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Femtosecond infrared coherent excitation of liquid phase vibrational population distributions (v > 5)

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Abstract

Femtosecond mid-infrared excitation of room temperature $W(CO)_6/n$ -hexane solutions resonant with the T_{1u} CO-stretching mode transfers vibrational population to at least v = 6. The population distribution in levels v = 0 to v = 5 was measured by transient infrared absorption spectroscopy. Resonance frequencies, anharmonic shifts and spectral broadening of observed ladder transitions were also characterized. Populating v = 6 deposits ~12000 cm⁻¹ in a single mode which is close to the dissociation energy of one W–C bond. These results constitute a significant step toward initiation and ultimate control of condensed phase, mid-infrared induced ground state reactions relevant to practical synthetic transformations. © 2004 Elsevier B.V. All rights reserved.

1. Introduction

Efficient preparation of highly excited vibrational states in molecular systems remains a significant objective in physical chemistry. Both frequency and time domain studies, employing nano- to picosecond laser pulses, continue to reveal important spectral features such as bandwidths, bandshapes, coupling strengths, and anharmonicities. Further investigation elucidates vibrational dynamics, relaxation processes, and the evolution of microscopic structure in complex molecules. Beyond the accumulation and elaboration of such data, attention is increasingly directed towards more actively influencing vibrational dynamics and reaction processes via controlled excitation of vibrational modes. Such efforts gain particular importance in view of the long-standing proposal that vibrational excitation along a reaction coordinate might lead to more efficient reaction [1]. Therefore, a central aspect of laser driven

chemistry is the ability to achieve the localized deposition of vibrational energy within a polyatomic molecule.

There are currently several vibrational population excitation techniques with the prospect of attaining this goal. Perhaps the most obvious, direct excitation of vibrational mode overtones, bears the disadvantage of rapidly decreasing transition moments with increasing energy. An alternative would be to achieve excitation via an excited electronic state, making use of stimulated emission pumping [2], Raman adiabatic passage (STI-RAP) processes [3], or fs Raman techniques [4]. These approaches suffer increased complexity due to the involvement of two or more laser pulses with very different frequencies, as well as the necessity of mapping a second electronic potential surface. The third excitation method, employed in the present study, has been termed vibrational ladder climbing. In this approach, the molecule is excited through the consecutive levels of a vibrational potential well by stepwise absorption of discrete photons, each of which possesses the correct frequency for the respective transition within the ladder system. The efficacy of ladder climbing excitation by ultrashort pulses was shown preliminarily in two experiments. In one approach, Heilweil and co-workers

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[5–7] employed picosecond pulses in the mid-IR (MIR) to populate v = 3 in the T_{1u} CO stretch of condensed phase W(CO)₆. Using fs MIR pulses from a free-electron laser, Noordam and co-workers [8] investigated vibrational ladder climbing in gaseous NO and detected population in v = 5 with a REMPI detection scheme.

The ladder climbing technique is particularly welladapted to excitation with fs pulses for two reasons. First, ultrashort pulses with high peak intensities effect excitation on a time scale faster than that of intramolecular vibrational energy redistribution (IVR), and thus energy dissipation to other modes does not hamper the efficiency of the ladder climbing process. Second, the broad spectral bandwidth of such pulses provides photons resonant with the changing level spacings of an anharmonic potential. In the last several years, considerable progress has been made in generating fs laser pulses in the MIR with increasingly higher pulse energies, thereby conceptually enabling more extensive studies and ultimately control of molecular dynamics in the ground electronic state. As an example, we recently demonstrated MIR induced dissociation of transition metal carbonyl compounds [9,10] and diazomethane [11], both in the gas-phase, requiring excitation to v = 7and v = 5 in the respective target modes. For both experiments, the dissociation itself was monitored and the extent of overtone excitation inferred from bond dissociation energies.

In this work we extend our studies to the synthetically more relevant liquid phase. We apply mid-infrared transient absorption spectroscopy to the detailed probing of vibrational ladder climbing. State population distributions are directly monitored and as such constitute a comprehensive visualization of the up-pumping process. Following the earlier work of Heilweil, we chose condensed-phase tungsten hexacarbonyl $W(CO)_6$ as a test system, since the T_{1u} CO-stretch has a large $0 \rightarrow 1$ transition dipole moment (~1 D) and sufficient anharmonicity that the consecutive transitions are spectroscopically well-resolved. In addition to directly controlling the population distribution, we obtain spectroscopic information such as anharmonicity parameters and spectral bandwidths for the higher lying transitions in the ladder. Further, we demonstrate that only recently available pulse energies are crucial for the observed progress in reaching higher vibrational levels such as v = 7 in metal carbonyl compounds, which lies above the dissociation threshold for eliminating one CO from the molecule.

