A newly developed approach based on nanosecond time resolved Fourier Transform IR Emission Spectroscopy (TR-FTIRES) has been applied to the investigation of the spectroscopy and structure of unknown transient radicals that are important in combustion processes. Several radicals including deuterated-vinyl, cyanooxomethyl (OCCN) and ketenyl (HCCO) whose vibrational structure has not been determined have been examined.

The transient radical species is produced with high vibrational excitation through UV photolysis of a precursor molecule. The IR emission from the highly excited species through its IR active vibrational modes is detected with fast time resolution using the TR-FTIR technique. A new two-dimensional cross-spectra correlation technique has been developed for analyzing the time-resolved FTIR emission spectra. This analysis reveals the common set of emission bands from the same target radical in the emission spectra obtained using different precursors.

The spectroscopic approach also allows the reactions of the excited radical and the photolysis reaction of the precursor molecules to be characterized. All these information are fundamentally important to the understanding of chemical dynamics of radicals as well as the combustion processes. A brief description of the progress is presented below.

I. Vibrational Bands of Vinyl-\(d_3\)
We have previously reported the detection of the fundamental transitions of all nine vibrational modes of the vinyl radical, for which only one mode was known prior to our work. To confirm the assignment of the nine vibrational modes of the vinyl radical, we have performed isotope substitution experiment. Comparing the ratio of the experimentally observed frequencies for the deuterated and non-deuterated vinyl radical with the theoretically predicted ratio allows the assignments to be examined. Deuterated vinyl bromide, vinyl chloride, methylvinyl ketone, and butadiene were used a precursor for the production of the vinyl-\(d_3\) radical. Four bands are attributed to vinyl-\(d_3\). The most intense band is the 985 cm\(^{-1}\) CD bend. Peaks in the CD stretching region appear at 2420 (CD stretch), 2345 (CD\(_2\) asym. stretch) and 2265 (CD\(_2\) sym. Stretch) cm\(^{-1}\) also have considerable intensity. The corresponding bands of the hydrogenated vinyl have all been identified. The correlation between the bands from the deuterated vinyl with those from the non-deuterated vinyl is established by a comparison of the peak shape, frequency and intensity.

II. The \(\nu_1\) and \(\nu_2\) Vibrational Bands of the OCCN Radical
The cyanooxomethyl radical, OCCN, has a significant role in the atmospheric medium. OCCN is an important dissociation product of many substituted carbonyls with the
general structure NC(CO)X, a class of carbonyl containing compounds that are major constituents of urban atmospheric pollution related to motor vehicles. Despite its importance, the vibrational modes in the electronic ground state of this small radical has, until this work, remained unreported.

The OCCN radical is produced through 193 nm photodissociation of carbonyl cyanide, CO(CN)\textsubscript{2}, pivaloyl cyanide, CO(CN)(CH\textsubscript{3})\textsubscript{3}, and methyl cyanoformate, CO(CN)(OCH\textsubscript{3}). Since all three precursor molecules all result in OCCN as the only common product in their dissociation, their emission spectra reveal common features that can be assigned to OCCN. The CN stretch (\(\nu_2\)) at 2093 cm\textsuperscript{-1} is the mode with the strongest transition intensity and can be readily identified in the emission spectra from all three precursors. The CO stretch (\(\nu_1\)) at 1774 cm\textsuperscript{-1} is more than one order of magnitude weaker and not as apparent as the strongest mode in the emission spectra but can be identified after the two-dimensional cross-spectra correlation analysis. \textit{Ab initio} calculation results confirm the assignment of both the frequency and relative intensity of the two modes.

