Solvent-dependent vibrational relaxation pathways after successive resonant IR excitation to $v=2$

Citation for published version (APA):

Bonn, M., Brugmans, M. J. P., & Bakker, H. J. (1996). Solvent-dependent vibrational relaxation pathways after successive resonant IR excitation to $v=2$. *Chemical Physics Letters*, 249(1-2), 81-86.
[https://doi.org/10.1016/0009-2614\(95\)01412-8](https://doi.org/10.1016/0009-2614(95)01412-8)

DOI:

[10.1016/0009-2614\(95\)01412-8](https://doi.org/10.1016/0009-2614(95)01412-8)

Document status and date:

Published: 01/01/1996

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Solvent-dependent vibrational relaxation pathways after successive resonant IR excitation to $v = 2$

Mischa Bonn^{a,b}, Marco J.P. Brugmans^a, Huib J. Bakker^b

^a FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

^b Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received 29 August 1995; in final form 11 December 1995

Abstract

With two subsequent resonant intense picosecond infrared pulses, we have succeeded in pumping a significant fraction of iodoform molecules in solution to the second vibrationally excited state of the C–H stretching mode. Transient populations of the vibrational levels are monitored with weak probe pulses. From these pump–pump–probe experiments, we find that the subsequent relaxation route depends critically on the solvent. In a strongly polar solvent (acetone) relaxation from $v = 2$ to $v = 0$ occurs predominantly via the $v = 1$ state, with time constants of $T_1^{2 \rightarrow 1} = 10 \pm 5$ and $T_1^{1 \rightarrow 0} = 60 \pm 5$ ps, respectively. In contrast, in a less polar solvent (chloroform) direct decay to the ground state is observed, with a time constant ($T_1^{2 \rightarrow 0} = 80 \pm 20$ ps), comparable to the energy lifetime of the first excited state ($T_1^{1 \rightarrow 0} = 125 \pm 5$ ps).

1. Introduction

A multitude of time-resolved experiments on small organic molecules in solution has provided insight into vibrational energy flow and dissipation mechanisms in these molecules [1]. In these pump–probe experiments, the C–H stretch vibration is excited to its first excited state, either by a resonant infrared pulse or by (stimulated) Raman excitation. A second, weaker, delayed probe pulse monitors the decay of the excited level. Some of these experiments have shown that after excitation of the C–H vibration there are *two* consecutive relaxation processes (see e.g. Refs. [2,3]). First, intramolecular vibrational relaxation (IVR) occurs: the energy is transferred to other low-frequency vibrations within the molecule. In the second process, called intermolecular energy transfer (IET), the excess energy is transferred to solvent molecules. It was found that the solvent has a large influence on the vi-

brational dynamics of small organic molecules [2]; the solvent not only modifies the rate of energy transfer to the solvent after vibrational relaxation within the molecule (IET), it also affects the intramolecular vibrational relaxation process (IVR) itself. With increasing polarity of the solvent, both relaxation processes are accelerated.

These insights were obtained from an abundance of experiments that have been performed on the lifetime of the first vibrationally excited state. In contrast, little is known about the relaxation rates and pathways of higher excited states. Lifetimes of higher excited states have previously been reported for (i) the C–O stretch of $\text{W}(\text{CO})_6$ [4], where due to the small anharmonicity of the vibration several higher transitions lie within the laser bandwidth, (ii) the C–D stretch of DCN [5] where a distribution of vibrationally excited states was observed after photogeneration of the molecule, and (iii) the C–H stretch of CHBr_3 [6], where the $v = 2$

state was populated directly by overtone absorption and the subsequent relaxation was monitored by anti-Stokes Raman probe scattering. In all of these cases, the relaxation rate was seen to increase with increasing vibrational quantum number and decay always occurred to the level directly below.