2. Experiment

MIR pulse generation of $\sim 12 \ \mu$ J energy pulses in a 160 cm⁻¹ FWHM envelope near 5 microns (2000 cm⁻¹) was accomplished by difference frequency mixing in

Fig. 1. The experimental setup is shown in schematic. A probe beam is reflected from a CaF_2 window (the back reflection is deflected by a window wedge). Both beams are collinearly collimated by a focussing mirror FM, here displayed as a lens, with f = 100 mm. At the spot of the focus, a SHG crystal or the sample cell can be alternatively placed. The pump is chopped at half the laser repetition rate.

AgGaS₂ of signal and idler pulses emerging from a tunable optical parametric amplifier (OPA). The OPA was pumped by 1.5 mJ, 100 fs, 800 nm pulses from a 1 kHz regeneratively amplified Ti:Sapphire laser system. The experimental setup, shown in Fig. 1, was a modified autocorrelator in which a wedged CaF2 window replaced the beamsplitter, so as to pass $\sim 90\%$ of the MIR pulse as a pump and reflect $\sim 5\%$ from the front surface as a probe. Both pump and probe were focused onto the sample cell, at a small crossing angle, by a gold-coated spherical mirror with 10 cm focal length. The time delay between pump and probe was adjusted by a mechanical delay stage that ranged from 150 fs to 1 ps in the measurements described below. After passing through the sample, the probe was dispersed in a monochromator and measured over a range of wavelengths using a biased liquid N₂-cooled single element HgCdTe detector. The single shot detector output was processed by a boxcar integrator and digitized by a PC for averaging.

Transient absorption spectra were collected by chopping the pump beam at half the laser repetition rate, phase locked to the laser emission, such that every other probe pulse measured the absorption of unpumped sample. The averages of 1500 pumped and 1500 unpumped shots were ratioed at each monochromator step (2 nm or \sim 4 cm⁻¹ resolution) and the log of this ratio yielded the differential absorbance. For the data displayed below, the monochromator frequency sweep was repeated 3-5 times and the resultant absorbance spectra further averaged. The signal was very sensitive to the focal overlap of pump and probe beams. This overlap was optimized by measuring the correlation between pump and probe by SHG in a 200 µm AgGaS₂ crystal that replaced the sample cell for the alignment procedure. Typical measurements yielded a MIR pulsewidth





Fig. 2. (A) The fs MIR laser pulse spectrum is shown (dashed line) superimposed on the FTIR absorption band (solid line) corresponding to the fundamental $0 \rightarrow 1$ transition in the T_{1u} CO-stretching manifold of W(CO)₆ dissolved in hexane. (B) The correlation trace of pump and probe pulses in a SHG crystal (200 µm AgGaS₂) is shown. The setup alignment is optimized via maximization of SHG signal at time zero.

of 160 fs, confirming that the pulses were approximately Fourier-transform limited, and also afforded a highly accurate time zero value (Fig. 2B). The maximum pump energy delivered at the sample position was measured to be 9.2 μ J. With a beam diameter of 160 μ m at the focus, measured by scanning a knife edge, this pulse energy corresponds to a peak intensity of 0.3 TW/cm².

Compounds were obtained commercially and used without further purification. Solid $W(CO)_6$ was dissolved in *n*-hexane and the concentration adjusted to produce an optical density (OD) of 0.6–0.8 at 1982 cm⁻¹ (the fundamental absorption frequency of the T_{1u} CO stretch). The static sample cell held this solution between two CaF₂ windows (2 mm thick) separated by a 950 µm Teflon spacer.

