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13. ABSTRACT (Maximum 200 words)

Within the last 12 months of the grant period, we had used our FTIR acquired from Bruker Optics via a DURIP grant to measure the transmission spectra of a few diatomic and triatomic molecules. As a result, we had observed distinct ro-vibrational and rotational transitions in carbon monoxide isotopic variants, nitrogen dioxide, and carbon dioxide. Furthermore, we had used the widely-tunable monochromatic THz source developed by us to measure the spectra of the same four molecules. We would like to note that the spectral measurements in the mid-IR and THz regions are essential to the accurate determination of rotational constants. Following our results, the transition frequencies measured by using two methods are quite consistent with each other.

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"Compact, Coherent, and High-Power THz Sources and Applications"

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Brief Summary

Within the last 12 months of the grant period, we had used our FTIR acquired from Bruker Optics via a DURIP grant to measure the transmission spectra of a few diatomic and triatomic molecules. As a result, we had observed distinct ro-vibrational and rotational transitions in carbon monoxide isotopic variants, nitrogen dioxide, and carbon dioxide. Furthermore, we had used the widely-tunable monochromatic THz source developed by us to measure the spectra of the same four molecules. We would like to note that the spectral measurements in the mid-IR and THz regions are essential to the accurate determination of rotational constants. Following our results, the transition frequencies measured by using two methods are quite consistent with each other.

1. Introduction

Chemical sensing is playing a more and more important role in counter-terrorism, counter-chemical-weapon, homeland security, and remote sensing. For example, being able to accurately determine the chemical concentrations of an unknown species or a mixture of the different species can be of vital importance to the U.S. soldiers in the battlefield. Most of the chemical species in the vapor phase exhibit a series of the absorption peaks due to the pure rotational transitions in the THz region of the electromagnetic spectrum if they possess permanent dipoles. In principle one could fingerprint each molecular species based on a set of the transition peaks in terms of the transition frequencies, strengths, linewidths, and overall profiles. Therefore, a compact and deployable spectrometer operating at room temperature is necessary for implementing such an application. Although the spectra of the rotational transitions are known for some molecules, it is necessary for our team to take the first step towards chemical sensing, i.e. to perform systematic spectroscopic studies on as many molecules as possible. On the other hand, it is worth mentioning that in the visible to mid-infrared regions there are always the congested and unresolved ro-vibrational transition peaks. Therefore, truly fingerprinting molecules may not be feasible in the regions from the visible to the mid infrared. In these regions, it is especially challenging for someone to come up with a scheme to determine the concentrations of the different species in an unknown chemical mixture.

In this final progress report, we summarize our new results on the direct measurements and analyses of the transmission spectra of the two carbon monoxide isotopic variants, nitrogen dioxide, and carbon dioxide using a widely-tunable monochromatic THz source developed by us recently. In addition, we compare these spectra with those measured by using FTIR as well as those predicted using the HITRAN database.

2. Experimental results and discussions

In our experiment, the THz source used by us was implemented by the mixing of two near-infrared laser beams in a GaSe crystal [1]. The output frequency of this THz source was tuned in a rather wide range from 2.8 cm^{-1} to 172 cm^{-1}, the linewidth is about 0.2 cm^{-1}, and the output peak power can be as high as 209 W at 196 μm. At each incident frequency, the transmitted power for a single pass was measured by using a bolometer. Each spectrum was then produced after taking an average over the 30 measurements taken at each frequency. For the spectra of the same molecules measured by using the IFS 66/v vacuum FTIR, the usable range of the FTIR is 0.4-500 μm and the spectral resolution is set to 0.25 cm^{-1}. Furthermore, for each FTIR spectrum illustrated below, 256 interferograms were taken and then averaged. Based on our results, see below, the signal-to-noise ratio by using our tunable THz source is much higher than that using the FTIR. Four identical gas cells each of which had a diameter of 9 mm and a length of 150 mm were filled with the four types of the pure gases with the pressures of 600 torr for the two CO isotopic variants with the atomic number for the carbon atom 12 and 13 (i.e. ^{12}CO and ^{13}CO) and 200 torr for the CO_2 and NO_2 molecules, respectively. The windows of these cells were all made from quartz. The purity of the gases was 99.96% for the ^{12}CO molecules and 99% for the rest of the molecules.

