The History of Improving Automobile Emissions: Infrared Spectroscopic Analysis of Tailpipe Exhaust over a Several-Decade-Model-Year Range

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Received September 9, 2003. Accepted September 25, 2003.

Abstract: In many urban areas, automobile transportation accounts for the majority of smog-forming emissions, and air pollution control legislation continues to spur the research and development of lower-emission automobiles. We describe here a laboratory project, suitable for the general chemistry or physical chemistry laboratory, which uses Fourier transform infrared (FTIR) spectroscopy for the analysis of automobile exhaust. Using this method, products of both complete and incomplete combustion of gasoline are identified in exhaust under various vehicle-operating conditions. By quantifying the level of carbon monoxide in exhaust from automobiles manufactured over a sixty-model-year range, students are able to understand the factors that reduce the emission of incomplete combustion products.

Introduction

The steady reliance on the automobile for transportation over the past several decades has resulted in a dramatic decline in our nation's air quality. Over 50% of all United States air pollution is generated by motor vehicles, and transportation accounts for over 75% of U.S. CO emissions, nearly 50% of U.S. oxide of nitrogen (NO_x) emissions, and 40% of the volatile organic compounds (VOC) emissions [1]. Ground-level ozone, the most problematic constituent of smog, forms when volatile organics combine with NO_x in the presence of sunlight; urban areas having sunny, warm climates are particularly prone to ozone problems [2]. A strong correlation between breathing smoggy air and an increased incidence of respiratory and cardiopulmonary disease is emerging. In general, slower lung growth in children appears to be associated with exposure to constituents of smog [3]. These findings continue to prompt new legislation associated with motor vehicle emission controls.

In the 1960s, a typical new car produced 228 pounds of smog-forming hydrocarbons in a year; today the typical new car produces less than five pounds annually [4]. Over the past four decades, emissions of carbon monoxide and oxides of nitrogen have also been substantially reduced. For example, a pre-1966 automobile emitted 84 g of CO/mile and 4.1 g NO_x/mile; the current federal standard is 3.4 g CO/mile and 0.4 g NO_x/mile (Tier 1) [5]. Aggressive air pollution control programs in the U.S. stimulated changes in engine design and emission control devices in the 1970s, and later use of reformulated gasoline and low-emission automobiles in some states also mitigated vehicle emissions. Since the phasing out of leaded gasoline in the 1970s, several oxygenated compounds, including ethanol and methyl *tert*-butyl ether, have been used to enhance octane ratings and to reduce carbon monoxide emissions.

Today's college freshmen were born well after many of these air pollution control technologies were implemented. In order for them to weigh the benefits and detriments of new lower-emission-vehicle technologies and legislation, they should have a basic understanding of the chemistry behind air pollution issues, including a knowledge of the constituents of tailpipe emissions, their role in smog formation, and the history of their reduction.

Most states in the U.S., and major metropolitan areas of the world, require annual testing of registered vehicles for CO and hydrocarbon emissions, and in some cities NO_x emissions, through an Inspection and Maintenance (I/M) or "smog-check" program. These programs analyze exhaust gas using a nondispersive infrared (NDIR) instrument, which, when calibrated, allows the measurement of hydrocarbon, CO, and CO_2 concentrations [6, 7]. This laboratory study enables students to collect and analyze their vehicles' gaseous emissions using Fourier transform infrared (FTIR) spectroscopy. The method also allows for specific hydrocarbon identification and quantification of carbon monoxide. We describe here a laboratory experiment that examines the emissions from a sixty-year range of automobiles, from a 1942 Packard convertible to a 2002 Toyota Prius (hybrid automobile). This experiment, and modifications thereof, has been used in our freshman chemistry laboratories, an environmental chemistry course, and the physical chemistry laboratory. Because our university campus is located near Los Angeles, CA, one of the smoggiest cities in the nation where the use of low-emission vehicles is encouraged, the results have been of great interest to students.

