Raman spectra and cross sections of ammonia, chlorine, hydrogen sulfide, phosgene, and sulfur dioxide toxic gases in the fingerprint region 400-1400 cm^{-1}

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Raman spectra of ammonia (NH_3), chlorine (Cl_2), hydrogen sulfide (H_2S), phosgene ($COCl2$), and sulfur dioxide (SO_2) toxic gases have been measured in the fingerprint region 400-1400 cm^{-1}. A relatively compact (< 2'x2'x2'), sensitive, 532 nm 10 W CW Raman system with double-pass laser and double-sided collection was used for these measurements. Two Raman modes are observed at 934 and 967 cm^{-1} in NH_3. Three Raman modes are observed in Cl_2 at 554, 547, and 539 cm^{-1}, which are due to the 35/35 35/37, and 37/37 Cl isotopes, respectively. Raman modes are observed at 870, 570, and 1151 cm^{-1} in H_2S, $COCl_2$, and SO_2, respectively. Values of $4.63\pm0.32\times10^{-31}$, $1.72\pm0.12\times10^{-29}$, $4.09\pm0.29\times10^{-30}$, $2.05\pm0.14\times10^{-29}$, and $3.87\pm0.27\times10^{-29}$ cm^2 were determined for the Raman cross section of the 967 cm^{-1} mode of NH_3, sum of the 554, 547, and 539 cm^{-1} modes of Cl_2, 870 cm^{-1} mode of H_2S, 570 cm^{-1} mode of $COCl_2$, and 1151 cm-1 mode of SO_2, respectively, using the Raman cross section of $4.5\pm0.18\times10^{-30}$ cm^2 for the 1285 cm^{-1} mode of CO_2 as the reference.

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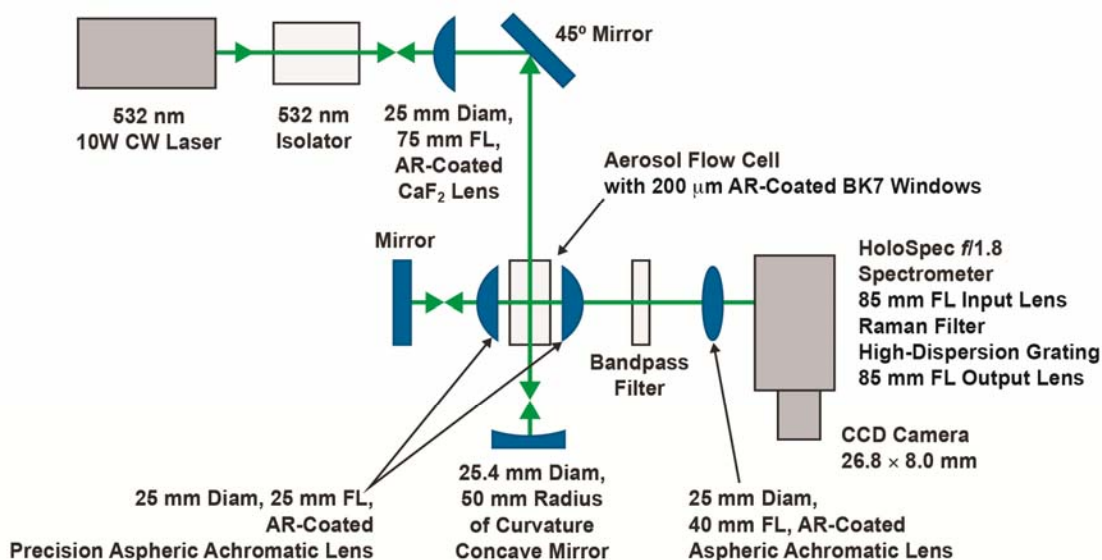
recommendations are those of the authors, and do not necessarily represent the view of the US Government.

I. INTRODUCTION

The Raman spectra and cross sections of toxic gases are important for the detection of these gases using Raman spectroscopy in the fingerprint region 400-1400 cm^{-1}. Raman cross sections of a number of gases (CH_4, C_2H_6, C_3H_8, C_6H_6, CO, CO_2, F_2, HBr, HCl, HF, H_2, H_2O, H_2S, N_2, NH_3, ND_3, NO, N_2O, O_2, O_3, and SO_2) have been reported previously.[1-6] In this paper, we report the measurement of the Raman spectra and cross sections of ammonia (NH_3), chlorine (Cl_2), hydrogen sulfide (H_2S), phosgene (CCl_2O), and sulfur dioxide (SO_2) toxic gases in the fingerprint region 400-1400 cm^{-1} using the Raman cross section of the 1285 cm^{-1} mode of carbon dioxide (CO_2) as the reference.[7]