2.1. Transmission spectra in the mid-infrared region

Fig. 1 shows the spectra for the four types of the molecules measured by using the FTIR in the mid-infrared region. The peaks appearing around 3600 cm^{-1} and 4500 cm^{-1} and low transmission in 2000-3000 cm^{-1} were caused by the absorption of the quartz windows. For the

two CO molecules, we observed two distinct peaks for each of them, which were located at 4237.1 cm^{-1} and 4294.1 cm^{-1} for the ^{12}CO molecules and 4123.3 cm^{-1} and 4201.5 cm^{-1} for the ^{13}CO molecules, respectively. The frequencies for these two peaks were differed by the amounts of 113.8 cm^{-1} and 92.6 cm^{-1} between the two isotopic variants. Such differences were due to the difference of the masses for the two isotopic carbon atoms. According to Ref. [2], these two peaks are assigned to the vibrational transition bands ($v = 0 \rightarrow 2$). It is important for us to note that due to the collision-induced linewidth broadenings under a relatively high pressure in our experiment, we could not resolve any single ro-vibrational transition line within each of the two apparent peaks in Fig. 1(a) and (b) [3].

For the NO$_2$ free radical, there were five distinct transition peaks appearing at the frequencies of 2635.0 cm^{-1}, 2917.8 cm^{-1}, 2981.7 cm^{-1}, 3119.0 cm^{-1}, and 3438.2 cm^{-1}, respectively. These five transition peaks were unusually sharp under the pressure of 200 torr. Based on Ref. [4] only two of these five peaks are close to 2907.4 cm^{-1} and 3199.0 cm^{-1} which were observed previously. On the other hand, for the CO$_2$ molecules there were also two absorption peaks located at 4223.6 cm^{-1} and 4287.4 cm^{-1}. These two transitions were quite close to those for the ^{12}CO molecules. However, they significantly deviated from those measured previously on the CO$_2$ molecules, i.e. 4006.0 cm^{-1}, 4030.3 cm^{-1}, and 4416.2 cm^{-1} [5]. One can also see a transition peak near 2265 cm^{-1}, see Fig. 1(c). Due to the very high absorption of the quartz window below 2500 cm^{-1}, however, this absorption peak was not very obvious. The transition frequency of this peak was close to those for a series of the ro-vibrational transition peaks centered at 2076.9 cm^{-1} [5].

2.2. Transmission spectra in the THz region

Using the widely-tunable THz source, we first measured the spectra of the ^{12}CO and ^{13}CO

molecules, respectively, see Figs. 2 and 3. For the ^{12}CO molecules, by comparing the spectra

measured using the two different techniques we had identified four transition peaks located at

30.1 cm^{-1}, 33.8 cm^{-1}, 38.3 cm^{-1}, and 41.3 cm^{-1}, respectively, from the spectrum obtained by using

our widely-tunable THz source, see Fig. 2(a). The frequencies of these transitions are in a good

agreement with 30.3 cm^{-1}, 33.0 cm^{-1}, 37.0 cm^{-1}, and 43.0 cm^{-1}, respectively, measured using the

FTIR. According to Ref. [6], these four frequencies correspond to the transitions of $7 \rightarrow 8$, $8 \rightarrow$

