Infrared Spectra of Reactive Species Generated by Flash Pyrolysis in a Free Jet

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Dedicated to Prof. K. Drauz on the occasion of his 60th birthday

We present the infrared spectra of reactive species recorded in the gas phase using free electron laser (FEL) radiation. We focus on the allyl radical, C₃H₅, as well as the pyrolysis products of trifluoromethylphenyl diazirine. The IR spectra are obtained by monitoring the ion-dip signal, using an IR/UV double resonance scheme. The work is motivated by our interest in devising a strategy to distinguish isomers of reactive species in a free jet. The suitability of IR/UV ion-dip experiments for this application has been shown before for the C₆H₅ isomers benzyl and tropyl. A FEL provides the required photon flux in the fingerprint region to record IR absorption spectra of diluted species in a supersonic expansion. We therefore wanted to elucidate whether IR/UV double resonance can be combined with the pyrolytic production of reactive intermediates to obtain structural information of reactive species.

Our first experiment concentrates on allyl, a species of importance in combustion chemistry, in particular in soot formation. The allyl radical also serves as a model system for radical spectroscopy and dynamics in general. Its structure is given in the inset of Figure 1. It is a suitable test case, because a) it can be generated cleanly and at high number density (estimated number density is on the order of 10¹⁴ cm⁻³), b) its UV spectrum is well understood, and c) most IR-wavenumbers are known from several linear absorption studies in rare-gas matrix and resonance Raman spectroscopy. However, its IR cross section is comparably low, because it lacks dipolar functional groups. Thus if an IR-spectrum of allyl can be recorded via IR/UV double resonance, this method would be applicable to a wide range of reactive species.

Allyl is produced by flash pyrolysis from allyl iodide. To record the IR absorption spectrum of allyl, as is shown in Figure 1, IR/UV ion-dip spectroscopy is applied employing FELIX, a free electron laser. In the UV step, allyl is excited at 248.1 nm by [1+1] two-photon ionization via the maximum of two bands, the most intense mode. Diode laser spectroscopy yields the rotational temperature of the pyrolytically produced radicals and the rather high IR energy necessary to obtain an ion-dip signal. Note that we follow the assignments given in the most comprehensive work by Nandi et al., who based them on isotopic labelling and on polarization studies. Their recommended IR wavenumbers and measured band absorbances are given as sticks in Figure 1. For comparison, wavenumbers of 801 and 983 cm⁻¹ for the ν₁ and ν₁₀ respectively were reported for the two modes in Ar-matrix. The ν₁ band is expected to be the most intense mode. Diode laser spectroscopy yields 801.719 cm⁻¹ for this ν₁ band. While the absorbance of the ν₁₁ relative to the strongest band is only 22% in the matrix spectrum, it appears with almost 60% in our ion-dip spectrum. In addition, at least one smaller band is observed in the ion-dip spectrum at around 1480 cm⁻¹. This band can be assigned to the symmetric and asymmetric CH₃ scissor vibrations ν₁ and ν₁₅, which cannot be separated in our experiment.

Absorbances of 6% and 17% relative to the ν₁₁ band were observed for these two bands in the matrix, where they appear at 1464 cm⁻¹ and 1478 cm⁻¹. In addition, a rather broad and reproducible feature shows up around 1300 cm⁻¹. Several modes could contribute to this feature, but all of them are expected to have a much smaller absorbance. Among...
investigated the femtosecond dynamics\textsuperscript{[15, 16]} as well as the photoionization\textsuperscript{[17]} of several phenylcarbenes Ph–C–X in the gas phase. While the dynamics of chlorophenylcarbene (X = Cl) could be rationalized with the aid of computations, the results for TFPC were less clear cut and could not be fully understood. We therefore wanted to verify the spin multiplicity of the carbene. Both earlier ESR experiments\textsuperscript{[18]} and computations\textsuperscript{[16]} have indicated a triplet ground state.