Experimental

A simple IR gas cell and collection assembly design allowed the collection of tailpipe gases directly into the IR gas cell. Economical gas cells with IR transparent windows were assembled using glass photochemical reactor cells (Ace Glass #7894) ordered with a 10-cm length and fitted with NaCl windows (McCarthy Scientific, SKU004). Cells were evacuated using a small vacuum manifold system (GlassContour Co., Laguna Beach, CA) equipped with thermocouple manometers (Hastings VT series). Exhaust gases were collected directly into the evacuated cell, eliminating the need to use the vacuum manifold for sample transfers. The exhaust sample collection was achieved by attaching a 40-cm length of vacuum tubing to the cell stopcock and placing the other end of the tubing approximately 15 cm into the car's tailpipe. The stopcock of the cell was slowly opened to

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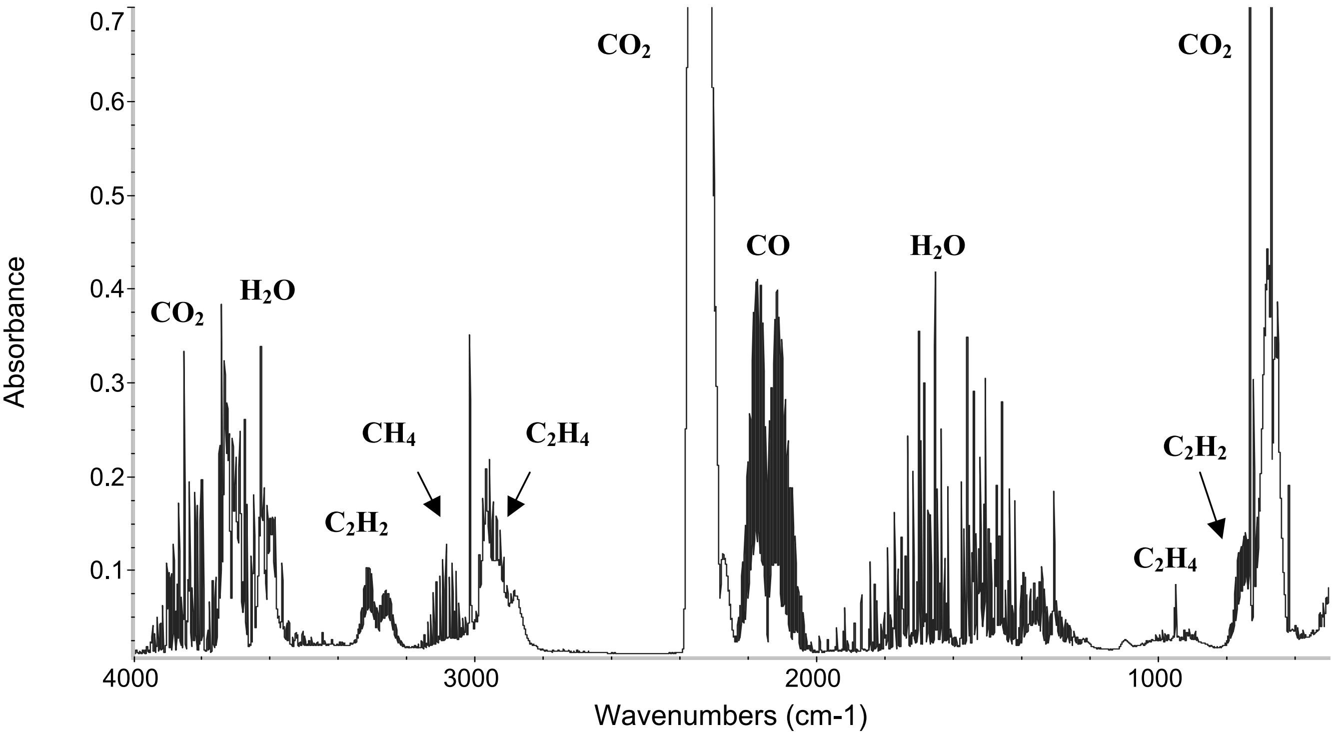

Figure 1. IR spectrum of 1942 packard exhaust (warm-start, idle condition).

draw in the exhaust sample and was closed after approximately 10 seconds. As water from the exhaust condensed on the vacuum tubing, dry lengths of tubing were used for each collection. After several exhaust collections (5 to 10), the IR cell's salt windows tended to fog from exposure to water vapor and were removed and polished using a crystal polishing kit (International Crystal Laboratories, 0009-492). All exhaust collections *must* be conducted outdoors, and we obtained permission from campus parking officials to park student vehicles near our chemistry facilities.