9, $9 \rightarrow 10$, and $10 \rightarrow 11$, respectively, where each pair of the integers on the two sides of each

arrow label the initial and final rotational quantum states. On the other hand, for the ^{13}CO

molecules, we identified eight peaks at 23.9 cm^{-1}, 26.9 cm^{-1}, 29.9 cm^{-1}, 32.6 cm^{-1}, 36.1 cm^{-1}, 39.3

cm^{-1}, 44.6 cm^{-1}, and 46.8 cm^{-1}, respectively, in the spectrum measured by using the tunable THz

source, see Fig. 3(a). The frequencies of these eight peaks are in a good agreement with those

measured by us using the FTIR, i.e. 24.6 cm^{-1}, 27.2 cm^{-1}, 30.7 cm^{-1}, 33.1 cm^{-1}, 36.8 cm^{-1}, 40.6

cm^{-1}, 44.8 cm^{-1}, and 47.9 cm^{-1}, respectively. In addition, these two sets of the transition

frequencies are consistent with those calculated via the HITRAN database [7]. By comparing the

two sets of the transition frequencies for the ^{12}CO and ^{13}CO molecules measured by using the

tunable THz source, one can see that the four frequencies for the ^{12}CO molecules are slightly

higher than the respective ones for the ^{13}CO molecules. In Table 1, we listed the differences of

the respective four transition frequencies measured by using the two techniques. According to

Table 1, the differences determined by using the tunable THz source are much closer to those

predicted by using the HITRAN database [7] than those using the FTIR. In addition, it appears to

us that using the tunable THz source, the signs of the differences are correct according to the

theory [8]. Moreover, the increasing trend of the frequency difference as the transition frequency

is increased is also consistent with the theory [8]. However, this is not the case for the frequency differences measured by using the FTIR. The small differences between the respective transition frequencies of the two isotopic variants can be attributed to the slightly larger rotational moment of inertia for the ^{13}CO molecules. This comparison illustrates the advantage of using our widely-tunable THz source in the low-frequency region. Basically, by measuring the differences of the respective transition frequencies for the two CO isotopic variants, we can differentiate between them.

We also measured the spectrum of the transmittance for the NO_2 molecules using the tunable THz source, see Fig. 4(a). According to Fig. 4, we identified five peaks for the frequency higher than 45 cm^{-1}, i.e. 47.2 cm^{-1}, 50.5 cm^{-1}, 52.1 cm^{-1}, 54.0 cm^{-1}, and 55.6 cm^{-1}, and five below it, i.e. 43.2 cm^{-1}, 40.9 cm^{-1}, 35.2 cm^{-1}, 30.5 cm^{-1}, and 29.4 cm^{-1}. These ten frequencies are consistent with those measured by using the FTIR, i.e., 29.5 cm^{-1}, 30.1 cm^{-1}, 34.7 cm^{-1}, 40.9 cm^{-1}, 44.4 cm^{-1}, 47.9 cm^{-1}, 49.7 cm^{-1}, 51.2 cm^{-1}, 53.5 cm^{-1}, and 55.0 cm^{-1}, respectively, see Fig. 4(b). Moreover, the transition frequencies of the five peaks above 45 cm^{-1} well matched those measured previously using the different FTIR [9]. In the frequency range of below 45 cm^{-1}, however, we have not found any measurements of the transition frequencies for the NO_2 molecules. It is well known that the O-N-O angle is approximately 134°. In addition, there are 17 valence electrons for each NO_2 radical. Therefore, such a radical exhibits a large number of the transitions due to the magnetic interactions among electron spin, molecular rotation, and nuclear spin. For example, within the range of 20-26 cm^{-1}, there are 1,000 transition lines predicted by the HITRAN database [7]. Therefore, more work definitely needs to be carried out by us on the NO_2 molecules in the future.

