Mid-infrared absorption spectra of dimethyl methylphosphonate as molecular simulant of nerve agents

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The fine mid-infrared absorption features of dimethyl methylphosphonate vapor have been characterized by using Fourier transforms infrared spectroscopy, and the nitrous oxide was used for calibration purpose. The results show that the main P—O—C and P=O bonds related absorption bands of dimethyl methylphosphonate vapor are peaked at 1050.01 and 1275.76 cm^{-1} respectively, those two bands show continuous characteristics at resolution of 0.125 cm^{-1}.

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Most of gaseous materials show characteristic optical absorptions, especially in the mid-infrared (400—4000 cm^{-1}) band. The optical fingerprints of different gases have made the absorption spectra the unique method of gas analysis for tens of years, both qualitatively and quantitatively. Based on this, the Fourier transforms infra-red (FTIR) spectroscopy has become a mature technique in various applications. However, the bulky and delicate spectroscopic instruments, in connection with the inconvenience of gas sample treatment, makes this method mainly be used in laboratories, strongly restricts its applications. The tunable diode laser absorption spectroscopy (TDLAS) method based on a compact single mode diode laser tuning over an interested wavelength range swiftly to fulfill the function of spectroscopy scan may overcome the drawbacks of FTIR, especially in field on-line applications. However, the lack of suitable diode laser in mid-infrared band strongly restricts its development for decades. The invention of mid-infrared quantum cascade lasers[1] accelerates the research in this field greatly; the appearance of single mode distributed feedback quantum cascade lasers (DFB-QCL)[2] makes the first demonstration of TDLAS in mid-infrared band using QCL[3] possible. Since then, a lot of works in different experimental schemes[4] have been developed.

In the TDLAS using diode lasers, normally the wavelength tuning range is restricted to only a few cm^{-1}, quite different from the scan range of FTIR of hundreds or thousands cm^{-1}, which also makes the measurement scheme and spectral information concerned of TDLAS different from those of FTIR. Therefore, in TDLAS the fine spectral characteristics of the target gases with resolution far below 1 cm^{-1} should be know in advance. For gases, the detailed data base such as HITRAN[5], including the information of about 40 ordinary gases, has existed already, whereas the data are still far from sufficient. Nowadays, the pollution, accidents as well as terrorism have become severe problems. For the development of TDLAS to detection and identification of toxic or pollution gases, more absorption data with higher resolution should be needed. Among great deal of gases, a group of nerve agents such as Sarin (GB), Soman (GD), and Tabun (GA) have attracted special attention because of the potential terroristic attack, but we are still in lack of their fine optical absorption data. The purpose of this work is to get the detailed optical absorption data of those gases at higher resolution. The nerve agents are extremely toxic, for example, the 50% lethal concentration (LC_{50}) of GB is about 5.7 μg/L or $\sim$ 910 ppbv for 10 minutes exposure[6], the airborne concentration sufficient to induce severe effects in 50% of those exposed for 30 minutes (EC_{50}) is < 0.8 μg/L or < 128 ppbv[7]. Because of this, the dimethyl methylphosphonate (DMMP) was selected firstly as the simulant. DMMP was used as fire suppressant in industry, which has similar chemical radicle and therefore similar absorption characteristics as sarin etc., whereas has quite low toxicity. Another gas nitrous oxide (N_2O), which has particular mid-infrared absorption features in conjunction with sufficient HITRAN data, was used as a frame of reference and for the calibration of FTIR spectrometer. The rotational absorption characteristics of DMMP in microwave band have been reported[8,9]. In this letter, the detailed FTIR characteristics of DMMP vapor and N_2O in mid-infrared band have been investigated qualitatively, and their absorption particularities also have been discussed.

DMMP is a colorless liquid at room temperature with boiling point $\geq$ 180 °C, its saturation vapor pressure at 20 °C is 14.5 mg/L or 2618 ppmv, quite similar to the GB of 16.1 mg/L or 2574 ppmv[7]. DMMP is also a preform of GB etc., the structure formulas of DMMP and GB are shown in Fig. 1, from which it can be seen that, the P=O, P—O—C, and P—C chemical bonds are exiting in both of them, so the analogical absorption fingerprint of those bonds should be traceable. The DMMP sample we used is industry liquid with $>$ 98% purity, no further purification was done. In the experiments we just utilized the self-vaporized vapor from the liquid at room temperature, no heating or bubbling was taken.

