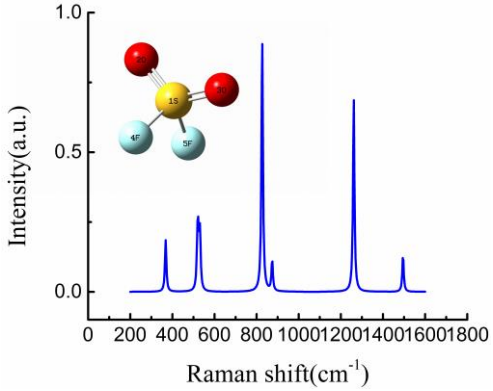

Figure 1: Molecular Structure and Calculated Raman spectra of SO_2F_2.

There are 9 vibration modes for SO_2F_2 molecule, they all have Raman active and they are formed into 9 Raman peaks. The comparison between its calculated shift with that actually measured by NIST is shown in Table 1. It can be seen from table that between Raman peak of SO_2F_2 actually measured by NIST and corresponding simulation result, the maximum deviation is 5.21% and the minimum deviation is 0.48%.

Table 1: Calculation Result of Raman Simulation of SO_2F_2

Calculated Raman shift/cm^{-1}	Calculated Raman active/(A^4/AMU)	Raman shift actually measured by NIST/cm^{-1}	Deviation/%
367.60	0.9314	385	-4.52
367.77	1.4044	388	-5.21
518.38	1.9891	539	-3.83
522.79	2.0200	544	-3.90
530.52	2.5743	553	-4.07
826.32	12.9190	848	-2.56
873.64	1.5533	885	-1.28
1260.83	10.6096	1269	-0.64
1494.77	2.1309	1502	-0.48

3.2 Geometrical Configuration of SOF_2 and Analysis of Simulation Result of Raman Spectra

SOF_2 is the quadrihedron type of molecule. There is also no imaginary frequency after optimization. The bond length is r(1,2)=143 pm and r(1,3)=r(1,4)=160.1 pm. The bond angle is θ(2,1,3)=θ(2,1,4)=106.7° and θ(3,1,4)=93.1°. Refer to Figure 2 for structure of SOF_2 molecule and its calculated Raman spectra.

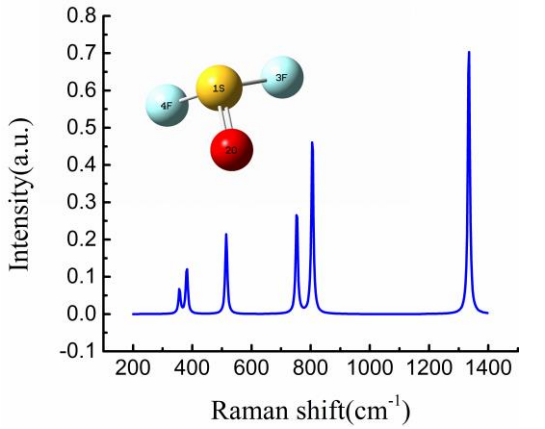

Figure 2: Molecular Structure and Calculated Raman spectra of SOF_2.

There are 6 vibration modes for SOF_2 molecule, they all have Raman active and they are formed into 6 Raman peaks. As shown in Table 2, it can be seen from table that between Raman peak of SOF_2 actually measured by NIST and corresponding simulation result, the maximum deviation is 5.62% and the minimum deviation is 0.05%.

Table 2: Calculation Result of Raman Simulation of SOF_2

Calculated Raman shift/cm^{-1}	Calculated Raman active/(A^4/AMU)	Raman shift actually measured by NIST/cm^{-1}	Deviation/%
356.77	0.8380	378	-5.62
381.43	1.5860	393	-2.94
514.65	2.7927	530	-2.90
753.11	3.8835	747	0.82
805.83	6.7855	808	0.27
1334.3	11.5427	1335	-0.05

3.3 Geometrical Configuration of SO_2 and Analysis of Simulation Result of Raman Spectra

SO_2 is the V-type molecule. After optimization, the bond length is r(1,2)=r(1,3)=143.7 pm and bond angle is θ(2,1,3)=119.2°. Refer to Figure 3 for molecule structure of SO_2 and its calculated Raman spectra.

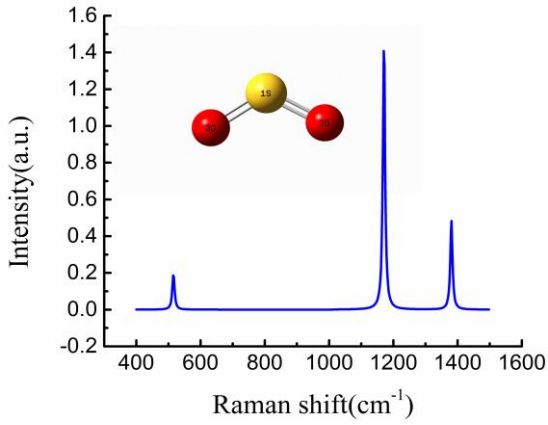

Figure 3: Molecular Structure and Calculated Raman spectra of SO_2.