Finally, for the CO_2 molecules we had also measured the transmission spectrum using the tunable THz source, see Fig. 5(a). By comparing this spectrum with that using the FTIR, see Fig. 5(b), we identified eight transitions with their frequencies 30.3 cm^{-1}, 32.9 cm^{-1}, 34.0 cm^{-1}, 35.2 cm^{-1}, 38.0 cm^{-1}, 41.7 cm^{-1}, 45.6 cm^{-1}, and 49.3 cm^{-1}, respectively. They are in a good agreement with those measured by using the FTIR, i.e. 30.7 cm^{-1}, 33.4 cm^{-1}, 34.6 cm^{-1}, 36.4 cm^{-1}, 38.5 cm^{-1}, 42.3 cm^{-1}, 46.9 cm^{-1}, and 50.7 cm^{-1}, respectively. It is important for us to point out that each CO_2 molecule does not possess any permanent dipole moment since the O-C-O angle is 180°. Theoretically speaking, any transition between the two rotational states is forbidden. However, according to Ref. [10], transient dipoles due to the collisions among the CO_2 molecules, i.e. quadrupole-quadrupole interaction, can be induced at a sufficiently high pressure. As a result, the transitions among the rotational states can then take place. For the CO_2 molecules, the frequency spacing between the adjacent rotational transitions was determined to be 1.56 cm^{-1} [10]. Based on the eight frequencies measured by us, the average spacing is about 2.7 cm^{-1}, which is within the same order of magnitude with 1.56 cm^{-1}. We believe that the more careful measurement should yield a better agreement between the two values.

3. Brief Conclusion

In conclusion, during the last 12 months of the grant period we had measured the transmission spectra of the two carbon monoxide isotopic variants, nitrogen dioxide, and carbon dioxide, by using the widely-tunable monochromatic THz source developed by us previously. We had compared our results with those obtained by us using the FTIR, as well as those predicted by using the HITRAN database. Following our measurements, we had identified many transition peaks for the four species of the diatomic and triatomic molecules. Based on our

results, one can see that these four molecules exhibit different rotational-transition peaks. In order to identify a specific molecular species, it may be possible for us to develop a rigorous software to match the transition peaks measured in the THz region with those stored in the data library in terms of the relative strengths, transition frequencies, and peak linewidths.

According to our results, the signal-to-noise ratio by directly frequency-tuning the monochromatic THz source is much higher than that using the Bruker-Optics FTIR. As a result, we have demonstrated that we could use our tunable THz source to differentiate between the two CO isotopic variants with ^{12}C and ^{13}C. There is an additional advantage of using a tunable coherent THz source over FTIR, i.e. when the multiple passes are used, the sensitivity of the measurements could be significantly improved. If the quartz windows are replaced by other materials for the gas cells, the signal-to-noise ratio could be further improved. Indeed, for all the spectra measured by us, see Figs. 2-5, the transmittances were significantly decreased as the transition frequency was increased due to the absorption of the quartz windows in the THz region.

Based on our results presented here and those for the relatively larger molecules published by us previously [11], there is a tradeoff when choosing the frequency range in the THz region for chemical sensing. This is due to the fact that the lower transition frequency the lower oscillator strength. After carefully analyzing our results, we conclude that the optimum frequency range for chemical sensing should be150 GHz – 3 THz (5-100 cm^{-1}). As a concluding remark, we believe that the direct measurement of the transmission spectrum by frequency-tuning our monochromatic THz source will eventually become an effective technique for the detection and identification of a chemical species in the vapor phase.

4. Publications

Under this support of this grant, we have published three journal papers in Appl. Phys. Lett. [1], Laser Phys. Lett. [11], and J. Nonlinear Opt. Phys. & Mats. [12], respectively, and three SPIE proceedings papers [13-15]. In addition, we have made eight presentations in the national and international conferences such as CLEO, LACSEA, LEOS, and SPIE [16-23].