In this Letter, we report the relaxation from the second vibrationally excited state of the C–H stretch vibration of CHI_3 , after resonant excitation from $v = 0$ to $v = 1$ and subsequent resonant excitation from $v = 1$ to $v = 2$. We find that the nature of the solvent not only determines the rate of the IVR process but also controls the IVR pathways of the $v = 2$ relaxation.

2. Results and interpretation

The systems under investigation are 200 and 1000 μm thick samples of 0.34 and 0.19 mol/l solutions of iodoform (CHI_3 99%, Merck) in deuterated acetone ($\text{C}_3\text{D}_6\text{O}$ 99.5 at% *d*, Aldrich) and deuterated chloroform (CDCl_3 99.8 at% *d*, Janssen Chimica), respectively. Two independently tunable (2500–4000 cm^{-1} , bandwidth $\sim 10 \text{ cm}^{-1}$ at 3000 cm^{-1}) 25 ps infrared pulses (rep. rate of 10 Hz) with energies of $\sim 100 \mu\text{J}$ are generated through downconversion of 1064 nm Nd:YAG pulses in LiNbO_3 (an extensive description of the apparatus can be found in Ref. [7]).

Transient spectra (showing the $(0 \rightarrow 1)$ -pump-induced spectral changes with a delay between pump and probe of 35 ps) are shown in Fig. 1. At the $0 \rightarrow 1$ transition around 3010 cm^{-1} the transmission increases due to the excitation of a considerable fraction of oscillators from $0 \rightarrow 1$. For these excited oscillators absorption from $1 \rightarrow 2$ becomes possible. This transient absorption band associated with the $v = 1$ excited state absorption, the so-called hot-band, is $\tilde{\nu}_{\text{anh}}$ shifted from the $0 \rightarrow 1$ transition, and is observed around 2900 cm^{-1} [8]. For iodoform in chloroform-*d* the transmission is seen to dip slightly at the red side of the $0 \rightarrow 1$ transition ($\sim 2980 \text{ cm}^{-1}$). This is due to an anharmonic shift: after excitation of the C–H stretch mode to $v = 1$, IVR decay occurs to $v_{\text{C-H}} = 0^*$, where $v_{\text{C-H}} = 0^*$ stands for $v_{\text{C-H}} = 0$ with other modes within the molecule excited [3]. The anharmonic coupling to these other low-frequency intramolecular modes leads to a red-shift of the $(v_{\text{C-H}} = 0^*) \rightarrow (v_{\text{C-H}} = 1^*)$ compared

Fig. 1. Transient spectra, transmission changes versus wavenumber, recorded with a $1 \mu\text{J}$ probe pulse from the first branch, with the $150 \mu\text{J}$ pump tuned to the $(v = 0) \rightarrow (v = 1)$ transition of the C–H stretch vibration of iodoform in (a) deuterated acetone ($\tilde{\nu}_{\text{pump}} = 3007 \text{ cm}^{-1}$) (upper panel) and (b) deuterated chloroform ($\tilde{\nu}_{\text{pump}} = 3017 \text{ cm}^{-1}$) (lower panel). Transient spectra were recorded at a delay time between the pump and the probe of 35 ps, to avoid power broadening. The lines represent calculations described in the text.

to the $(v_{\text{C-H}} = 0) \rightarrow (v_{\text{C-H}} = 1)$ transition [3,9], as observed in Fig. 1b. Subsequently, the $v_{\text{C-H}} = 0^*$ will decay to $v_{\text{C-H}} = 0$. The anharmonic shift (difference between $(0^* \rightarrow 1^*)$ and $(0 \rightarrow 1)$) was found to be $29 \pm 3 \text{ cm}^{-1}$ for the solvent CDCl_3 . For CHI_3 in $\text{C}_3\text{D}_6\text{O}$ this is not observed (Fig. 1a), since in this case the $0^* \rightarrow 0$ relaxation is much faster [9].