Infrared spectra of exhaust samples were collected using a Thermo-Nicolet Nexus 670 FTIR spectrometer equipped with a MCT detector. Depending upon the analysis, spectral resolutions of either 2 cm^{-1} or 0.125 cm^{-1} were used. Each sample spectrum was obtained by averaging 32 scans and ratioed to a background spectrum of the evacuated gas cell. A background spectrum was collected a few minutes prior to each exhaust sample collection.

The identification of exhaust gas spectral peaks present in the FTIR spectra was achieved by comparison to spectra of the pure standard gases. The vapor from subliming dry ice and evaporating hot water was used to generate spectra of carbon dioxide and water. This was accomplished without the use of gas cells by placing the water/carbon dioxide in a small beaker inside the FTIR sample compartment and allowing the material to pass into the gas phase within the enclosure for approximately 1 min. Students in our physical chemistry laboratories, two of whom served as teaching assistants for the freshman chemistry laboratories, assisted in collecting spectra of pure carbon monoxide and several gaseous hydrocarbons. A 4.00 % CO/air calibration standard (Airgas) was used for CO quantitation studies, or CO/air mixes were prepared by the instructor at percentages ranging from 0.1 to 10% using the vacuum manifold system. All CO gas cylinders were kept inside a laboratory fume hood at all times, and gas cells containing CO/air mixtures were evacuated using the vacuum manifold system in a ventilated fume hood. Laboratory natural gas ports were used as a convenient source (although not a pure one) of methane, and lecture bottles of ethylene (Airgas, 99.5%) and acetylene (Airgas, 99.6%) were supplied from local vendors. Because NO$_x$ emissions are generally present only at ppm levels in exhaust gases of idling vehicles, it was not possible to detect NO$_x$ using 10-cm gas cells; however, other studies have incorporated long-pathlength IR spectroscopy to measure NO$_x$ in automobile exhaust [8].

Tailpipe gases were collected under both warm-start and cold-start conditions. Automobiles that had been driven a considerable distance to our campus were assumed to be running at normal operating temperature, and collections were done while the car was idling or at particular rpm values if the car was equipped with a tachometer. Cold-start emission samples were collected by starting a vehicle and collecting the exhaust after approximately 15 s had elapsed. This time delay was necessary to purge the exhaust manifold of atmospheric gases. Vehicle engines that had been previously started were allowed to cool down for at least one hour before a cold-start collection was initiated.

Results and Discussion

Exhaust samples taken from automobiles with no air pollution control devices yielded the richest infrared spectra. The infrared spectrum of exhaust from a 1942 Packard convertible is shown in Figure 1. Spectral peaks were assigned by comparison to those of the pure standard gases. Freshman students were able to easily identify CO, CO$_2$, CH$_4$, and water vapor in the Packard's exhaust. Other peaks in the C–H stretching and bending regions were assigned by our physical chemistry laboratory students, two of whom served as freshman chemistry teaching assistants, during a high resolution IR rovibrational spectroscopy project. Using published methods, these students collected and analyzed the high resolution (0.125 cm^{-1}) IR spectra of acetylene (C$_2$H$_2$, a linear molecule) [9], methane (CH$_4$, a spherical top) [10], and ethylene (C$_2$H$_4$, a symmetric top). By determining fundamental frequencies and rotational constants from the spectra of the pure gases [9], they then identified these three hydrocarbon constituents in the exhaust sample. It is very likely that the broad spectral band near 3000 cm^{-1} encompasses several overlapping hydrocarbon absorptions, and hydrocarbons other than these three were present in the exhaust sample.