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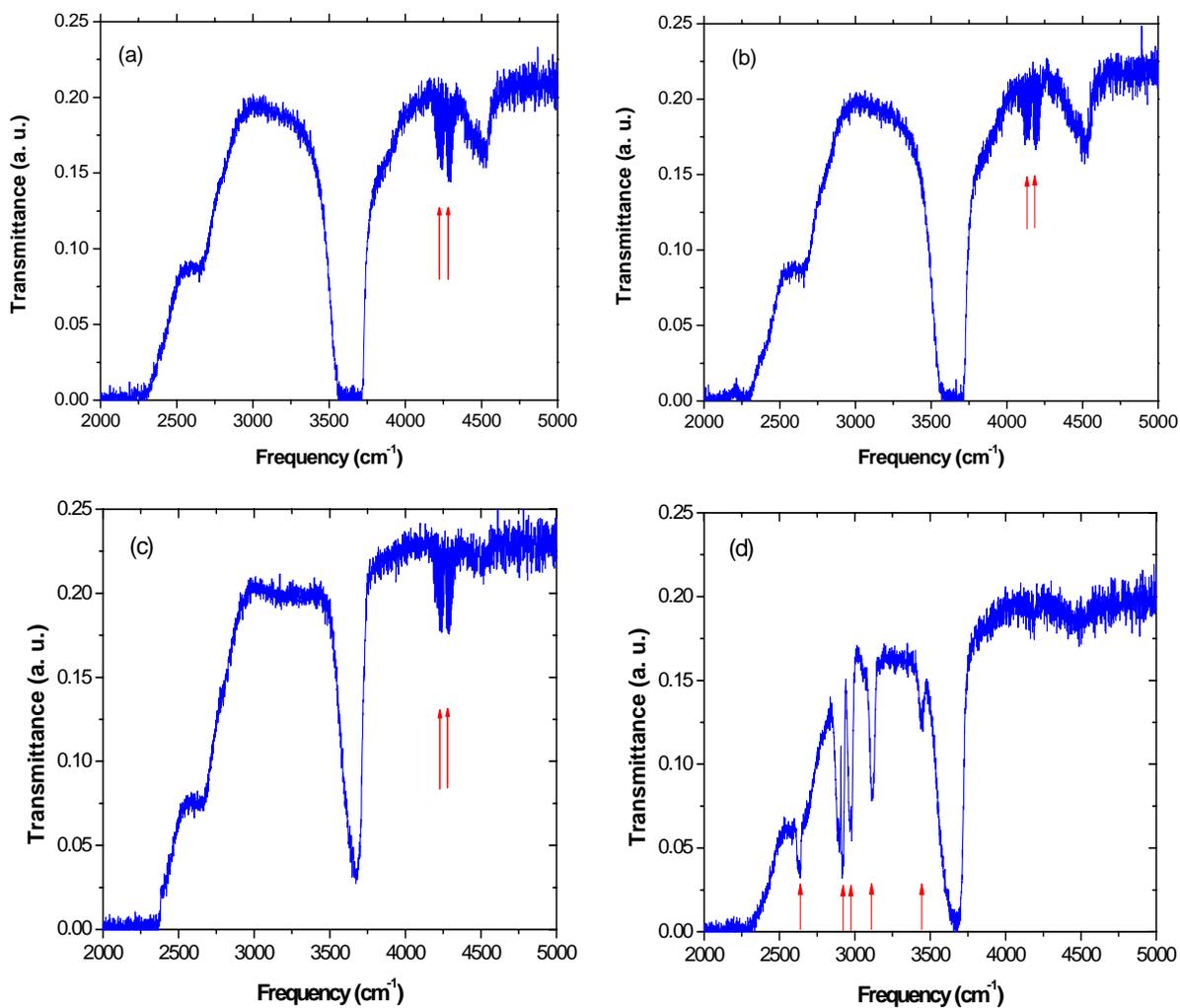
Fig. 1. Transmission spectra in the mid-infrared region measured for (a) ^{12}CO, (b) ^{13}CO, (c) CO_2, and (d) NO_2 molecules. Arrows indicate observed transitions.