3. Results and discussion

Fig. 2A shows the laser pulse spectrum superimposed on the solvent-subtracted FTIR absorption spectrum of $W(CO)_6$ in *n*-hexane solution. The laser frequency is deliberately slightly red-shifted with respect to the T_{1u} fundamental at 1982 cm⁻¹ in order to afford spectral overlap with higher transitions of the anharmonic ladder (up to at least v = 7). The difference spectrum with a pump power of 8.5 µJ is displayed in Fig. 3. The probe delay was set to 1 ps, which is long enough to separate both beams clearly in time and avoid coherence artifacts in the transient absorption signal. Further increasing the probe delay time may also be disadvantageous, since short-lived higher-level populations might relax prior to probing. There is a strong bleach of the fundamental transition at 1982 cm⁻¹, accompanied by five new absorption bands corresponding to the first five overtone transitions: $1 \rightarrow 2$ at 1966 cm⁻¹, $2 \rightarrow 3$ at 1951 cm⁻¹, $3 \rightarrow 4$ at 1930 cm⁻¹, $4 \rightarrow 5$ at 1907 cm⁻¹, and finally $5 \rightarrow 6$ at 1882 cm⁻¹. It is clear by inspection that higher transitions have broader absorption bandwidths. By fitting each band to a Gaussian peak shape, we obtained



Fig. 3. A transient absorption (Δ OD) trace of W(CO)₆ in hexane is shown as a function of probe frequency. There is a strong bleach of the fundamental at 1982 cm⁻¹ and induced absorption bands due to population in the first 5 vibrationally excited levels of the T_{1u} COstretching mode. The delay between pump and probe was set to 1 ps.

the following FWHM parameters (in cm^{-1}) for the fundamental through fourth overtone: 5.6 (± 0.1), 7.0 (± 0.3) , 7.1 (± 0.3) , 8.8 (± 0.5) , 11.1 (± 0.8) (type A errors, k = 1). The signal-to-noise level was insufficient to measure the width of the fifth overtone accurately. In interpreting these values, it must be noted that the monochromator resolution was approximately 4-5 cm^{-1} , and thus the width of the fundamental is artificially increased from the intrinsic width of 3.5 cm^{-1} FWHM measured at higher resolution by FTIR. Note that probe absorption for the $5 \rightarrow 6$ transition corresponds to population transfer by the probe to v = 6. Given the fact that the pump pulse affords spectral amplitude a factor of ~ 20 higher at this resonance frequency, we conclude that the pump generates a nonzero population in v = 6, although direct observation is limited to v = 5 in the current setup. The principal limitation in the ladder climbing progression is the available laser pulse spectrum. In the current study, the bandwidth should allow excitation of the $6 \rightarrow 7$ transition, although the spectral amplitude there is small (Fig. 2A).

Inference of vibrational state populations from the band areas in the spectrum is nontrivial, since stimulated emission competes with absorption when the probe passes through the excited sample. In addition, the expected increase in absorption cross section with each successive transition must also be taken into account. We modelled the excitation process under the assumption that the cross section would scale as it does in a strictly harmonic potential, such that the oscillator strength for the *n*th overtone transition is (n + 1) times larger than the fundamental oscillator strength. We assumed, further, that population in v = 6 was negligible, and we then calculated relative populations using the formula $A_n = (n + 1)(P_n - P_{n+1})$, where A_n is the area of the *n*th overtone band and P_n is the population of the v = n vibrational level. Using this analysis, the bleached ground state population and the total excited population agreed to within 10% of one another. We calculated that a total of $\sim 25\%$ of the molecules present in the probe path were excited from the ground state, distributed as follows in the higher vibrational levels: $16 (\pm 2)\%$ excited to v = 1, 5.5 (±0.6)% to v = 2, 2.8 (±0.3)% to $v = 3, 1.3 \ (\pm 0.1)\%$ to v = 4, and 0.18 $\ (\pm 0.02)\%$ to v = 5.

The excited state population distribution was modeled theoretically by numerical solution of the modified Bloch equations and applying the density matrix formalism [6]. Briefly, the model incorporated a Morse oscillator manifold of anharmonic vibrational levels (v = 0-9 with constant $\Delta v = 15$ cm⁻¹ anharmonicity), absorption cross-sections that scale with level n (see above), fixed population lifetimes much longer than the pulse duration, and no cross-manifold relaxation channels. We also included damping (via coherence lifetimes between all interacting vibrational states) that increases by a factor of two for each ascending level to mimic the observed transition bandwidths. We estimated a T₂ coherence lifetime of 5 ps for the $v = 0 \rightarrow 1$ transition from the observed 4 cm⁻¹ (FWHM) bandwidth of the fundamental absorption (assuming a Gaussian band profile). The pump pulse electric field was input as a Gaussian envelope function possessing no chirp (e.g., transform limited). The pulse duration, bandwidth and center frequency were input from the measured pulse characteristics described above. From these vibrational state and pulse properties, the computer model predicts the relative ground and excited state vibrational populations as a function of Rabi frequency. The results of this modeling are shown in Fig. 4.