N_2O are widely used in industry and surgery, it is also an important greenhouse gas. N_2O has plentiful and accurate HITRAN data, in which 47835 transitions with

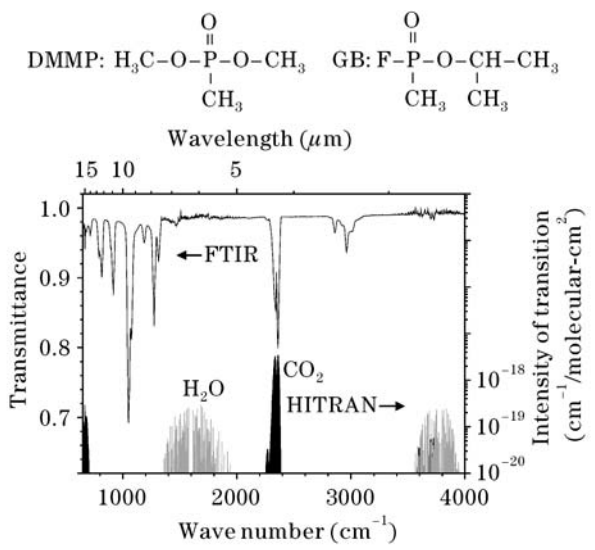

Fig. 1. Measured transmittance spectrum of DMMP vapor at resolution of 4 cm^{-1} (up trace) and HITRAN 2000 data of CO_2 and H_2O (low trace).

precise position and intensity are listed. HITRAN data show that the absorption features of N_2O are quite distinctive, especially in the wavelength range we interested, so is suitable for calibration purpose. N_2O sample we used is standard gas in pressure bottle with > 99.9% purity.

In the measurements, a Nicolet Magna-860 FTIR spectrometer with highest resolution of 0.125 cm^{-1} was used. For better mid-infrared performance, KBr beam splitter and LN_2 cooled MCT-A detector were installed. A home-made single-pass gas cell with gas inlet and outlet valves and gas pumping line was inserted into the sample chamber of the spectrometer. The pathlength of the gas cell is 15 cm with KRS-5 windows at both sides; the reflection loss of each window is about 33% for two surfaces at mid-infrared band, so the total light throughput of the gas cell is around 50%.

In Fig. 2, the measured transmittance spectrum of pure N_2O gas at atmosphere pressure in 700—4000 cm^{-1} region with resolution of 4 cm^{-1} was shown at upside, for comparison, the HITRAN 2000 absorption intensity data of N_2O was also plotted at underside. Comparing the

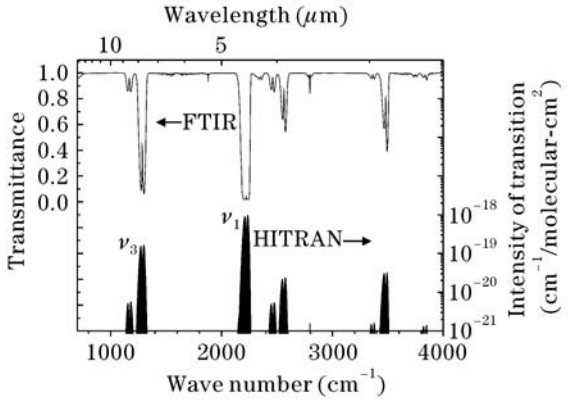

Fig. 2. Measured transmittance spectrum of N_2O (up trace) at resolution of 4 cm^{-1} and HITRAN 2000 data of N_2O (low trace).

measured spectrum with HITRAN, all structural details reflect on the measured result, each peak matches precisely, confirmed the reliability of the HITRAN data and the measurement system. For N_2O molecular with linear structure, the basic symmetric stretching mode ν_1 and asymmetric stretching mode ν_3 appear around at 2224 and 1285 cm^{-1}, respectively. Those two modes show the first and second strong intensities. From Fig. 2 it can be seen that, for our 15-cm gas cell, the absorption of ν_1 band has saturated, the ν_3 band is near saturation.

To practically evaluate the FTIR system in more detail, the absorptance of ν_3 band of N_2O has been measured at resolution of 0.125 cm^{-1} as shown in Fig. 3. In the measurements the N_2O is in three different pressures of high (H), medium (M), and low (L) as labeled. From Fig. 3(a) it can be seen that, almost all HITRAN individual lines in this band with separation in order of 1 cm^{-1} appear in the measured results, the peak positions match to the HITRAN data with precision better than the minimum data spacing of the FTIR spectrometer of 0.06 cm^{-1}. In those measurements, for high pressure sample the absorption has saturated in some region, whereas for medium pressure sample still remains unsaturated. To have a clear look, the absorptance in 1280—1290 cm^{-1} range is enlarged in Fig. 3(b) for medium pressure sample. The HITRAN peaks nearby with separation of about 0.2 cm^{-1} and intensity difference less than one order can be clearly distinguished from the measured results, otherwise only a broadening can be observed. The minimum peak width observed in this band is about 0.24 cm^{-1}, or 4 data spacing.