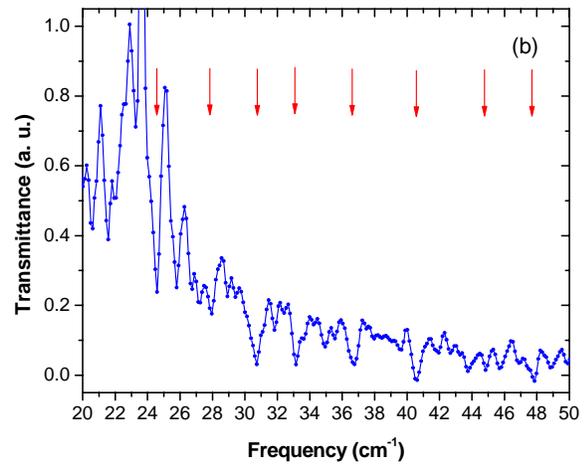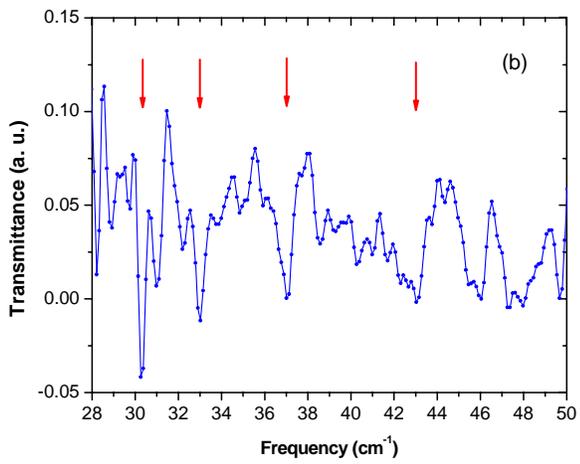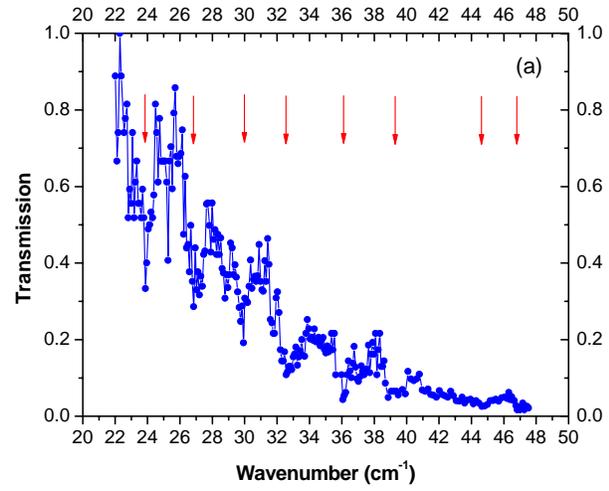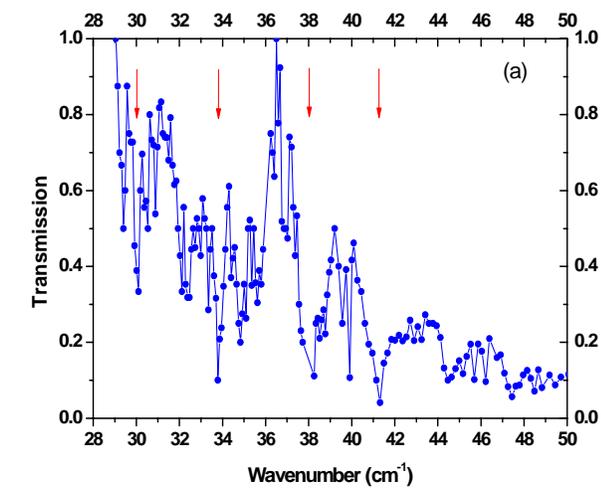
Fig. 2. Transmission spectrum for ^{12}CO molecules using (a) tunable THz source and (b) FTIR. Arrows mark rotational transitions.

