Raman Spectra Characteristics of Carbon Monoxide and Carbon Dioxide Based on the First-Principles Calculation

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Abstract

Carbon monoxide CO and carbon dioxide CO2 are typical and crucial fault characteristic gases extracted from oil immersed power transformer. The Raman spectral characteristics of CO and CO2 are the basis of online detection and analysis with Raman technology. Gas molecular models were established with Gauss View procedure and 6-31G* basis set was selected to simulate the gas molecule atomic orbits. The first first-principles calculation was conducted based on the Gaussian 09W with the B3LYP hybrid density functional theory to research the Raman spectra characteristics of CO and CO2. In this study, the calculation Raman vibration frequency, the calculation Raman activity and the correction Raman vibration frequency were discussed in detail. These results lay a solid foundation for qualitative and quantitative detection of CO and CO2 with Raman method.

Keywords

Raman spectra characteristics, carbon monoxide, carbon dioxide, the first first-principles, density functional theory.

1. Introduction

A security, economic, stable and reliable electrical power system is the basis of the rapid development of national economy and social stability. Power transformer plays an important role in the power transmission and distribution project, and its safe and reliable operation is extremely important for the whole power system. Presently, most power transformers still employ oil-paper insulation. Once faults have happened in a power transformer due to aging, overheating or discharge, some low molecular weight characteristic fault gases like hydrogen H_2, carbon monoxide CO, carbon dioxide CO_2, and some low molecular hydrocarbons are generated and dissolved in the transformer oil[1]. It has been recognized for many years that online monitoring of the concentrations and rates of generation of these gases is one of the most effective methods for transformer condition assessment and fault diagnosis oil.

Over the past few decades, dissolved gas-in-oil analysis (DGA) has been world widely accepted as an effective diagnostic technology for the detection of incipient transformer faults. At present, gas chromatography, electrochemical method, palladium gate field effect transistors, catalytic combustion sensors, semiconductor chemical sensors, Fourier infrared spectrum and photoacoustic spectrum are the mainly methods applied to detect these characteristic fault gases. When used for DGA, some limitations exist. In recent years, Raman spectroscopy has been widely used in detecting and analyzing solid, liquid or gaseous materials with the development of laser technology and charge-coupled devices [2-3]. Based on the Raman effect, laser Raman spectroscopy can infer the structures and properties of solid, liquid or gaseous material by directly measuring its Raman scattering intensity [4-7]. Thus, in this study, gas molecular models of CO and CO_2 were established firstly and then a first first-principle calculation combined with density functional theory was

conducted based on the Gaussian 09W. Finally, their Raman variations of CO and CO_2 were discussed in detail.

2. The Basics Theory of Raman Spectroscopy

Raman occurs when light with the energy of $h\nu_0$ impinges upon a molecule and interacts with the electron cloud and the bonds of that molecule, as shown in Fig. 1. Rayleigh scattering is elastic scattering where there is no energy exchange between the incident light and the molecule. Stokes scattering happens when there has an energy absorption from the incident light, while anti-stokes scattering happens when the molecule emits energy to the incident light.

According to Boltzmann distribution law, the intensity of Raman Stokes is larger than scattering Raman anti-Stokes scattering and the previous one will be used in our experiments. Raman Stokes scattering spectra can be used to simultaneously identify different chemical species because the Raman variation Δν are indicative and reflect the particular structure information of the molecules.

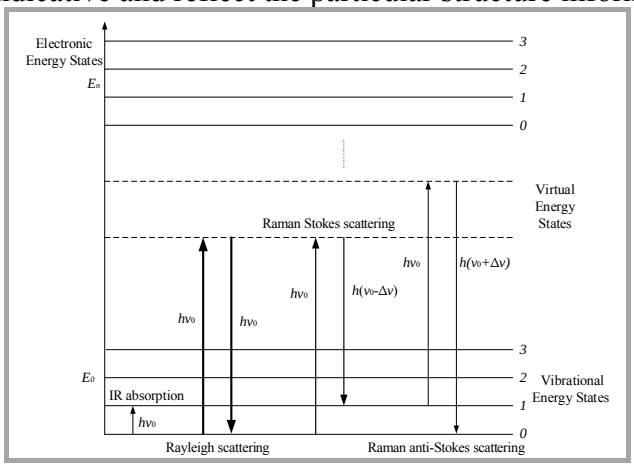

Fig. 1 The principle of Raman scattering

The Raman variation depends on the atomic masse and the bond strength of a molecule [13]. For a diatomic molecule, the Schrodinger equation for the relative motion of two atoms of masses m_1 and m_2 with a parabolic potential energy is

$$-\frac{\hbar^2}{2m_{eff}}\frac{d^e\psi}{dx^2}+\frac{1}{2}kx^2\psi=E\psi \tag{1}$$

Where ħ and k is the reduced Planck constant and force constant of vibrational mode respectively. The effective mass, m_{eff} , is

$$m_{eff}=\frac{m_1m_2}{m_1+m_2} \tag{2}$$

And the Raman variation of the vibrational mode of a diatomic molecule is

$$\Delta\nu=\frac{1}{2\pi c}\left(\frac{k}{m_{eff}}\right)^{1/2} \tag{3}$$

In polyatomic molecules there are several modes of vibration because all the bond lengths and angles may change. For a linear molecule that consists of N atoms, there are 3N - 5 independent modes of vibration.