Table 3: Calculation Result of Raman Simulation of SO_2

Calculated Raman shift/cm^{-1}	Calculated Raman active/(A^4/AMU)	Raman shift actually measured by NIST/cm^{-1}	Deviation/%
515.29	2.4649	518	-0.52
1170.85	21.4065	1151	1.72
1380.64	7.5057	1362	1.37

There are 3 vibration modes for SO_2 molecule. As shown in Table 3, it can be seen from table that the maximum deviation is 1.72% and the minimum deviation is 0.52%.

3.4 Geometrical Configuration of CF_4 and Analysis of Simulation Result of Raman Spectra

CF_4 is the regular tetrahedron type of molecule. After optimization, the bond length is r(1,2)=r(1,3)=r(1,4)=r(1,5)=132.1,
pm and bond angle is θ(2,1,3)=θ(2,1,4)=θ(2,1,5)=θ(3,1,4)=θ(3,1,5)=θ(4,1,5)=109.5°. Refer to Figure 4 for its structure and its calculated Raman spectra.

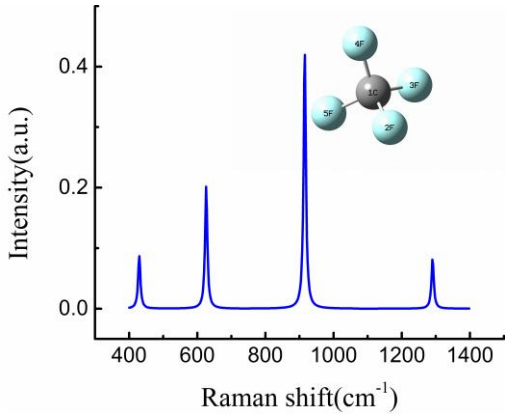

Figure 4: Molecular Structure and Calculated Raman spectra of CF_4.

There are 9 vibration modes for CF_4 molecule, due to CF_4 molecule is symmetrical that different vibration modes may result in the same Raman shift. The comparison between its calculated shift with that actually measured by NIST is shown in Table 4. The maximum deviation is 1.21% and the minimum deviation is 0.71%.

Table 4: Calculation Result of Raman Simulation of CF_4

Calculated Raman shift/cm^{-1}	Calculated Raman active/(A^4/AMU)	Raman shift actually measured by NIST/cm^{-1}	Deviation/%
429.74	0.5477	435	-1.21
429.74	0.5477	435	-1.21
626.07	0.8811	631	-0.78
626.07	0.8811	631	-0.78
626.07	0.8811	631	-0.78
915.49	5.9642	909	0.71
1290.59	0.4207	1280	0.83
1290.59	0.4207	1280	0.83
1290.59	0.4207	1280	0.83

In order to describe the relation between calculated value of Raman spectra and value actually measured by NIST more directly with calculated value as x shaft and actually measured value as y shaft to draw scatter diagram of peak value of Raman spectra of SO_2F_2, SOF_2, SO_2, and CF_4, conduct linear regression and calculate correlation coefficient R^2, just as Figure 5 shows.

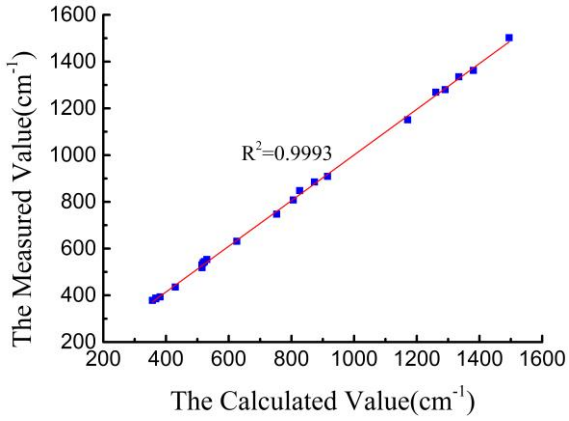

Figure 5: Diagram on Relativity of Calculated Value and Actually Measured value.

4. Conclusions

Structural optimization and Raman spectra calculation of main SF_6 decomposition gas products of electrical equipment are conducted on the level of 6-31G (2df,p) basis set by utilizing DFT and B3LYP method in this research. In addition, calculated shift is compared with shift actually measured by NIST, and the relativity between theoretical calculated value and value actually measured by NIST of Raman spectra of SF_6 decomposition gas products is researched by utilizing correlation coefficient R^2 through linear regression. Following conclusions can be drawn:

Gained theoretically calculated Raman peak is greatly agreed with data actually measured by NIST as the value of correlation coefficient R^2 is 0.9993, verifying reliability of adopting DFT to calculate Raman spectra of SF_6 decomposition products.

This research lays a good foundation for quantitative inspection of SF_6 dissolved gases of electrical equipment based on Raman spectra technique.

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