Fig. 3. Transmission spectrum for ^{13}CO molecules using (a) tunable THz source and (b) FTIR. Arrows mark rotational transitions.
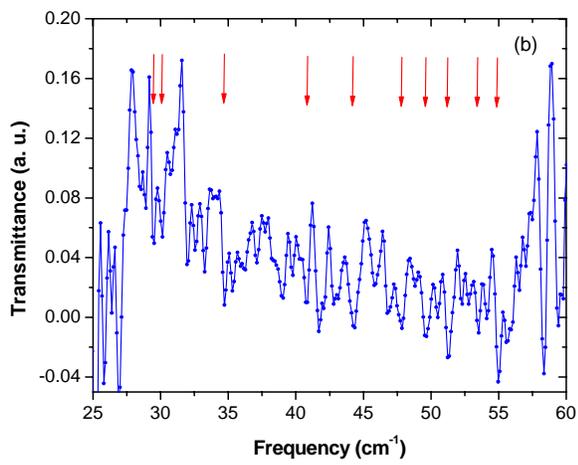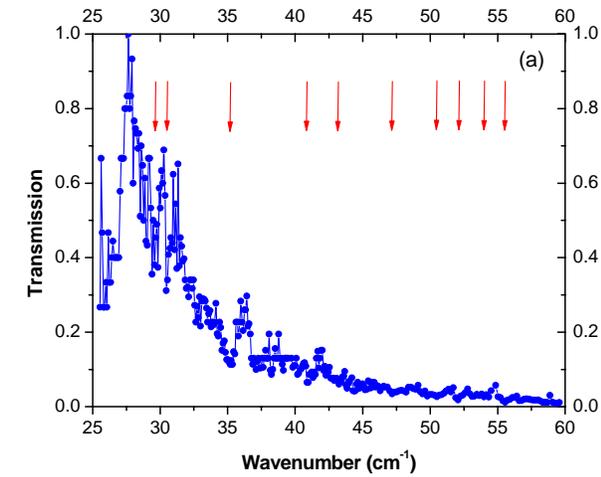
Fig. 4. Transmission spectrum for NO₂ molecules using (a) tunable THz source and (b) FTIR. Arrows mark rotational transitions.
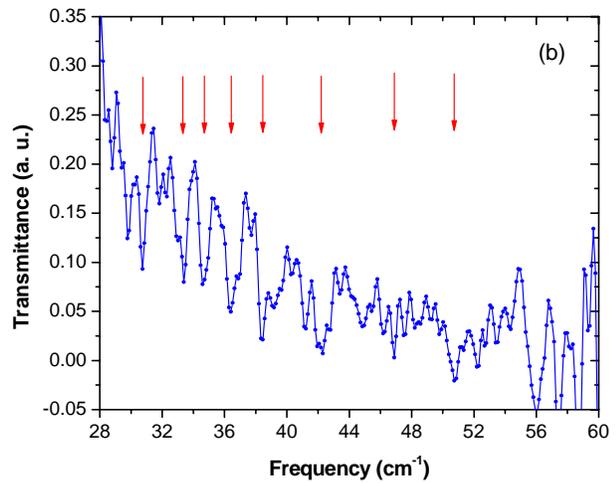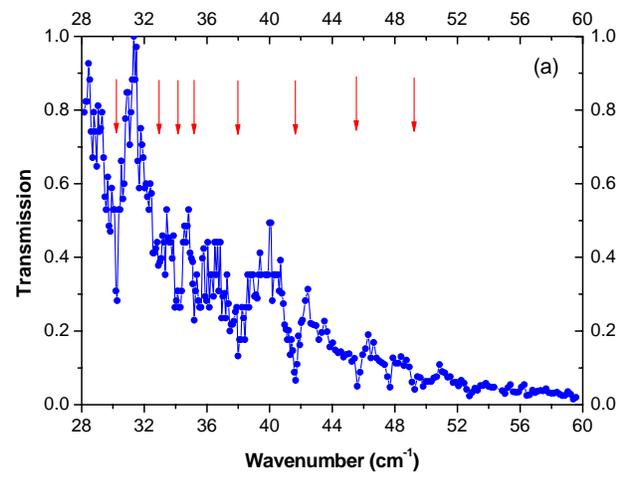
Fig. 5. Transmission spectrum for CO₂ molecules using (a) tunable THz source and (b) FTIR. Arrows mark rotational transitions.

Table 1. Frequency differences between ^{12}CO and ^{13}CO molecules for respective four transitions measured by using widely-tunable THz source and FTIR, and predicted by HITRAN database.

Transition	7→8	8→9	9→10	10→11
Tunable THz source (cm^{-1})	0.2	1.2	2.2	2.0
FTIR (cm^{-1})	-0.4	-0.1	0.2	2.4
HITRAN (cm^{-1})	1.4	1.5	1.7	1.9