If the molecule is nonlinear, there are 3N-6 independent vibrational modes. Each normal mode, q, behaves like an independent harmonic oscillator when anharmonicity is neglected, so the Raman variation of the vibrational mode of q is

$$\Delta v_q = \frac{1}{2\pi c}\left(\frac{k_q}{m_q}\right)^{1/2} \tag{4}$$

3. The Basics Theory of Density Functional Theory

Raman spectroscopy is a modulating molecular vibration frequency with the incident light, namely a molecular vibration spectrum. The molecular vibration spectra of fault characteristic gases can be conducted by quantum chemical calculation method, especially the density functional theory calculation.

Gaussian 09W procedure is a powerful and integrated quantum chemical calculation software package. It possesses the function of spectrum prediction and could calculate all kinds of spectra and spectral characteristics of solid, liquid or gaseous materials. Thus in this study, the gaseous molecular models of CO and CO_2 were firstly established and then imported into Gaussian 09W for theoretical calculation. Various kinds of quantum chemical calculation methods were embraced in Gaussian 09W like ab initio calculation, semi-empirical algorithm, and so on. And the B3LYP hybrid density functional theory was selected to research the Raman spectra characteristics of CO and CO_2 here. The basic component elements for CO and CO_2 were C and O, thus 6-31G* basis set was selected to simulate the gas molecule atomic orbits throughout the theoretical calculation.

4. Results and Discussion

The simulation calculation process is as follows. The molecular structures of each established model (bond length, bond Angle, etc.) were optimized to obtain the optimum geometric configuration with the lowest total energy. And then the Raman vibration frequency, the Raman activity under corresponding vibration frequency were calculated and analyzed. It should be stated that the calculated Raman vibration frequency values are somewhat larger than the measured ones with Gaussian 09W procedure, and a reduction factor should be multiplied for correction. The correction factor was set at 0.9614 in this study for the selected B3LYP hybrid density functional theory and 6-31G* basis set.

Fig. 2 The optimized molecular structure of CO and CO2

CO gas is composed of one C atom and one O atom, and CO_2 gas is made up one C atom and two O atoms. The optimized molecular structure of CO and CO_2 are represented in Fig. 2, and the corresponding bond length of C-O in CO and CO_2 are 114.7pm and 118.5 pm.

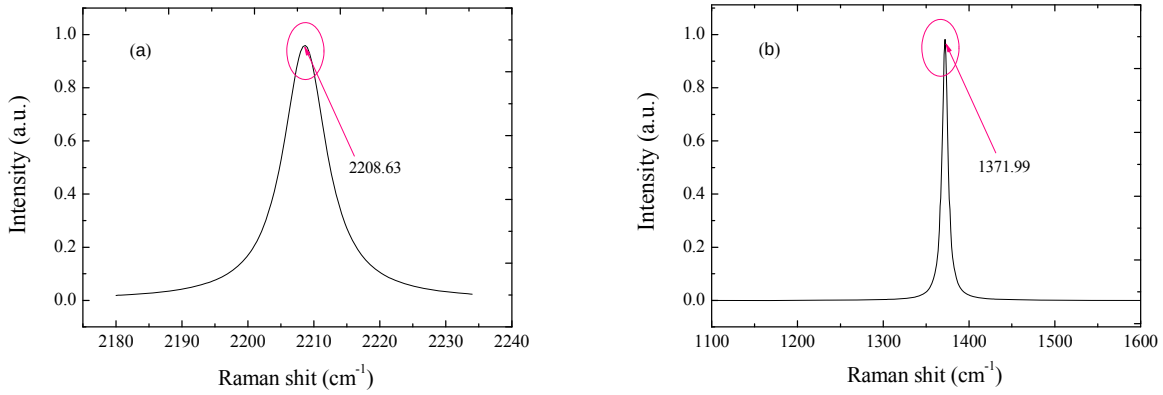

Fig. 3 The calculated Raman spectra of (a) CO and (b) CO2

Fig. 3 shows the calculated Raman spectra of CO and CO_2 gas, and the corresponding calculating results of CO and CO_2, including the calculation Raman vibration frequency, the correction Raman vibration frequency and the calculation Raman activity are displayed in Table 1.

Table 1 The Raman simulation results of CO and CO2

gas	the calculation Raman vibration frequency/cm^{-1}	the correction Raman vibration frequency/cm^{-1}	the calculation Raman activity/(A^4/AMU)
CO	2208.63	2123.38	12.06
CO_2	1371.99	1319.03	14.55

As shown in Table 1, the calculated characteristic Raman variations of CO and CO_2 were 2208.63 cm^{-1} and 1371.99 cm^{-1}, respectively. As mentioned above, the calculated Raman vibration frequency values are usually somewhat larger than the measured ones with Gaussian 09W procedure, and a reduction factor should be multiplied for correction. In this work, the correction factor was set at 0.9614. Therefore, the correction Raman vibration frequency for CO and CO_2 were 2123.38 cm^{-1} and 1319.03 cm^{-1}, respectively.

5. Conclusion

Gas molecular models of CO and CO_2 gases were established with Gauss View procedure and 6-31G* basis set was selected to simulate the gas molecule atomic orbits. Based on the B3LYP hybrid density functional theory, a first first-principles calculation was conducted to research the Raman spectra characteristics of CO and CO_2 gases. The calculated characteristic Raman variations of CO and CO_2 were 2208.63 cm^{-1} and 1371.99 cm^{-1}, respectively. And the correction Raman vibration frequency for CO and CO_2 were 2123.38 cm^{-1} and 1319.03 cm^{-1}, respectively. These theoretical results lay a solid foundation for qualitative and quantitative detection of CO and CO_2 with Raman technology.

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