

Studies of mechanisms of intramolecular vibrational dynamics using time-resolved photoelectron spectroscopy

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Introduction

The simplest prototype system for intramolecular vibrational energy redistribution (IVR) is the Fermi Resonance. A Fermi Resonance comprises two near-degenerate harmonic oscillator levels in two different vibrational modes which are coupled by anharmonicity to give two eigenstates each with some character from each of the coupled levels. In the most interesting example, one of the harmonic oscillator levels in an electronically excited state is optically accessible by symmetry and is connected to the ground state by a significant Franck-Condon factor (the “bright state”), whereas the other is either optically inaccessible by symmetry, or is connected by a negligible Franck-Condon factor (the “dark state”). This then is the IVR prototype: energy redistributes from the bright state to the dark state and back again, with a period determined by the eigenstate energy separation. In the more chemically interesting IVR problem there will be a set of dark states, and depending on their density the bright state population may either exhibit recurrences or simply decay.^[1,2] A key goal in studies of IVR is the identification of the dark states, and techniques that lend themselves to a direct determination of these are therefore very valuable.

Experiment

Laser pulses of ~1 ps duration were generated by a 1 kHz titanium sapphire regenerative amplifier (Spectra-Physics Spitfire) configured for the chirped-pulse amplification of picosecond pulses. The output was frequency tripled to generate a beam at ~264 nm, and split 50:50 to form ‘pump’ and ‘probe’. The timing between these two beams could be varied between 0 ps and 1 ns using an optical delay line on the probe arm. The beams were overlapped spatially on a microscope slide in an equivalent plane to the sample. The beams were loosely focused, with a typical beam diameter of around 100 μm. Energies were in the range 2-3 μJ per pulse and each beam had a bandwidth of around 15 cm⁻¹.

A skimmed supersonic molecular beam of toluene seeded in He was intersected at right angles by the two laser beams which were co-propagating and linearly polarized at right angles to their mutual direction of propagation, and to that of the molecular beam. Photoelectrons produced by resonant two-photon ionization were focused by a three-element electrostatic lens, configured to work in velocity-mapping mode,^[3] and the resulting image was captured by a CCD camera.^[4] The experiment was repeated until the signal-to-noise ratio reached an acceptable level, typically 30,000 times at a rate of 50 Hz. The typical operating pressure was around 10⁻⁵ mbar, with a base pressure of around 10⁻⁷ mbar.

At each of the time delays studied three images were recorded; one each for the two beams in isolation and one for the combination signal. To minimize systematic errors, these three images were recorded in interspersed 20 second bursts until sufficient repetitions had been performed. The blocking and unblocking of the beams was controlled by a pair of electro-mechanical shutters (EOPC) and a user-generated script within the data collection software (Photek). The final pump + probe image at each time delay was subjected to an inverse Abel transform, and then converted to deduce a photoelectron spectrum as a function of photoelectron kinetic energy.^[5] This kinetic energy can be straightforwardly converted to ion internal energy by use of the known ionization potential of toluene.^[6]

Results and Discussion

In Figure 1 we show the photoelectron spectrum as a function of ion internal energy obtained when the 1 ps pump and probe pulses are overlapped in time, with the pump pulse preparing the Fermi resonance in S₁ toluene at ~460 cm⁻¹.^[7] Based on reference^[8] we assign the compound peak at ~510 cm⁻¹ ion internal energy to 6a¹ + 10b¹16b¹ in the ion, where the two components are separated in energy but not fully resolved. It looks likely that at least one more transition also contributes to this compound peak. The peak at ~990 cm⁻¹ is assigned to 6a² + 10b²16b² in the ion

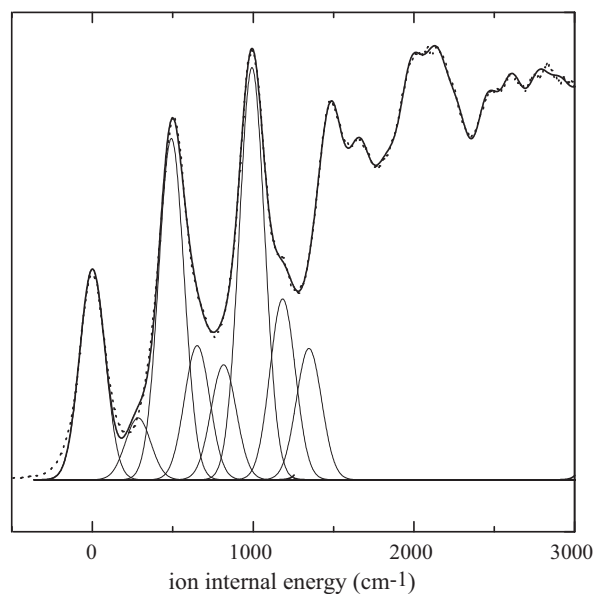


Figure 1. Photoelectron spectrum following the preparation of the Fermi resonance at ~460 cm⁻¹ (dotted line). Also shown is a fit to a set of Pearson VII functions to the first 1300 cm⁻¹ wavenumber portion of the spectrum (solid line, with thin lines for individual functions).

with the same caveat. For our purposes here we are interested in two peaks: the first at 0 cm^{-1} corresponding to $v = 0$ in the ion, and the second at $\sim 510\text{ cm}^{-1}$ which we label the “ $\Delta v = 0$ peak”.