II. EXPERIMENTAL

Figure 1 shows a schematic of the optical setup of the Raman system.[8] Pump laser propagates in the horizontal direction (z-axis) through the flow cell. The laser was polarized perpendicular to the direction of propagation (z-axis). The Raman signal is collected along the x-axis. The magnification M of the image of the laser focal spot on the spectrometer slit is 1.6, which is the ratio of the 40 mm focal length focusing lens and the 25 mm focal length collection lens. The diameter D of the laser focal spot, located in the center of the flow cell, was 50 μm.

FIG. 1. Schematic of the optical setup used for the Raman system.

Ammonia (34 L of 200 ppm balance nitrogen) was purchased from Icon Safety. Hydrogen sulfide (34 L of 50 ppm balance nitrogen) was purchased from Cross Company. Carbon dioxide (103 L of 4.97 ppm balance air), chlorine (103 L

of 4.60 ppm balance air), phosgene (103 L of 0.90 balance nitrogen), and sulfur dioxide (103 L of 1.00 ppm balance air) were purchased from Airgas. The actual gas concentrations of CO_2, Cl_2, $COCl_2$, and SiO_2 were determined to ±5% accuracy by Airgas by direct comparison to calibration standards traceable to N.I.S.T. weights and/or N.I.S.T. Gas Mixture reference materials. The accuracy of the other gases is also assumed to be ±5%. The flow rate of the gases through the flow cell was ~ 0.5 LPM.

III. RESULTS and DISCUSSION

Figure 2 shows the Raman spectrum for the 1265 and 1285 cm^{-1} modes of the 4.97-ppm CO_2 obtained with 10 W laser power and 15 second signal integration time. The spectrum of Fig. 2 is the average of 9 scans for a total signal integration time of 135 s. The Raman signal for the 1285 cm^{-1} mode integrated over the 1280-1290 cm^{-1} spectral range and corrected for the underlying background is 1.73×10^3 counts. The Raman cross section for the 1285 cm^{-1} mode of CO_2 is 4.5×10^{-30} cm^2 deduced from the measured value of 51.6×10^{-36} m^2/sr for 488 nm excitation in Ref. 7.
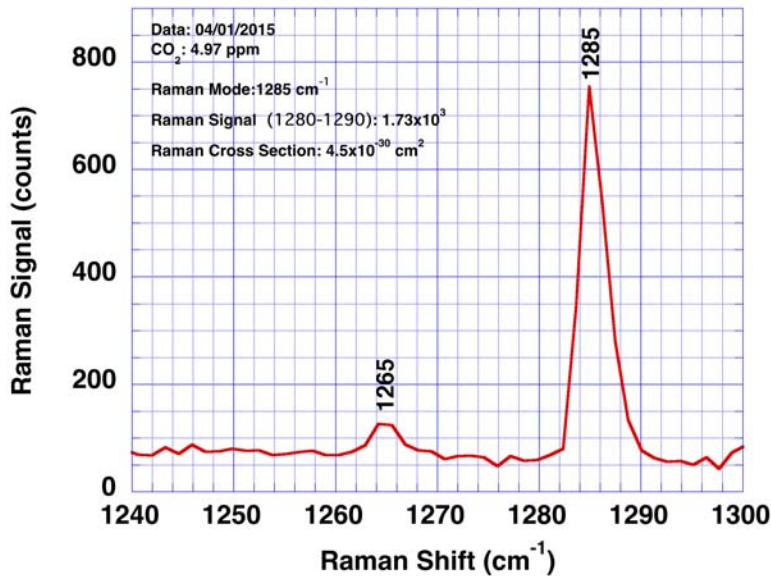

FIG. 2. Raman spectrum (average of 9 scans) for the 1265 and 1285 cm^{-1} modes of 5 ppm CO_2 obtained with 10 W laser power and 15 s signal integration time for each scan.

