IR Spectroscopy

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Ultrafast Hopping from Band to Band: Assigning Infrared Spectra based on Vibrational Energy Transfer**

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Infrared spectroscopy is widely used in fundamental and applied chemical research. Applications cover tasks in analytical chemistry, such as process monitoring or product identification,[1] as well as cutting-edge studies elucidating reaction mechanisms[2] or resolving ultrafast biomolecular dynamics and functions.[3] Typically, analysis of an IR spectrum starts with assignment, that is, with establishing a connection between the bands observed in the spectrum and the moieties of the molecule that are involved in the corresponding vibrations. For small molecules, vibrations often can be assigned based on experience, aided by databases that list functional groups and the typical wavenumber range of their absorption bands. However, the database approach quickly becomes unfeasible if several groups are present that cause vibrations in the same wavenumber range or if a certain group is present several times in a molecule. A way to obtain assignment information in such cases is isotope labeling, which might involve complex synthesis. Very frequently, quantum-chemical computations are used for assignment. However, even for seemingly simple cases, contradicting results can be obtained from different computational methods, as illustrated by the results presented herein. Furthermore, there are cases where the computation of vibrational modes can be intrinsically difficult, such as excited states or reaction mixtures containing unknown species. A broadly applicable experimental approach to aid assignment is therefore highly desirable.

Herein we show how time-dependent infrared pump–probe spectroscopy allows assignment problems to be solved. For this purpose, a vibration of the molecule is selectively excited using an infrared excitation pulse with narrow bandwidth and the response of the other vibrations is investigated by a delayed probe pulse. The initially excited vibration relaxes; low-frequency modes become excited, and intramolecular vibrational energy transfer (VET) across the molecule occurs between low-frequency modes.[4] Through-bond transfer rates of 2.6–5.5 Å ps^{-1} have been reported for different molecules.[4b,5] The high-frequency vibrations investigated herein are anharmonically coupled to the low-frequency modes and respond to VET by red-shifting.[6] Because transfer times correlate with through-bond distances,[4b,5,7] the order in which the bands in the spectrum respond to the initial excitation reflects the distance between the vibrating groups in the molecule. This is critically important information for band assignment.

As an example for the broadly applicable method of VET-based assignment, we chose the artificial amino acid *p*-azido-L-phenylalanine,[8] which is used as a protein label for IR spectroscopy (Figure 1). We investigated the boc-protected form (abbreviated N_3Phe), thereby adding a peptide bond to the model system. Figure 1 shows the FTIR absorption spectrum. Referring to a database of group frequencies,[9] as is typically done for IR band assignment, we expect several bands in the wavenumber range shown in Figure 1.

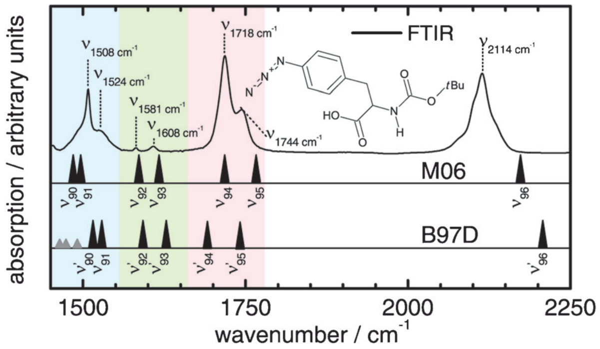

Figure 1. Structure and IR absorption spectrum of N_3Phe. The band positions obtained from DFT computations using the M06 functional and the B97D functional are indicated with black triangles (scaling factors of 0.962 and 1.015 are used for M06 and B97D, respectively). Small gray triangles indicate methyl group absorptions of the *tert*-butyl moiety. Their absorption is less than 5% of the neighboring vibration ν'_{90}. The background colors blue, green, and red mark the different spectral regions discussed in the text.

Asymmetric azide stretching is usually observed at wavenumbers between 2080 cm^{-1} and 2170 cm^{-1}, and we therefore assign the band at 2114 cm^{-1} to the azide moiety. The structure of the band is attributed to a Fermi resonance.[10] Carbonyl stretching of the carboxylate moiety is expected

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between 1705 cm^{-1} and 1730 cm^{-1}; carbonyl stretching of the carbamate moiety (amide I) is expected between 1705 cm^{-1} and 1722 cm^{-1}.[9] We observe two bands (at 1744 cm^{-1} and 1718 cm^{-1}) in the corresponding wavenumber range, but it is not possible to definitively assign which belongs to the carboxylate and which belongs to the carbamate. An amide II vibration of the carbamate moiety is expected as well;[9] this should occur between 1510 cm^{-1} and 1550 cm^{-1}, and we observe bands at 1508 cm^{-1} and 1524 cm^{-1}. Furthermore, several ring vibrations are expected in the range from 1450 cm^{-1} to 1665 cm^{-1}. Ring vibrations are therefore the likely cause for the small absorption signals at 1581 cm^{-1} and 1608 cm^{-1}. However, a ring vibration could also be responsible for one of the bands in the amide II range.