In Figure 2 we show a three-dimensional plot that illustrates the behaviour of the photoelectron spectrum as a function of the time delay between excitation and ionization. For clarity, we have omitted the portion of each spectrum above ion internal energies of 2500 cm^{-1} . The photoelectron spectra have each been normalized to the total photoelectron count which itself varies negligibly with time delay. From inspection of this Figure it is clear that the normalized intensities of both the $v = 0$ peak and the $\Delta v = 0$ peak oscillate as a function of time delay, with the $v = 0$ peak particularly sensitive to this. The sensitivity of the photoelectron spectrum is particularly interesting given the compound nature of the “ $\Delta v = 0$ peak” which easily could have masked the observed effect. It is however clear that if there had been no dispersion of photoelectron kinetic energies no oscillation would have been observed.

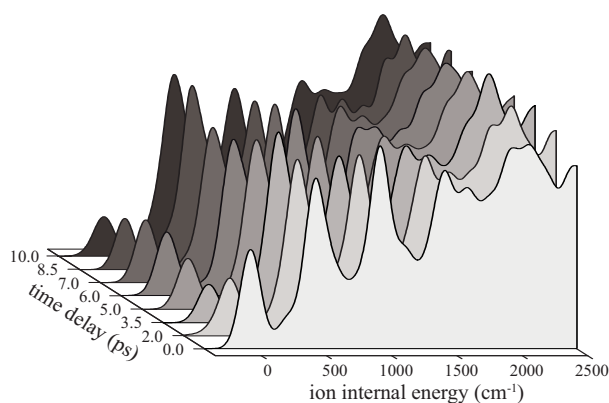


Figure 2. Photoelectron spectra as a function of the time delay between excitation and ionization.

In order to quantify the observed oscillation we plot the ratio of the intensities of the $\Delta v = 0$ to $v = 0$ peaks as a function of time in Figure 3; we use this ratio in order that we can neglect any small changes in the total

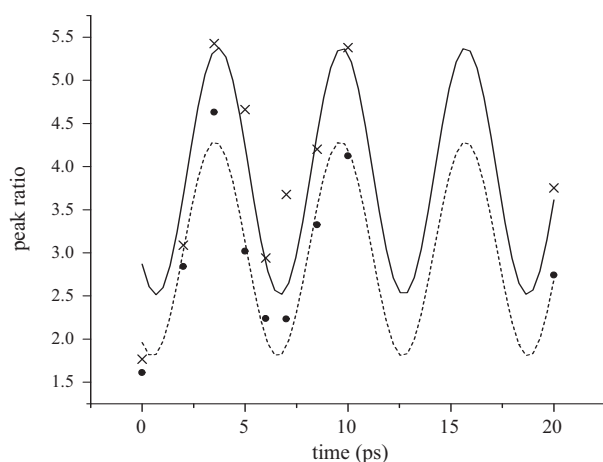


Figure 3. Ratio of the intensities of the “ $\Delta v = 0$ ” to $v = 0$ photoelectron peaks (see text) as a function of time delay: single function model (crosses) and multifunction model (solid circles).

photoelectron count with time delay. Various choices could be made in order to determine the ratio; in Figure 3 we show two limiting cases. (i) We make a crude fit of each of the two peaks to a single Gaussian function and take the ratio of the areas (the single function model). (ii) We use multiple Pearson VII functions as shown in Figure 1 and take the ratio of the areas of the function that contributes most to each peak (the multifunction model). The reason for the use of the Pearson VII functions (which are an approximation to Voigt functions) is that the peak shapes are instrumentally limited and these functions appear to best reproduce the observations. It is clear that although each choice gives a slightly different result, there is no ambiguity over the effect seen, *i.e.*, an oscillation as a function of time delay.

In each case we fit the time dependent ratio, $R(t)$, to the function

$$R(t) = B + A \cos\left(\frac{2\pi t}{T} - \phi\right) \quad (1)$$

and show these fits also in Figure 3. The fit yields oscillation periods, T , of $6.0 \pm 1\text{ ps}$ and $6.1 \pm 1\text{ ps}$ from the single and multifunction models, respectively, and phase shifts $\phi = 0.23 \pm 0.4\pi$ and $0.16 \pm 0.4\pi$, respectively. The period of the oscillation is trivially related to the measured eigenstate energy separation^[9] which has been determined to be $4.8 \pm 0.5\text{ cm}^{-1}$. This would give rise to a period of $6.4 \pm 0.7\text{ ps}$, in good agreement with our values, within error bars.

The major significance of this work is that it gives a means of efficiently studying intramolecular vibrational redistribution (IVR) processes in which unknown dark states can be detected and identified as a function of time, without the need to reconstruct the harmonic oscillator levels from eigenstates. In preliminary work we have already shown the possibilities in this regard.^[4] Although our observations indicate the power of time-resolved VMI, it is clear that yet more information could be gained if the energy resolution of the photoelectron detection method were comparable to the bandwidth of the laser pulses used ($\sim 15\text{ cm}^{-1}$ in this case), as is the case in ZEKE.^[10] However, the disadvantage of ZEKE is the lengthy wavelength scans that have to take place at each time delay in order to detect the formed cation vibrational states. It seems likely therefore that when the aim is to unravel complicated IVR processes VMI and ZEKE would be an extremely powerful complementary pair.

Conclusion

We have shown that photoelectron spectra in which ion vibrational states are only partially resolved can be very sensitive to wavepacket evolution in an excited state of a polyatomic molecule. The method demonstrated could easily be extended to the study of the more complicated wavepackets, such as those typically prepared prior to energy redistribution, and would be particularly powerful when the bandwidth of the laser pulse allows full vibrational resolution, and when combined with a photoelectron detection method which has a resolution comparable to this bandwidth. In the work presented here the laser bandwidth and pulse duration were a happy compromise enabling sufficient resolution in both frequency and time for these observations to be made.

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