In the calculations (lines in Fig. 1) the transient spectrum is calculated: input parameters are the absorption band and the spectral profile of the pulses. The excited fraction of oscillators (typically 20%) is adjusted to the experimental $0 \rightarrow 1$ signal amplitude.

For the hotband, the width, the $1 \rightarrow 2$ cross section and the anharmonicity are adjustable parameters. The shape of the hotband and the $0^* \rightarrow 1^*$ transition (for CHI_3 in CDCl_3) are assumed to be that of the $0 \rightarrow 1$ absorption band. For both transients the hotband was found to be 1.65 ± 0.10 broader than the fundamental absorption band. The integrated cross-sections for $1 \rightarrow 2$ were found to be 1.95 ± 0.10 times that of $0 \rightarrow 1$, close to the value of 2 for a harmonic oscillator [10]. The anharmonicities are 118 ± 1.5 and $122 \pm 1.5 \text{ cm}^{-1}$ for CDCl_3 and $\text{C}_3\text{D}_6\text{O}$, respectively.

For the pump-pump-probe experiments, the delay between the $(1 \rightarrow 2)$ -pump and the $(0 \rightarrow 1)$ -pump was fixed at 16 ps (the time at which the effect of the $(0 \rightarrow 1)$ -pump is maximal). In these experiments, the delay of the probe pulse, of the same frequency as the $(1 \rightarrow 2)$ -pump, is varied. In Fig. 2 the transmission of the probe tuned to the $1 \rightarrow 2$ absorption with and without the second pump pulse is shown. Clearly, the $(1 \rightarrow 2)$ -pump excites a significant number of oscillators to their second excited state. With the $(0 \rightarrow 1)$ -pump blocked, no signal was observed, confirming that the transmission changes due to the $(1 \rightarrow 2)$ -pump result from up-pumping of the C–H oscillators to their second vibrationally excited state. The large anharmonicity of the C–H stretch vibration (the $\sim 120 \text{ cm}^{-1}$ difference between ground and excited state absorption) indicates the $\nu = 2 \rightarrow \nu = 3$ transition is not involved in this measurement (assuming a Morse potential, the $\nu = 2 \rightarrow \nu = 3$ transition frequency is readily calculated to be 2780 cm^{-1}). In the experiment, the polarizations of the pulses were parallel. From the observation that the $0^* \rightarrow 1^*$ absorption rises with the same time-constants as the $\nu = 1$ decays [9], it is apparent that reorientational motion (and the associated polarization diffusion) is either very fast or very slow compared to both the pulse duration and vibrational relaxation times, presumably very fast (see Ref. [11]). Hence, contributions to the signal arising from polarization diffusion play no role in the interpretation of the data.

There is a remarkable difference between the results of the pump-pump-probe experiment for the two solutions (Fig. 2): whereas for CHI_3 in CDCl_3 the transmission with the second pump remains larger than the transmission without the second pump at all delays, for CHI_3 in $\text{C}_3\text{D}_6\text{O}$ the two signal curves cross (see inset in Fig. 2a). The latter can be understood

Fig. 2. Transient transmission changes at the $1 \rightarrow 2$ frequency, after excitation with the $(0 \rightarrow 1)$ -pump, with and without the $(1 \rightarrow 2)$ -pump pulse. The increased transmission with the second pump pulse is due to excitation to the second excited state, whereafter absorption from $\nu = 1$ to $\nu = 2$ can no longer occur. Data are obtained in one experimental run: every other $(1 \rightarrow 2)$ -pump pulse is blocked. The lines are numerical solutions to the rate equations of the three-level system, assuming decay from $(2 \rightarrow 1)$ for (a) acetone (upper panel) and direct decay to the ground state $(2 \rightarrow 0)$ for (b) chloroform (lower panel).

as follows: the probe pulse is monitoring the population difference between the $\nu = 1$ and $\nu = 2$ levels. If the oscillators in $\nu = 2$ decay to $\nu = 1$, then the long-time effect of the second pump pulse will be that there are more oscillators in $\nu = 1$ than without the second pump pulse; the oscillators have been put 'on hold' in the $\nu = 2$ state for a time $T_1^{2 \rightarrow 1}$, so that the hotband ($1 \rightarrow 2$ absorption) will effectively live somewhat longer with than without the second pump pulse. For CHI_3 in CDCl_3 , such a crossing is not observed.