Keep above results in mind, the absorption features of DMMP vapor have been investigated. Figure 1 shows the measured transmittance spectrum of DMMP vapor

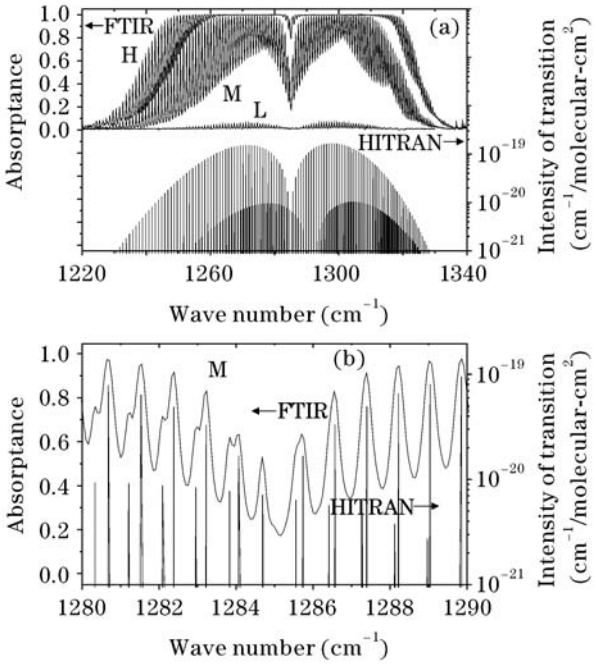

Fig. 3. Measured absorptance spectra (a: up trace) of ν_3 band of N_2O in three different pressures of high (H), medium (M), and low (L) at resolution of 0.125 cm^{-1} and HITRAN 2000 data of N_2O (a: low trace), the 1280—1290 cm^{-1} range is enlarged in (b).

in 700—4000 cm^{-1} region with resolution of 4 cm^{-1}. The HITRAN data of CO_2 and H_2O are also plotted for reference. The first and second strong absorption bands of DMMP appear around 1050 and 1275 cm^{-1}, from the knowing data those two bands can be assigned to the absorption of P—O—C and P=O bonds of DMMP respectively, other weaker bands still need to be assigned. Because of the existence of CO_2 and H_2O in DMMP vapor, their absorption also appears in the measured results, especially the very strong absorption of CO_2 around 2360 cm^{-1}.

To verify whether there exists any fine structure in the P—O—C and P=O absorption bands of DMMP, the absorptances of those two bands were measured at resolution of 0.125 cm^{-1}, as shown in Fig. 4. Those two bands are peaked at 1050.01 and 1275.76 cm^{-1} respectively, spectral continuum extending over a broad range of wavelength, no noticeable sharp lines as that of N_2O can be distinguished at this resolution. The minor fluctuations

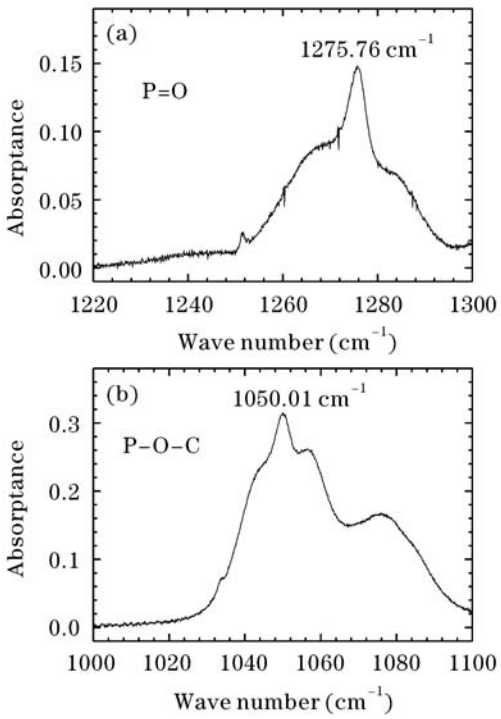

Fig. 4. Measured absorptance spectra of DMMP vapor at resolution of 0.125 cm^{-1}.

in Fig. 4(a) were also caused by trace water. From the results it can be deduced that, the main absorption bands of P—O—C and P=O bonds of DMMP and therefore the nerve agents with similar molecular structure should be continuous bands without sharp lines as those of N_2O. If those bands were used for TDLAS purpose, different strategies should be considered.

In summary, the fine mid-infrared absorption features of DMMP vapor and N_2O have been characterized by using FTIR spectroscopy. The results show that the main P—O—C and P=O bonds related absorption bands of DMMP peaked at 1050.01 and 1275.76 cm^{-1}, respectively, those two bands show continuous characteristics at resolution of 0.125 cm^{-1}.

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