To apply these results to experimental conditions, it was necessary to take the beam geometry and intensity profile into account, since the Rabi frequency varies considerably across the beam, even at the focus. We used a Gaussian spatial intensity profile of the laser

Fig. 4. The traces shown above indicate the calculated relative populations of the first seven levels in the T_{1u} CO-stretching mode plotted as a function of Rabi frequency, which is proportional to the applied laser field and the molecular transition dipole. The calculations were based on the Bloch equation model described in the text.

beam discretized at the focus into a series of concentric rings. The Rabi frequency pertaining to each ring was calculated and weighted by the area of the ring. The correspondingly weighted vibrational population profiles at each Rabi frequency were obtained from Fig. 4 and summed to afford a net relative population distribution across the full beam. As anticipated for this nonlinear excitation process, resultant distributions were highly sensitive to the input beam focal size. Excellent agreement with the experimental data was achieved for a focal diameter of 400 µm (FWHM), which led to the following theoretical population profile: 74% in v = 0, 14% in v = 1, 6.1% in v = 2, 3.2% in v = 3, 1.5% in v = 4, and 0.5% in v = 5. While this focal diameter is somewhat larger than the experimentally measured value, we believe the discrepancy is easily compensated for by imperfect pump-probe overlap in the experimental setup.

To achieve population transfer to vibrational levels as high as v = 5, the pulse energy of the applied laser field is crucial. Fig. 5 shows the transient absorption spectra as a function of pump pulse energy, which was varied using a gold-coated CaF₂ gradient filter. Three measurements are shown, taken with 9.2, 5.2 and 2.6 µJ of pump energy at the sample, with all other experimental parameters held constant. The probe delay for these measurements was set to 150 fs. On the one hand, this minimized relaxation effects; but on the other hand, coherence artifacts such as the nonzero values in ΔOD for wavenumbers larger than the $0 \rightarrow 1$ transition appear, which are absent from the measurement at 1 ps delay shown in Fig. 3. For the highest fluence, we again observe population up to v = 5. As the fluence is reduced, the populations of levels 2–5 steadily decrease, while the population in level 1 increases. At low fluence, excitation proceeds mostly to v = 1, but too few photons are present to induce higher overtone population. This





Fig. 5. Transient absorption (Δ OD) traces are shown as a function of probe frequency for three different pulse energies. Note the increase of population in level 1 with decreasing pulse energy, with concomitant depopulation of levels 2–5. The probe delay was 150 fs.

finding supports a true ladder climbing mechanism, in which excitation is restricted to transitions between consecutive levels. Moreover, it suggests that to within the uncertainties noted, no competing excitation channel, such as ladder switching due to accidental degeneracies for higher steps in the ladder occurs. Thus, the observed ladder climbing is a true single mode process, as was shown previously for the excitation of gas phase metal carbonyls [9,10].

As mentioned earlier, we employed MIR pulses of similar energy and focal parameters to induce CO dissociation from metal carbonyl complexes in the gas phase [9,10]. The thermodynamics of these bond scissions require excitation at least to v = 7. The important question arises whether one can also induce ground state molecular dissociation in the condensed phase. Due to the observed spectral broadening of the absorption features and the current signal-to-noise ratio of our detection system, it is difficult to make a conclusive estimate of whether any population of v = 7 is achieved in the present study. However, even assuming that some small fraction of molecules were excited to the dissociation threshold, inducing molecular dissociation in the condensed phase remains a greater challenge than the analogous gas phase reaction. Upon excitation of the T_{1u} CO stretch, IVR is required to channel vibrational energy into the W-C reaction coordinate. In solution, collisions with solvent compete with this process and may rapidly remove energy from the excited molecule, thereby obstructing dissociation. Moreover, cumulative dissociation measurements in solution would be hindered by diffusional recombination of CO with the unsaturated $W(CO)_5$ fragment on a microsecond timescale. Therefore, in the absence of a more sensitive probe than transient absorption, clear detection of condensed-phase IR-induced dissociation remains inconclusive.