To clarify the assignment of the carbonyl bands and the assignment in the amide II range, we computed the normal modes using density functional theory (DFT). The vibrational wavenumbers computed using the M06 and the B97D functionals[11] (M06/6-31 + G(d,p)/PCM/UFF and B97D/6-31 + G-(d,p)/PCM/Bondi; see the Supporting Information for computational details) are displayed below the experimental data in Figure 1. Figure 2 shows the localization of the respective normal modes. The localization of modes ν_{96} to ν_{92} is almost identical in both computations, with the highest wavenumber mode being the azide stretching vibration. Both methods suggest that the carbonyl stretching of the carboxylate (ν_{95}) is at higher wavenumber than the carbonyl stretching (amide I) of the carbamate (ν_{94}). The two modes with next lower wavenumbers in both computations are localized on the phenyl ring, with the higher mode involving predominantly the four H-substituted C atoms (ν_{93}) and the lower involving mainly the other two C atoms (ν_{92}). In the amide II wavenumber range, the computations predict two modes: an additional ring mode and an amide II vibration of the carbamate. Although the two computations are in agreement about the localization of the two vibrations, there is disagreement about the order of the modes. The computation using the M06 functional predicts the ring mode at higher wavenumber, whereas the computation using the B97D functional predicts a higher wavenumber for the amide II mode.

To resolve the uncertainty resulting from the computations, unambiguous assignment of the vibrational modes can be obtained from measurements that monitor VET using ultrafast IR pump–probe spectroscopy. Both vibrations are located at different through-bond distances from the azide and VET originating from the excited azide group will lead to a much faster response of the ring vibration compared to the amide II vibration; this allows clear assignment of the bands in the absorption spectrum to the vibrational modes.

Figure 3 shows the change of the absorption of the bands as a function of time after direct excitation of ν_{96} at 2114 cm^{-1} (the azide stretch vibration). t_{max} indicates the time of maximum signal obtained by bi-exponential interpolation of the data in the vicinity of the maximum.[5b] The upper panel shows the responses of the two bands at 1744 cm^{-1} and 1718 cm^{-1}, which are attributed to carbonyl vibrations. Both DFT computations attribute the higher wavenumber band to the carboxylate moiety (ν_{95} and ν'_{95} in Figure 2, spatially closer to the azide) and the lower wavenumber band to the carbamate moiety (ν_{94} and ν'_{94} in Figure 2, which are spatially further from the azide). The experiment strongly supports this assignment, as the higher wavenumber band responds earlier in time ($t_{\text{max}}^{1744\,\text{cm}^{-1}} = 2.3$ ps) than the lower wavenumber band ($t_{\text{max}}^{1718\,\text{cm}^{-1}} = 3.6$ ps). The middle panel shows the time dependence of the absorption bands that are attributed to the ring modes. The response is much faster than that of the carbonyl modes with $t_{\text{max}}^{1608\,\text{cm}^{-1}} = 1.4$ ps and $t_{\text{max}}^{1591\,\text{cm}^{-1}} = 1.3$ ps and reflects the proximity of the azide group and the phenyl ring. In these cases the two DFT computations agree well with each other as well as with the information from time-resolved spectroscopy. To further distinguish modes, such as ν_{92} and ν_{93}, that are delocalized over a similar set of atoms and therefore yield similar t_{max}, the angles between transition dipoles of excited and probed modes could be obtained from polarization resolved measurements and compared to computed angles. The assignment of the bands at 1524 cm^{-1} and 1508 cm^{-1} remains unclear from the computations because the results are contradictory. The computed band intensities (see the Supporting Information) are not conclusive for assignment. Both computations predict a higher intensity for the amide II

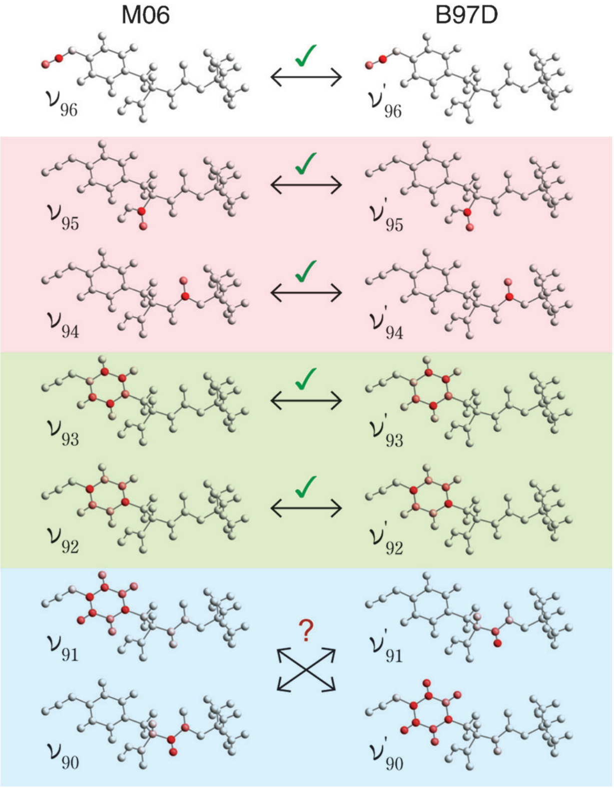

Figure 2. Localization of vibrational normal modes computed using DFT with the M06 and the B97D functionals. The red color coding of the molecular structures represents the vibrational energy per atom. The color scale is normalized to the maximum vibrational energy localized at a single atom for each mode. Both computations agree on the assignment of the azide asymmetric stretch (ν_{96}), which is the mode excited in the pump–probe measurements, the two carbonyl modes (ν_{95} and ν_{94}), and two of the ring modes (ν_{93} and ν_{92}). However, the order of the amide II mode of the carbamate and the third ring mode is interchanged. Red, green, and blue background colors correspond to the spectral regions marked in Figure 1.