Figure 3 shows the Raman spectrum (average of 9 scans) of 200 ppm NH_3, which shows two Raman modes at 934 and 967 cm^{-1}, in agreement with the infrared (IR) spectrum.[9] The Raman signal for the 967 cm^{-1} mode integrated over the 950-981 cm^{-1} spectral range and corrected for the underlying background is 7.17×10^3 counts. Using values of 7.17×10^3 and 1.73×10^3 counts for the Raman signals of NH_3 and the 1285 cm^{-1} mode of CO_2, values of 200 and 4.97 ppm for the concentration of NH_3 and CO_2, respectively, and a value of 4.5×10^{-30} cm^2 for the Raman cross section of the 1285 cm^{-1} mode of CO_2, we obtain a value of $4.63 \pm 0.32 \times 10^{-31}$ cm^2 for the

3

Raman cross section of the 967 cm^{-1} mode. The Raman signal for the 934 cm^{-1} mode integrated over the 921-950 cm^{-1} spectral range and corrected for the underlying background is 6.93x10^3 counts, which yields a value of 4.48±0.31x10^{-31} cm^2 for the Raman cross section of the 934 cm^{-1} mode. The 0.3 (7%) accuracy of the Raman cross section of the 967 and 934 cm^{-1} modes of NH$_3$ is due to the 5% accuracy of the NH$_3$ concentration and 4% accuracy of the Raman cross section of CO$_2$, and 3% accuracy of the Raman signal.
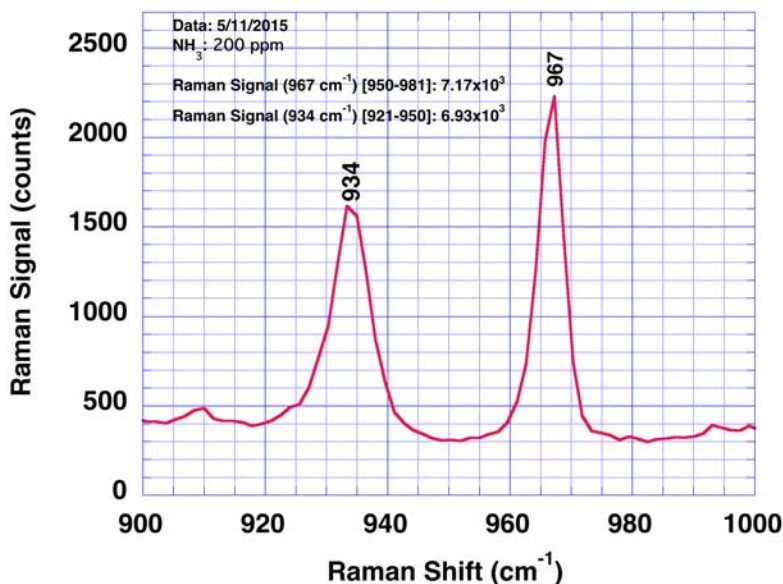

FIG. 3. Raman spectrum (average of 9 scans) for the 934 and 967 cm^{-1} modes of 200 ppm NH$_3$ obtained with 10 W laser power and 15 s signal integration time for each scan.

Chlorine is a diatomic molecule, which has a single vibrational mode that is Raman active. But Cl$_2$ has two stable isotopes ^{35}Cl (78.76%) and ^{37}Cl (24.24%). Therefore, we expect three Raman modes, which are due to the ^{35}Cl^{35}Cl, ^{35}Cl^{37}Cl, and ^{37}Cl^{37}Cl isotopic molecules. Figure 4 is the Raman spectrum (average of 9 scans) of 4.60 ppm Cl$_2$, which shows three Raman modes at 554, 547, and 539 cm^{-1} in agreement with those reported by Hochenbleicher and Schrotter.[10] The 554 cm^{-1} mode is due to the more abundant isotopic molecules ^{35}Cl^{35}Cl. The 547 cm^{-1} mode is due to the ^{35}Cl^{37}Cl isotopic molecules. The 539 cm^{-1} mode is due to the ^{37}Cl^{37}Cl isotopic molecules. Frequency separation between these modes is expected to be 7.4 cm^{-1} based on the masses of the two isotopes. The relative Raman signals of the 554, 547, and 539 cm^{-1} modes should be 1.00, 0.31, and 0.10, respectively, based on the relative abundance of ^{35}Cl and ^{37}Cl isotopes. The relative strengths of the observed modes is consistent with those expected.