The ion-dip spectrum obtained upon excitation around 270 nm is depicted in the top trace of Figure 3. A depletion of 60\% was observed on the strongest peaks upon adding the IR radiation. The stick spectrum calculated by density functional theory (B3LYP functional, 6-311++G** basis set) is depicted in the center trace. The vibrational wavenumbers are unscaled. They are given together with the computed IR-intensities in the Supporting Information. The blue sticks correspond to the triplet carbene, the red sticks to the singlet. While satisfactory agreement is visible in the low energy range, two intense bands at 1748 cm\textsuperscript{-1} and 1289 cm\textsuperscript{-1} are not adequately represented. No bands close to these positions were reported in earlier matrix isolation spectra.\textsuperscript{[17]} We therefore computationally investigated possible isomerization products of the carbene. One possible isomerization product is trifluorostyrene, depicted in the lower trace of Figure 2. Its calculated stick spectrum is shown in the bottom trace of Figure 3. As visible, the peaks at 1748 cm\textsuperscript{-1} and 1289 cm\textsuperscript{-1} are matched by calculated bands of this isomerization product. In particular the 1748 cm\textsuperscript{-1} band is quite unique and can be assigned to an olefinic C–F stretching mode. It also appears prominently in the solution-phase IR-spectrum of trifluorostyrene.\textsuperscript{[19]} Several other bands like the double peak at 1070 and 1095 cm\textsuperscript{-1} and the weak band at 1230 cm\textsuperscript{-1} might be better represented by the calculated stick spectrum of the carbene. The intense band at 1154 cm\textsuperscript{-1} as well as several low-wavenumber bands that correspond to vibrations of the aromatic ring are equally well described in the calculated spectra of both species. We conclude from the spectrum in Figure 3 that both species, TFPC (carbene) and trifluorostyrene, are present, but that there is substantial isomerization from the carbene to trifluorostyrene. DFT-calculations using the BMK functional reveal that trifluorostyrene is 185 kJ\textsuperscript{mol}\textsuperscript{-1} lower in energy than the carbene. However there are significant barriers of 178 kJ\textsuperscript{mol}\textsuperscript{-1} (triplet transition state) and 167 kJ\textsuperscript{mol}\textsuperscript{-1} (singlet transition state) present for an F-atom shift, as calculated by QST3 with a subsequent frequency computation. A figure summarizing the results is also given in the Supporting Information. One thus expects a dependence of the degree of isomerization on the pyrolysis temperature. Indeed the relative intensity of the band at 1748 cm\textsuperscript{-1} seemed to grow with temperature. However, at the lowest pyrolysis power chosen in our earlier work,\textsuperscript{[16]} the signal intensity was not sufficient to record a satisfying infrared spectrum.

The discovery of a partial isomerization in the pyrolysis nozzle impacts the interpretation of the earlier femtosecond experiments. Three time constants are unravelled in this earlier work. Although lower pyrolysis temperatures have been used in the femtosecond work, the time constants might have to be assigned to two different species, TFPC and trifluorostyrene, that show an independent dynamics. Future experiments on this species should thus focus on a variation of excitation wavelengths.

In conclusion we reported IR-spectra of the fingerprint region of pyrolytically generated reactive species in a free jet, recorded by IR/UV double resonance spectroscopy employing FELIX as the IR source. Even a weak IR-absorber like allyl can be studied under these conditions. The IR-spectrum of the pyrolysis of trifluoromethylphenyl diazirines indicates substantial isomerization of trifluoromethylphenyl carbene to trifluorostyrene. The results show that a large number of reactive intermediates can be studied by this technique and information on isomerization processes can be obtained, provided that the UV

**Figure 2.** Trifluoromethylphenyl carbene can be generated from the corresponding diazirines precursor (top). Trifluorostyrene is formed as a second product in the pyrolysis (bottom).

**Figure 3.** The pyrolysis of trifluoromethylphenyldiazirine yields the IR spectrum depicted in the top trace. The stick spectra represent calculations of singlet (red) and triplet (blue) trifluoromethylphenyl carbene and of trifluorostyrene (black).
spectrum is known. Note that the UV-spectrum does not necessarily have to show high resolution structure\cite{10,11} to carry out ion-dip experiments with FEL radiation.

**Experimental Section**

The experiments were carried out at the FELIX free electron laser (FEL) facility at the FOM Institute of Plasma Physics Rhinhuizen. The principles of the experiment have been described in detail elsewhere.\cite{5,6} Measurements were performed in a differentially pumped molecular beam set-up. All species were produced by flash pyrolysis in a source following the design in the literature.\cite{3} Allyl iodide was purchased from Aldrich, trifluoromethylphenyl diazirine was synthesized following the literature procedure.\cite{18} The precursors were seeded in 1 bar of argon. The skimmed free jet of reactive species enters the ionization region of a time-of-flight mass spectrometer, where it is crossed by IR and UV laser radiation. A frequency-doubled dye laser, pumped by a Nd:YAG laser, was employed for UV excitation, delivering around 2 mJ of UV light. The IR-FEL was fired temporally around 100 ns before the UV laser and scanned over the fingerprint region of the molecule (500–1600 cm$^{-1}$). When the IR light is resonant with a vibrational mode of the species, the ion signal is depleted, because only the molecules left in the ground state can be resonantly ionized. Note that the determination of absolute cross sections is difficult, because absorption of more than one IR-photon on resonance cannot be ruled out. At each wavenumber step we recorded 32 shots with and without IR-radiation present and 32 shots without. The signal obtained with IR-radiation present and 32 shots without is divided by the signal observed without the IR-radiation present. To obtain the spectrum in Figure 1 several scans were averaged, while the spectrum in Figure 3 is based on a single scan.

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