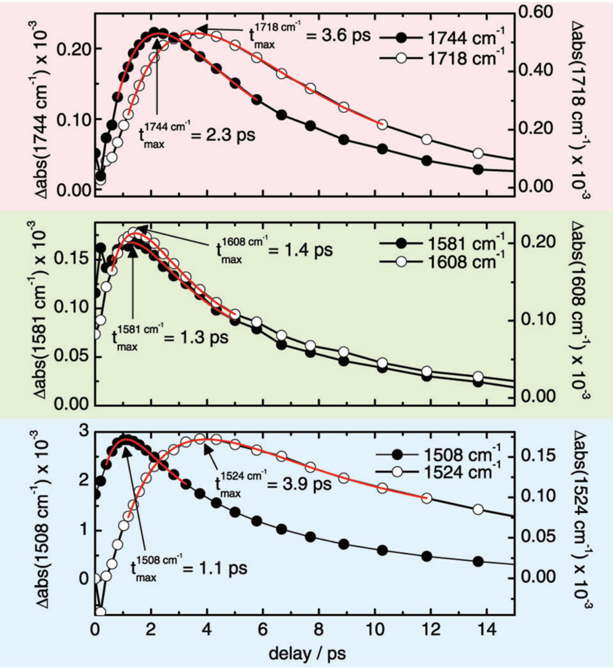

Figure 3. Absorption change of the bands as a function of time after excitation of ν_{96} (azide vibration at 2114 cm^{-1}). The red lines are bi-exponential interpolations in the vicinity of the maximum that are used to obtain t_{max}, the time of maximum signal. The black lines connect the measured data points and serve as a guide to the eye. Signals in the middle panel are vertically offset for better visibility (note the different origin of the y axes). The scales of each panel are chosen such that the two curves have the same positive amplitude. Red, green, and blue background colors correspond to the color coding in Figure 1 and Figure 2.

band, but different orders of bands. The energy transfer times, however, decide in favor of the assignment suggested by the B97D computation: the lower wavenumber mode responds very fast with $t_{max}^{1508\,cm^{-1}} = 1.1$ ps, which is in agreement with its assignment as a ring mode (ν'_{90} in Figure 2). The t_{max} observed for this mode corresponds with the times observed for the two other ring modes. In contrast, the higher wavenumber mode is slower, with $t_{max}^{1524\,cm^{-1}} = 3.9$ ps. This time is comparable to the value of $t_{max}^{1718\,cm^{-1}} = 3.6$ ps obtained for the carbonyl group of the carbamate. The assignment of the band at 1524 cm^{-1} as an amide II vibration of the carbamate suggested by the B97D computation (ν'_{91} in Figure 2) is therefore strongly supported; the contradicting assignment as a ring mode proposed by the M06 computation must be discarded. However, a superiority of the B97D functional over the M06 functional in computing vibrational frequencies should not be deduced from this single result. With increasing density of vibrational bands in larger molecules, harmonic DFT computations that are frequently employed to aid assignment cannot be expected to predict exactly the right order of bands.[12] High-level ab initio methods with anharmonic corrections, which have the desired accuracy to address the assignment problem, are not applicable in the majority of cases owing to the prohibitive computational effort required.[12c,13] Therefore, an experimental approach to assignment, such as the one presented herein, is of great importance.

In summary, this work shows how VET-induced signals obtained from ultrafast IR-pump–IR-probe spectroscopy can aid the exact assignment of absorption bands. We make use of the fact that the time dependence of VET-induced absorption changes reflects the spatial proximity of the two modes that correspond to the excited and the responding absorption bands. In the present case of a molecule with little branching and no intramolecular hydrogen bond (see the Supporting Information), it has been sufficient for assignment to measure a data set with VET starting from one mode at the end of the molecule. For molecules with a more complex structure, two or more measurements with VET starting from modes located at different points in the molecule can be used to obtain additional assignment information. Also weaker bands than azide can be used to inject vibrational energy, as the low noise allows for the detection of smaller signals. Additionally, small signals can be increased by increasing infrared pump intensity, concentration, or sample thickness. VET based assignment will be particularly useful when assignment using databases or quantum chemical computations is difficult, for example, in molecules where vibrational frequencies of different functional groups are similar or for species that are difficult to compute, such as reactive intermediates and excited states. In mixtures, the technique can reveal which absorption bands belong to the same species. Disentangling IR spectra of reaction mixtures that might contain unknown species is therefore another promising application when investigating reaction mechanisms.

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