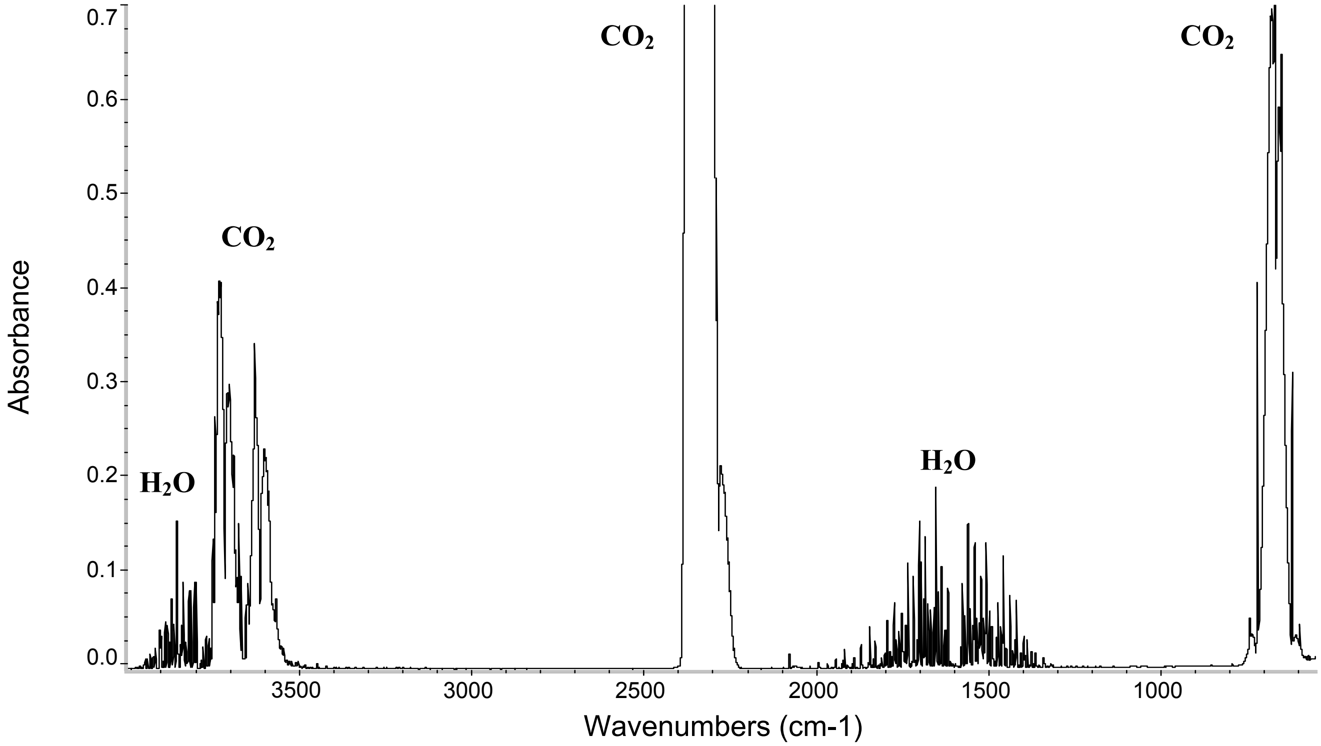

Figure 2. IR spectrum of 2002 Toyota Prius exhaust (warm-start, idle condition).

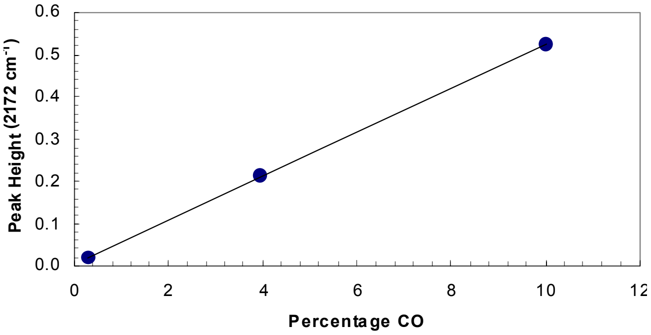

Figure 3. Carbon monoxide calibration plot.