Fig. 3. Transient (1→2)-pump pulse induced transmission changes at the 1→2 transition frequency: the logarithm of the transmission with both pump pulses (T_{wp}) normalized to the transmission without the second pump (T_{np}) for (a) acetone and (b) chloroform as solvent. Dots are data with the second pump and the probe tuned to the peak of the hotband, open squares with 12 cm^{-1} detuning to the red. The line through the 2873 cm^{-1} data (red side of hotband) for chloroform is the same as the calculation for the 2885 cm^{-1} data, scaled to signal amplitude. Clearly, the $v = 2$ does not relax to an anharmonically shifted $v = 1^*$.

The effect is even clearer in Fig. 3, where the transmission changes induced by the second pump pulse are plotted versus delay.

The data for CHI_3 in $\text{C}_3\text{D}_6\text{O}$ can be adequately described by numerically solving the rate equations for a three-level system, assuming a $2 \rightarrow 1 \rightarrow 0$ decay path (see lines in Figs. 2a and 3a). The energy decay time of the $1 \rightarrow 0$ transition was determined in a separate 2-colour ($0 \rightarrow 1$)-pump ($1 \rightarrow 2$)-probe experiment to be 60 ± 5 ps. From the width and the amplitude of the bleaching signal, the energy decay time $T_1^{2 \rightarrow 1}$ was

found to be 10 ± 5 ps. For CHI_3 in CDCl_3 , the data cannot be described by a $2 \rightarrow 1 \rightarrow 0$ decay path.

It could be that, for CHI_3 in CDCl_3 , the decay from $v = 2$ occurs to a level $v = 1^*$, where $v = 1^*$ stands for $v_{\text{C-H}} = 1$ with other modes within the molecule excited, resulting in an anharmonic red-shift as described above (Fig. 1b). If this anharmonic shift is sufficiently large, the $1^* \rightarrow 2^*$ absorption shifts out of the ($1 \rightarrow 2$)-probe laser bandwidth, after deexcitation from $2 \rightarrow 1^*$, and the transmission of the probe will remain larger than without the $1 \rightarrow 2$ pump pulse at all delays. We checked for this effect by ($1 \rightarrow 2$)-pumping and -probing the red side of the hotband (open squares in Fig. 3b). In this experiment, decay to a $v = 1^*$ state would result in a signal with a decreased transmission at delay times where IVR has, but IET has not yet occurred ($\gtrsim 35$ ps), as in Fig. 1b. It is clear, however, from Fig. 3b that the data collected at the red side of the hotband show the same decay as the data at the peak of the hotband. Hence, we can exclude the $2 \rightarrow 1^*$ relaxation path for CHI_3 in CDCl_3 , and conclude that relaxation occurs directly from $2 \rightarrow 0^*$. Probing the $0 \rightarrow 1$ transition, no significant effect of the second pump pulse was observed. This supports the direct relaxation from $2 \rightarrow 0^*$: it can be expected that the anharmonic shift of the $0^* \rightarrow 1^*$ after direct decay from $v = 2$ will be larger than after decay from $v = 1$, permitting the $v = 0^*$ to $v = 1^*$ transition to shift out of the laser bandwidth, resulting in a smaller signal probing the $0 \rightarrow 1$ transition.