III. The \(\nu_1\) CH-Stretching Mode of the Ketenyl (HCCO) Radical

The ketenyl radical is either a product or a transient intermediate in the combustion of many small hydrocarbons including acetylene, ethane, and ethene. The \(\nu_1\) CH stretch, a previously uncharacterized mode of the ketenyl (HCCO) radical, has been identified at 3232 cm\textsuperscript{-1} through time-resolved Fourier transform infrared emission spectroscopy. The ro-vibrationally excited ketenyl is generated, along with ethyl (CH\textsubscript{2}CH\textsubscript{3}), with near unit quantum efficiency via the 193 nm photodissociation of ethyl ethynyl ether. IR emission from the vibrationally excited photoproducts was detected with both temporal and frequency resolution. Spectral assignments were supported by comparison with theoretical calculations as well as 2D correlation analysis.

IV. Two Dimensional Cross-Spectra Correlation Analysis of Time-Resolved FT Emission Spectra

Based on the principles of the generalized two-dimensional vibrational spectra correlation analysis, a new approach for deciphering the correlation among the spectral peaks of two \textit{different} spectra is developed. This 2D \textit{cross}-spectral correlation (2DCSC) analysis is aimed at revealing the vibrational features associated with a common species in two different spectra, each obtained from a system containing multiple species with at least one common species. The cross-spectral correlation is based on the premise that the spectral features of the same species should have the same time- and frequency-response toward similar perturbations. The effectiveness of the cross-spectral correlation analysis is first tested with model systems, with spectral peaks decaying linearly or exponentially with time.

This 2DCSC has been applied to analyzing time-resolved emission spectra obtained, by a Fourier transform IR spectrometer, for samples consisting of the vibrationally excited transient radicals including cyanooxomethyl (OCCN), ketenyl (HCCO), and vinyl (C\textsubscript{2}H\textsubscript{3}). 2DCSC among the different sets of time-resolved spectra collected following the photodissociation of different precursor molecules allows the identification of the spectral features associated with the same radical species that have similar intensity decay.
patterns. This procedure has assisted in the identification of many previously unidentified vibrational modes of these radicals.

V. Photodissociation of Acrylonitrile: Determination of the Transition State Structure
Acrylonitrile, also known as vinyl cyanide, is an important molecule whose photodissociation reaction following UV irradiation has been intensively studied previously using molecular beam techniques. The TR-FTIRES technique can be used to monitor the identity of the dissociation products as well as their internal energy content. The IR emission approach complements the Mass spectrometry detection in molecular beam studies as the latter can only discern the atomic make up of the molecule and the translational energy but not necessarily its structure and vibrational modes. The combination of the two sets of information has proven valuable for the understanding of this dissociation reaction. Based on the detection of the HCN species through Mass spectrometry, molecular beam studies have detected a dissociation channel through a 3-centered transition state following 193 nm irradiation. The time-resolved IR emission study on the other hand shows that there is also product in the form of the HNC isomer. This finding provides evidence for a dissociation channel through a 4-centered transition state that is suggested by a most recent theoretical calculation. A rotational contour simulation of the most intense emission peak is also performed in order to determine the symmetry of the normal mode responsible for this peak.

VI. Publications since 2004 acknowledging support from this grant

The $\nu_1$ and $\nu_2$ Vibrational Bands of the OCCN Radical Detected Through Time-Resolved Fourier Transform IR Emission Spectroscopy
William McNavage, William Dailey and Hai-Lung Dai

Two-dimensional cross spectral correlation analysis and its application to time-resolved fourier transform emission spectra of transient radicals
William McNavage and Hai-Lung Dai

Time-Resolved FTIR Emission Spectroscopy of Transient Radicals
Laura T. Letendre, William McNavage, Charles Pibel, Ding-Kuo Liu, and Hai-Lung Dai

Nanosecond Time-Resolved IR Emission from Molecules Excited in A Supersonic Jet: Intramolecular Dynamics of NO₂ near Dissociation
Jianqiang Ma, Peng Liu, Min Zhang, and Hai-Lung Dai

The ν₁ CH Stretching Mode of the Ketenyl (HCCO) Radical
*J. Phys. Chem. A*, submitted
Michael J. Wilhelm, William McNavage, Raymond R. Groller and Hai-Lung Dai

Two other manuscripts on deuterated vinyl and acrylonitrile are also in preparation.