The Raman signal of Cl$_2$ integrated over the 530-561 cm^{-1} spectral range and corrected for the underlying background is 6.11x10^3, which yields a value of 1.72±0.12x10^{-29} cm^2 for the Raman cross section of Cl$_2$.
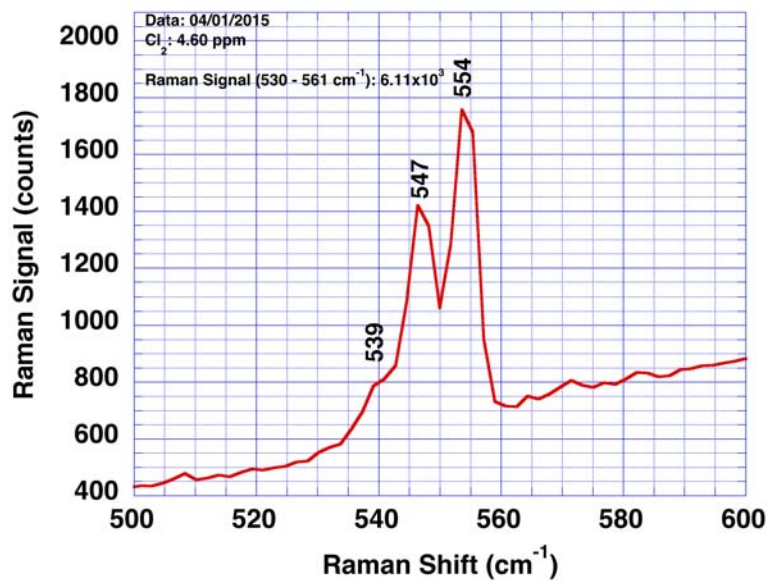
FIG. 4. Raman spectrum (average of 9 scans) for the 539, 547, and 554 cm^{-1} modes of 4.6 ppm Cl_2 obtained with 10 W laser power and 15 s signal integration time for each scan.

Figure 5 is the Raman spectrum (average of 9 scans) of 50 ppm H_2S, which shows the Raman mode at 870 cm^{-1}. This mode has not been reported previously. The Raman cross section of the mode at 2611 cm^{-1} was reported previously. [1, 6]
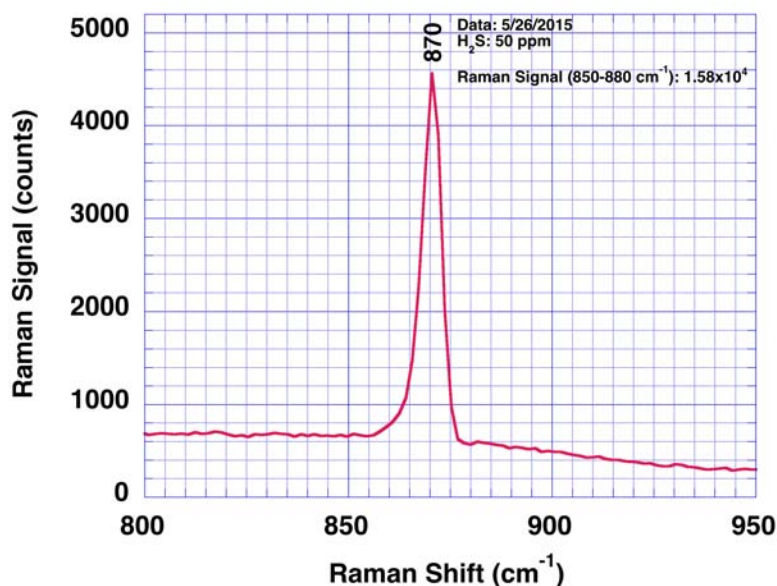

FIG. 5. Raman spectrum (average of 9 scans) for the 870 cm^{-1} modes of 50 ppm H_2S obtained with 10 W laser power and 15 s signal integration time for each scan.

Value of the Raman signal of H_2S integrated over the spectral range 850-880 cm^{-1} range and corrected for the underlying background is 1.58×10^4, which yields a value of $4.09 \pm 0.29 \times 10^{-30}$ cm^2 for the Raman cross section of the 870 cm^{-1} mode of H_2S.