Indeed, the data for CHI_3 in CDCl_3 can be described by calculations assuming direct decay of $v = 2$ to $v = 0$ (with $T_1^{1 \rightarrow 0}$ separately determined to be 125 ± 5 ps). The calculations for this system indicate two possible ranges of $T_1^{2 \rightarrow 0^*}$, smaller than 12 ps and between 60 and 100 ps. However, fast decay can be ruled out owing to the following considerations: (i) For the fast decay process, our numerical calculations predict a smaller effect of the second pump pulse than observed when probing the $1 \rightarrow 2$ transition. In contrast, when slow decay is assumed the transmission change due to the second pulse is well reproduced. (ii) Our calculations further show that, for fast decay from $v = 2$ to $v = 0$ the signal $\ln(T_{wp}/T_{np})$ (Fig. 3) probing the $0 \rightarrow 1$ transition would be equal to that probing the $1 \rightarrow 2$ transition. For fast decay from $v = 2$ to $v = 0^*$, the signal $\ln(T_{wp}/T_{np})$ probing the $0 \rightarrow 1$ transition would be half of that probing the $1 \rightarrow 2$ transition. For slow decay the

0→1 signal becomes even four times smaller than the 1→2 signal. The data probing the 0→1 transition are not shown here, since no significant 1→2-pump induced transmission changes could be observed. This points to a signal much weaker than that probing the 1→2 transition, indicating that slow decay occurs from $v = 2$. The results of the calculations assuming slow decay ($T_1^{2 \rightarrow 0^*} = 80$ ps) from the second excited state are shown as lines in Figs. 2b and 3b.

3. Discussion

Recently, a theoretical model was developed which describes the effect of intermolecular (solute–solvent) interactions on the intramolecular energy transfer in small organic molecules [9]. This theory successfully describes the dependence of the $v_{\text{C-H}} = 1$ IVR relaxation rate on solvent. The theory predicts that the rate of IVR is determined by (i) the anharmonic coupling matrix element (describing the anharmonic coupling between the C–H stretching mode and the accepting modes, which are excited upon de-excitation of the C–H stretching mode), (ii) the energy difference between the C–H stretching mode and the combination of anharmonically coupled accepting modes (a measure of how good the resonance is) and (iii) the width of the absorption lines associated with vibrational transitions in the molecule (a measure of how important perfect resonance is). In the third lies the solvent-effect: the solvent influences the relaxation rate by influencing the transition energy distributions (i.e. the width of the absorption lines). Broader lines will imply larger possible overlap of the original mode with accepting mode combinations, resulting in faster decay.

Comparing the 2→1 to the 1→0 relaxation, the first and the last effects will increase the relaxation rate for both solvents, since (i) the $v = 2$ wavefunction will be more spread out than the $v = 1$, increasing the anharmonic coupling and (ii) as shown in Fig. 1, in both solvents the 1→2 absorption line is broadened compared to the 0→1 absorption line. However, the fact that in CDCl_3 relaxation from $v = 2$ occurs directly to $v = 0$ shows that in this case the 2→1 relaxation is slow, and probably even slower than the 1→0 relaxation. Apparently, the energy mismatch is large for the 2→1 process compared to the 1→0. For the two so-

lutions discussed in this Letter one would expect similar intramolecular anharmonic couplings. Also, the energy mismatches are expected to be quite similar (although it must be noted that the solvent determines the *exact* position of the (0→1) and the (1→2) transitions, as can be seen in Fig. 1). Therefore, differences in relaxation paths and rates must be mainly due to differences in energy mismatch compensation capacity of the solvent. In principle, the solvent effect on the energy mismatch compensation is twofold: The solvent affects both the width of the C–H stretching mode and the width of low-frequency modes within the molecule, which act as accepting modes in the relaxation process.