Nevertheless, given the efficiency of vibrational excitation demonstrated above, and realizing that for the MIR spectral range great potential exists for improving experimental conditions with respect to pulse energy, chirp and bandwidth, the present results are cause for optimism in the quest to achieve condensed phase ground state reaction control. As an example of future possibility, CO dissociation or rearrangement might be induced not only in homoleptic metal carbonyls, but in complex and biologically relevant systems such as myoglobin, currently an area of active research [12].

4. Summary

We applied resonant MIR fs pulses for efficient vibrational energy deposition in a single vibrational mode within molecules in solution. The generation of a vibrational population distribution up to v = 6 in the T_{1u} CO-stretching mode of condensed phase tungsten hexacarbonyl (corresponding to a single mode vibrational temperature of T = 2500 K) has been achieved by vibrational ladder climbing. The anharmonic transitions, including center frequencies and spectral broadening for each step in the ladder, have been determined up to v = 5 by transient absorption spectroscopy. Decreasing the pump fluence yielded an increase in the v = 1 population and accompanying depopulation of higher levels, in accordance with a stepwise ladder climbing mechanism. With a maximum energy of $12\,000-13\,000$ cm⁻¹ deposited in a single mode, the molecule is excited to a level in the range of the dissociation threshold of its W-C bond. Therefore, experiments are in reach that will aim at inducing ground state molecular dissociation in the condensed phase and detecting dissociation products on a shot-to-shot basis, so as to circumvent the problem of diffusional recombination. Furthermore, as an extension of coherent control studies to the liquid phase, application of modulated MIR laser pulses [13,14] might potentially generate non-Boltzmann population distributions in a selected mode and ultimately control the excitation or select between two or more reaction products. In the present case both concept-driven and tool-driven arguments converge to open new possibilities for controlling condensed phase quantum chemistry.

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- References
- [1] J.C. Polanyi, Acc. Chem. Res. 5 (1972) 161.
- [2] H.L. Dai, R.W. Field (Eds.), Advanced Series in Physical Chemistry, vol. 4, World Scientific, London, 1995.
- [3] N.V. Vitanov, T. Halfmann, B.W. Shore, K. Bergmann, Ann. Rev. Phys. Chem. 52 (2001) 763.
- [4] T.C. Weinacht, J.L. White, P.H. Bucksbaum, J. Phys. Chem. A 103 (1999) 10166.
- [5] V.D. Kleiman, J.S. Melinger, E.J. Heilweil, in: A. Douhal, J. Santamaria (Eds.), Femtochemistry and Femtobiology: Ultrafast Dynamics in Molecular Science, World Scientific Publishing, Singapore, 2002.

- [6] V.D. Kleiman, S.M. Arrivo, J.S. Melinger, E.J. Heilweil, Chem. Phys. 233 (1998) 207.
- [7] S.M. Arrivo, T.P. Dougherty, W.T. Grubbs, E.J. Heilweil, Chem. Phys. Lett. 235 (1995) 247.
- [8] D.J. Maas, D.I. Duncan, A.F.G. van der Meer, W.J. van der Zande, L.D. Noordam, Chem. Phys. Lett. 270 (1997) 45.
- [9] L. Windhorn, T. Witte, J. Yeston, D. Proch, M. Motzkus, K.L. Kompa, W. Fuss, Chem. Phys. Lett. 357 (2002) 85.
- [10] T. Witte, T. Hornung, L. Windhorn, D. Proch, R. de Vivie-Riedle, M. Motzkus, K.L. Kompa, J. Chem. Phys. 118 (2003) 2021.
- [11] L. Windhorn, J. Yeston, T. Witte, W. Fuss, M. Motzkus, D. Proch, K.L. Kompa, C.B. Moore, J. Chem. Phys. 119 (2003) 641.
- [12] U. Liebl, G. Lipowski, M. Negrerie, L.C. Lambry, J.L. Martin, M.H. Vos, Nature 401 (1999) 181.
- [13] T. Witte, D. Zeidler, D. Proch, K.L. Kompa, M. Motzkus, Opt. Lett. 27 (2002) 131.
- [14] T. Witte, K.L. Kompa, M. Motzkus, Appl. Phys. B 76 (2003) 476.