Figure 6 is the Raman spectrum of 0.90 ppm $COCl_2$, which shows the Raman mode at 570 cm^{-1}; there is appreciable fluorescence background of unidentified origin. This mode is due to the Cl-Cl stretch. Our value of 570 cm^{-1} is consistent with the value of 573 cm^{-1} for liquid $COCl_2$ reported by Ananthakrishnan.[11] The value of the Raman signal integrated over the 559-580 cm^{-1} range and corrected for the underlying background is 1.43×10^3, which yields a value of $2.05 \pm 0.14 \times 10^{-29}$ cm^2 for the Raman cross section of $COCl_2$.
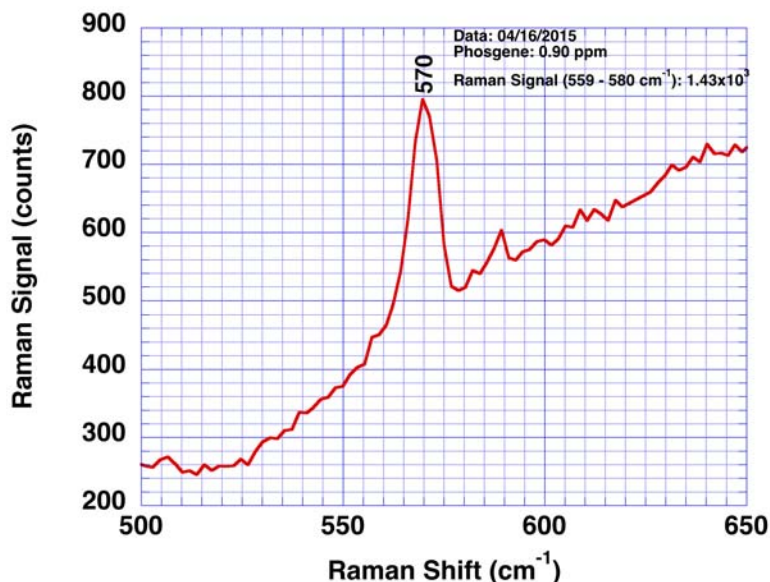

FIG. 6. Raman spectrum (average of 9 scans) for the 570 cm^{-1} mode of 0.90 ppm $COCl_2$ obtained with 10 W laser power and 15 s signal integration time for each scan.

Figure 7 is the Raman spectrum of 1.00 ppm SO_2, which shows the Raman mode at 1151 cm^{-1}. This value of 1151 cm^{-1} is consistent with the value of 1145 cm^{-1} for the liquid SO_2 reported by Dickinson and West.[12] The value of the Raman signal integrated over the 1140-1161 cm^{-1} range and corrected for the underlying background is 2.99×10^3, which yields a value of $3.87 \pm 0.27 \times 10^{-29}$ cm^2 for the Raman cross section of SO_2. Our value of $3.87 \pm 0.27 \times 10^{-29}$ cm^2 for Raman cross section of SO_2 is larger by 1.5x than the value of 2.57×10^{-29} cm^2 deduced from the value of 2.38×10^{-30} cm^2/sr for 514.5 nm excitation reported by Fouche and Chang[1,2] for 514.5 nm excitation. The reason for this discrepancy is not known.
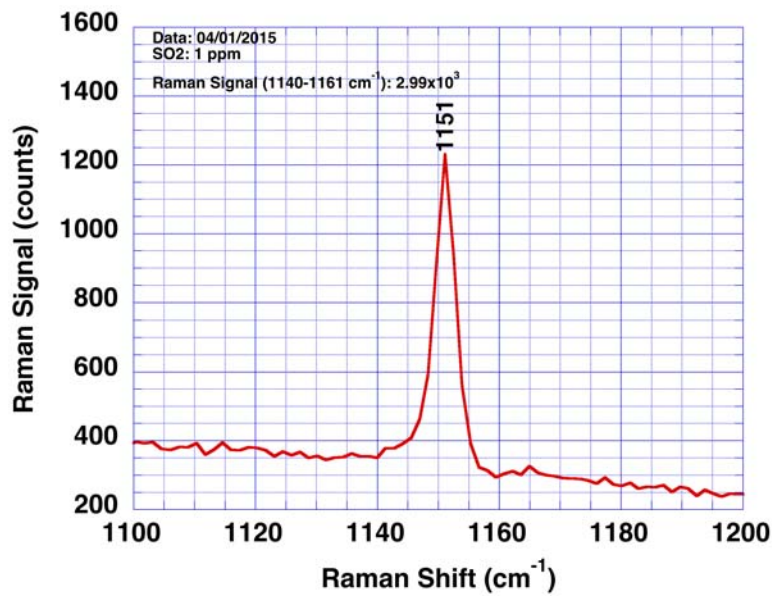
FIG. 7. Raman spectrum (average of 9 scans) for the 1151 cm^{-1} mode of 1.0 ppm SO_2 obtained with 10 W laser power and 15 s signal integration time for each scan.

SUMMARY

The Raman spectra of toxic gases ammonia (NH_3), chlorine (Cl_2), hydrogen sulfide (H_2S), phosgene ($COCl_2$), and sulfur dioxide (SO_2) have been measured in the fingerprint region 400-1400 cm^{-1}. The Raman cross sections of these gases have been determined using the Raman cross section of the 1285 cm^{-1} mode of CO_2 as the reference.

ACKNOWLEDGMENTS

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