Table 1. Comparison of CO Content of Exhaust from Various Vehicles

Year, Model, and Emission Standard of Passenger Vehicle	Mean % CO (± 1σ) (Idle Conditions)
1942 Packard Model 110 Convertible	8.0 ± 2%
1964 Ford Ranchero	4.5 ± 1%
1980 Mercedes 450 SLC	2.0 ± 0.5%
1990 Toyota Camry	1.0 ± 0.5%
1998 Acura CL (TLEV)	0.4 ± 0.1%
2001 Honda Civic (ULEV)	<0.2 %[a]
2002 Toyota Prius (SULEV)	<0.2 %[a]

[a] below detection limit

The infrared spectrum of the 1942 Packard exhaust was compared to that from a 2002 Toyota Prius (Figure 2). The Prius is a hybrid automobile powered by a four-cylinder gasoline engine boosted by a battery. Under warm-start conditions, no hydrocarbons or carbon monoxide were detected in the Prius' exhaust. Hybrid vehicles like the Toyota Prius and Honda Insight were initially manufactured for use in CA under its aggressive low-emission vehicle (LEV) regulations. Under this program, the Prius is classified as a SULEV (super-ultra-low-emission vehicle), and is now available in most states. SULEVs emit 70% less CO and 96% less hydrocarbons than the minimum federal (Tier 1) standard, and there are several 2003–2004 model year compact and subcompact cars available nationwide that fall under this certification [11]. Carbon monoxide levels measured in all of the SULEV vehicles in this study were below the method's detection limit (0.2% CO, vide infra), assuming the vehicles were warmed up to normal operating conditions. All SULEVs, however, showed detectable CO under cold-start conditions.

Exhaust carbon monoxide content from vehicles manufactured over a 60-year range was quantified using a three-point CO calibration plot where the absorbance at 2172 cm^{-1} was measured (R(7) rotational line, chosen for its intensity and relative distance from overlapping CO_2 and H_2O absorptions) as a function of CO concentration. A typical calibration plot is shown in Figure 3. Because exhaust samples were collected at ca. 1 atm pressure, calibration studies also used CO/air mixtures at 1 atm to avoid problems with pressure broadening, which was found to be significant at 1 atm. A one-point calibration using the purchased 4% calibration mix was sufficient for routine studies. The method detection limit for CO was determined to be 0.2% based on three standard deviations greater than spectral baseline noise. Analyses of the carbon monoxide content of several warmed-up vehicles are summarized in Table 1. Although quantitative comparisons

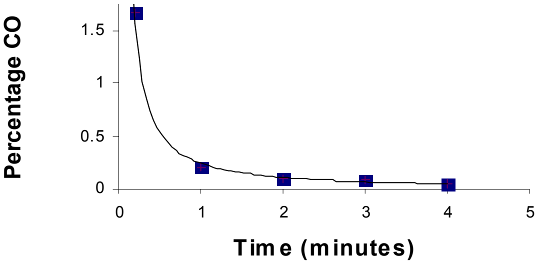

Figure 4. Percentage carbon monoxide in 1998 Acura CL exhaust as a function of time (smooth spline fit to data).

between vehicles are not possible due to different engine types, variations in idle rpm, ambient temperature differences, and other factors, the exhaust from newer-model year vehicles generally showed lower CO levels. Carbon monoxide levels in exhaust from warm-started cars classified in the low-emission-vehicle program (1990 model year and newer in CA) were usually below the method detection limit, except for cars with higher mileage. In general, automobiles utilizing carburetion rather than fuel injection showed higher exhaust CO levels, and automobiles which were not equipped with catalytic converters (pre-1975 model years) showed higher CO and hydrocarbon emissions. A check on the validity of the method was possible as two of the vehicles underwent a CA smog check during the same month that the laboratory experiment was performed. Under idle conditions, the % CO in exhaust measured by the FTIR method differed by no more than 20% from the smog-check result (NDIR method), well within variations expected for ambient temperature, fuel composition, idle RPM and many other factors [7].

Exhaust carbon monoxide levels are the highest when the engine is operated under fuel-rich conditions; that is, when the air in the fuel–air mixture that enters the engine cylinder is insufficient to convert all of the fuel carbon to CO_2. Fuel-rich mixtures are often used during engine warm-up, and, in older cars, at idle, for combustion stability [6]. Hydrocarbon emissions primarily occur because of wall quenching; this occurs when the combustion flame approaches the cooler cylinder walls and the combustion reaction is quenched, leaving an incompletely combusted air–fuel mixture. If these hydrocarbon gases survive combustion in the exhaust manifold and are not further oxidized in a catalytic converter, they are emitted into the atmosphere [6].