The hotband of CHI_3 in $\text{C}_3\text{D}_6\text{O}$ is extremely broad (Fig. 1a), indicative of the ability to compensate for large energy mismatches. This explains that in $\text{C}_3\text{D}_6\text{O}$ the 2→1 relaxation can occur despite a large energy mismatch. Due to this large mismatch, the 2→1 relaxation for CHI_3 in CDCl_3 is slow. As a consequence, the 2→0 relaxation becomes the dominant relaxation path, despite the fact that the anharmonic coupling can be expected to be much smaller for this transition. However, the direct 2→0 process can become relatively efficient, due to a small energy mismatch between the mode and the combination of accepting modes. It is unknown which specific low-frequency modes act as accepting modes, but when a larger amount of energy must be disposed of, more low-frequency mode combinations are resonant with the energy: the low-frequency modes within the CHI_3 molecule [12] show that with four accepting modes there is only one combination that lies within 100 cm^{-1} of the (1→0) transition. For the (2→0) transition, with eight accepting modes, there are six possible relaxation channels within 100 cm^{-1} of this transition.

The 2→0 process could also occur for CHI_3 in $\text{C}_3\text{D}_6\text{O}$, presumably with a rate similar to that of the 2→0 transition, as in CDCl_3 , since for this transition there is no necessity for compensating large energy mismatches. However, the rate will be negligible compared to the 2→1 relaxation rate, and the 2→0 process is therefore not observed in the experiment.

Summarizing, the 2→1 process requires a large energy mismatch compensation from the solvent, readily obtained from acetone, but not from chloroform. In chloroform, direct relaxation to the ground state becomes the principal relaxation pathway.

4. Conclusions

We have succeeded in resonantly climbing the vibrational ladder of the C–H stretch vibration in CHI_3 to the second excited state. The decay from this state depends crucially on the solvent. For a strongly polar solvent decay from $\nu = 2$ first occurs to $\nu = 1$, whereafter the first excited state decays to the ground state. For a less polar solvent, direct decay to the ground state is the dominant relaxation pathway. The difference is qualitatively explained in terms of the energy mismatch compensation by the solvent in the IVR process; apparently, for the $\nu = 2$ to $\nu = 1$ decay process, there is a large energy mismatch between the energy associated with this transition and the combination of the anharmonically coupled accepting modes. In the case of a strongly polar solvent (acetone), this energy mismatch is easily compensated for, resulting in the $2 \rightarrow 1 \rightarrow 0$ relaxation route. In a less polar solvent (chloroform), the energy mismatch compensation is not so efficient and direct decay from $\nu = 2$ to $\nu = 0$ occurs.

Acknowledgement

The work described in this Letter is part of the research program of the Stichting Fundamenteel On-

derzoek van de Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Research).

References

- [1] J.C. Owruksy, D. Raftery and R.M. Hochstrasser, *Ann. Rev. Phys. Chem.* 45 (1994) 519.
- [2] H.J. Bakker, P.C.M. Planken and A. Lagendijk, *Nature* 347 (1990) 745.
- [3] H. Graener, *Chem. Phys. Letters* 165 (1990) 110.
- [4] S.M. Arrivo, T.P. Dougherty, W.T. Grubbs and E.J. Heilweil, *Chem. Phys. Letters* 235 (1995) 247.
- [5] D. Raftery, E. Gooding and R.M. Hochstrasser, in: *Ultrafast phenomena*, Vol. IX, eds. P.F. Barbara et al. (Springer, Berlin, 1994).
- [6] H. Graener and A. Laubereau, *Chem. Phys. Letters* 102 (1983) 100.
- [7] M.J.P. Brugmans, H.J. Bakker and A. Lagendijk, submitted for publication.
- [8] H. Graener, R. Dohlus and A. Laubereau, *Chem. Phys. Letters* 140 (1987) 306.
- [9] H.J. Bakker, *J. Chem. Phys.* 98 (1993) 8496.
- [10] P.W. Atkins, *Molecular quantum mechanics* (Oxford Univ. Press, Oxford, 1992).
- [11] G. Seifert and H. Graener, *Opt. Commun.* 115 (1995) 216.
- [12] T. Shimanouchi, *Table of molecular vibrational frequencies, consolidated*, Vol. I, NSRDS-NBS Circular No. 39 (US GPO, Washington, 1972).