The more complete the combustion reaction, the higher the carbon dioxide percentage in the exhaust gas. The exhaust of a normally running engine will contain 13.8 to 15.0% CO_2 by volume [7]. Most state's I/M programs use a four-gas analyzer that measures the amount of CO_2 and O_2 present in exhaust so that the engine's combustion efficiency can be assessed. A very rich fuel mixture will result in high CO and high hydrocarbon readings, with low CO_2 and O_2 readings. In most automobiles equipped with a catalytic converter, carbon monoxide levels in exhaust are the highest when the vehicle is started up cold. As the catalytic converter catalyst begins to warm to operating efficiency (approximately 750 ºC), levels of CO will drop as CO is oxidized to CO_2. Many newer automobiles are equipped with a "mini" or "warm-up" converter located immediately after the exhaust manifold, which reaches the required temperature much more rapidly than the larger, main converter. Over the short time period for converter warm-up (from less than 1 minute to a few minutes depending on vehicle year and model), levels of hydrocarbons in the exhaust will also decline due to (1) precise adjustment of the fuel–air mixture, and (2) oxidation of hydrocarbons to CO_2 and H_2O by the catalytic converter. The decreasing CO content of a vehicle's exhaust as it warms up from a cold start is shown in Figure 4. Spectra over this time period are shown in Figure 5, where the decrease in CO from time zero (startup) to five minutes (warm) can be noted qualitatively with the increases in the CO_2 and H_2O exhaust levels. These results confirm the importance of reducing one's car trips during a given day, as cold-start emissions can account for up to 50% of vehicle CO emissions during a typical vehicle trip [7].

Students were asked to visit their home state's air pollution control board Web site and obtain vehicle emission regulation information in order to evaluate their vehicle's results in light of state and federal emission control inspection standards. In the freshman laboratories, the project complemented a chapter in our lecture textbook on atmospheric gases and pollution. The project was augmented in an environmental chemistry course to investigate other student hypotheses including (1) the effect of engine speed on levels of hydrocarbons and CO, (2) the effect of gasoline octane number and type of oxygenate used (ethanol versus methyl *tert*-butyl ether) on levels of emissions, and (3) a comparison of exhaust constituents from diesel and gasoline-powered passenger cars. Because Pepperdine University students are allowed to use their own cars in the study and are well aware of the Los Angeles air pollution problem, they have been especially interested in the outcomes of these experiments.

The project described here is best adapted to a relatively small laboratory class size (less than 18 students), which has two supervisors available (e.g., one instructor and one teaching assistant) to assist in the exhaust collection and FTIR operation. It was possible to collect an exhaust sample from at least 15 vehicles over a 3-hour laboratory period with efficient student supervision and nearby vehicle parking. A second week was necessary to study the effect of warm-started versus cold-started vehicles. If two supervisors are not available, or if laboratory classes are larger, students could be polled about their vehicle type and year before the exercise to avoid collecting exhaust samples from very similar vehicles. Alternatively, a comparison between exhaust collected from one new vehicle and from an older one lacking a catalytic converter (pre-1975) is sufficient to demonstrate the objective of the project.

Conclusions

Laboratory projects that demonstrate the application of chemistry to an essential consumer product, such as the automobile, can be especially effective in communicating chemical concepts. We have described here an experiment that simulates automobile I/M programs required in most states, but uses a FTIR spectrophotometer to further understand and extend the results from a chemical perspective. Utilization of a FTIR allows identification of CO, CO_2, H_2O, and specific hydrocarbons in automobile exhaust, and quantitation of carbon monoxide is easily achieved. By studying vehicles manufactured over an extensive model-year range, and under both cold and warm operating conditions, students are able to note the advances made by pollution control devices in reducing smog-forming emissions.

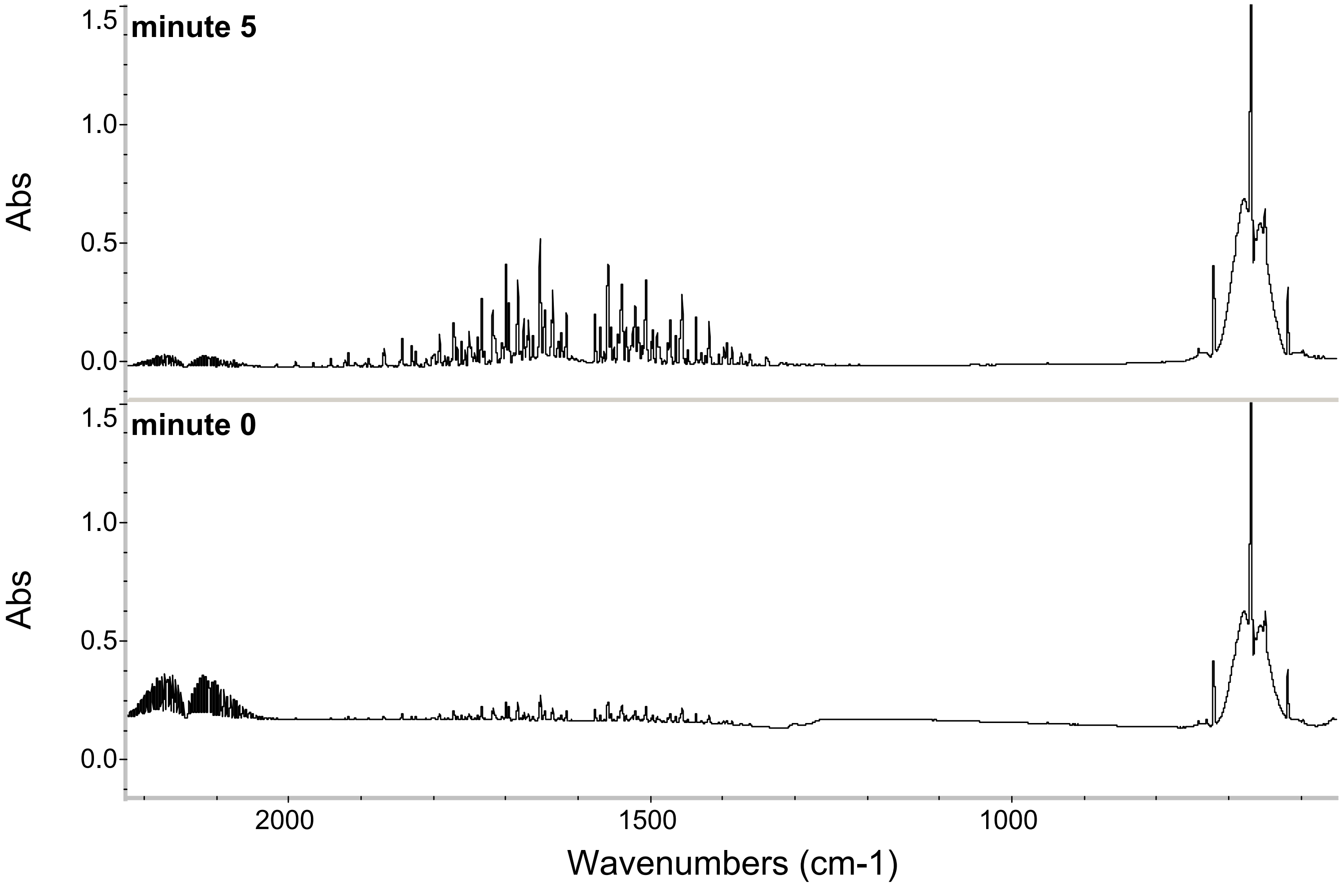

Figure 5. IR spectra of 1998 Acura CL exhaust at start-up (0 min) and after warm-up (5 min), showing a decrease in CO (2149 cm^{-1}) and an increase in both H_2O (1595 cm^{-1}) and CO_2 (667 cm^{-1}).

Acknowledgment. This work was supported by a grant from the Camille and Henry Dreyfus Special Grant Program in the Chemical Sciences and by the Pepperdine University Research Council. The author acknowledges Cathryn McFearin, head general chemistry laboratory teaching assistant, and Pepperdine students in the honors general chemistry laboratory classes of 2002 and 2003 for testing this experiment using their automobiles. Special thanks is extended to Mike Brandt in the Auto Technology program at Santa Monica College for helpful discussions and testing of one of the vehicles in the study and Professors Harry Pappas and Randy Maddox for use of their automobiles in the study.

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