Free-electron laser as a tool for pump-probe measurements of the vibrational relaxation in condensed phases

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Received 23 February 1995

Abstract

In this communication, we discuss the interest of the infrared free-electron laser (CLIO) for measurements of vibrational relaxation rates at the picosecond scale by a one-color pump-probe experiment. We report the results of preliminary experiments involving small molecules (CO, CO2) in low-temperature argon matrices and intermediate-size molecules (acetonitrile, benzonitrile) in room-temperature CCl4 solutions.

1. Introduction

The vibrational relaxation of polyatomic molecules in condensed phases has been studied for twenty years using the pulsed excitation of selected vibrational levels and probing the population of excited levels by time-resolved IR fluorescence [1], transient IR absorption [2], laser induced visible/UV fluorescence [3] and Raman scattering [4].

It was shown that the relaxation of a polyatomic molecule is a sequential process (Fig. 1). The first stage corresponds to the population transfer from the initial prepared doorway level |s⟩ (typically the v1 = 1 level of the IR-active ith normal mode) to close lying levels |l⟩ corresponding to different combinations of lower-frequency modes. Only a small fraction of the vibrational energy is transferred to the lattice. The second stage consists of a series of non-radiative steps at a

\[ K_1 \]

Fig. 1. Schematic representation of the vibrational relaxation pathways in a polyatomic molecule.

ladder of intermediate vibrational states until the whole energy excess is dissipated and the initial population of the fundamental |0⟩ level is recovered. The decay associated with the first step may be considered as exponential with the rate constant k1 while the time scale of the further ones may be approximated by k2 – the rate

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SSD/0030-4018 (95)00219-7
of the slowest, rate-determining step (usually, the relaxation from the lowest excited to the ground vibrational level). The values of $k_1$ and $k_2$ differ by orders of magnitude: $k_1$ varies in the $10^4$ to $10^{12}$ s$^{-1}$ range in low-temperature matrices [3] and in room-temperature liquid solutions [4], while for molecules such as CH$_3$F (CD$_3$F) in low-temperature matrices, $k_2$ (strongly dependent on the host) varies in the $10^4$ to $10^6$ s$^{-1}$ range [2].

In a one-color pump-probe experiment, the $|0\rangle \rightarrow |s\rangle$ transition is pumped by a pulse at $t = t_0$ and then the $|0\rangle \rightarrow |s\rangle$ absorption is interrogated by a probe pulse after a variable $\Delta t = t - t_0$ delay. The absorption depends on the difference between the populations of $|0\rangle$ and $|s\rangle$ levels: \( \Delta N = N_0 - N_s \). In the low-temperature limit where $k_e \gg kT$ for all vibrational modes, at $t < t_0$, $N_s = 0$ and $N_0 \equiv N$ (where $N$ is the total number of molecules in the sample) so that $\Delta N (t < t_0) = N$. If the fraction $\alpha$ of molecules is transferred to the $|s\rangle$ state by the pump pulse, we have $N_0(0) = N(1 - \alpha)$, $N_s(0) = \alpha N$ and $\Delta N(0) = N(1 - 2\alpha)$, i.e. the absorption is reduced to the $1 - 2\alpha$ fraction of its initial value. If $k_1 \gg k_2$, the further evolution of populations is given by

\[
N_s(t) = \alpha N \exp[-k_1(t - t_0)] ,
\]

\[
N_0(t) = N[1 - \alpha \exp[-k_2(t - t_0)]] ,
\]

hence the variation of population difference (and of the optical density at $\nu = E_i/h$) may be approximated by a bi-exponential:

\[
\Delta N(t) = N - \alpha N \exp[-k_1(t - t_0)]
- \alpha N \exp[-k_2(t - t_0)] .
\]

The interest of a one-color pump-probe experiment (in spite of obvious limitations) consists in the possibility to determine both $k_1$ and $k_2$ constants in the same experiment.

### 2. The light source - the CLIO free-electron laser

The free-electron laser CLIO has been described in detail elsewhere [5,6]. This source is continuously tunable in the 4 to 16 μm (600 to 2500 cm$^{-1}$) spectral range with possible extension to the far infrared. The radiation is emitted in the form of macropulses with a ca. 10 μs duration and 6.25 or 25 Hz repetition rate. Each macropulse consists of a train of ~600 (or 300) micropulses with a FWHM $\delta \tau \approx 1$ ps and a time interval between pulses of $T = 16$ or 32 ns. The measured spectral width of a macropulse (ca. 15 cm$^{-1}$) is slightly larger than the homogeneous (Fourier-transform limited) width of the micropulse. The average power measured at the exit window of the light line is of the order of 800 mW at 25 Hz, which corresponds to an energy of ~20 μJ per micropulse and a peak power of the order of 20 MW. The laser beam, limited to the TEM$_{00}$ mode, has a diameter of ~1 cm.

In the pump-probe experiment with an optical delay between pump and probe beams and usual IR detectors with a response time of $10^{-6}$ to $10^{-7}$ s we cannot separate individual micropulses. The observed effect of the pump on transmission of the probe beam is the average upon two "combs" of micropulses delayed by $\Delta \tau$ which may be varied. The information which can be extracted depends on the relative magnitude of relaxation times ($\tau_i = 1/k_i$) and of the time interval between micropulses ($T$).

In the case of a rapid relaxation ($\tau \ll T$) we are dealing with individual pulses and Eq. (2) may be applied to the experimental data provided that a finite width of the pump and probe pulses ($\delta \tau$) is taken into account in the case of $\tau = \delta \tau$.

If $\tau \gg T$, the pileup of the excited level population must be taken into account. For each component of the bi-exponential given in Eq. (2), the population of the excited state at the time $t$ after the $n$th exciting pulse is given by

\[
N_s(t + nT) = \alpha N \sum_n e^{-k_1(nT)}
\]

\[
\rightarrow \frac{\alpha N}{1 - e^{-k_1T}} e^{-k_1t} \quad \text{for} \ n \to \infty ,
\]

while for the ground state population we get

\[
N_0(t + nT) = N \left( 1 - \alpha \sum_n e^{-k_2(nT)} \right)
\]

\[
\rightarrow N \left( 1 - \frac{\alpha e^{-k_2T}}{1 - e^{-k_2T}} \right) \quad \text{for} \ n \to \infty .
\]

The population difference is reduced to a value oscillating between the limits
\[ \Delta N = N \left( 1 - \frac{2 \alpha}{1 - e^{-\Delta T}} \right) \text{ for } t = 0, \]
\[ \Delta N = N \left( 1 - \frac{2 \alpha e^{-\Delta T}}{1 - e^{-\Delta T}} \right) \text{ for } t = T, \]

and nearly constant when \( kT \ll 1 \). Note that even in this case the relaxation rate may be estimated from the measured \( \Delta N \) value if \( \alpha \) is evaluated from the transition probability and the laser fluence.

3. Experimental

The experimental setup used in this work is of the current type (Fig. 2):

- The beam of the CLIO laser is first sent to a ZnSe beamsplitter. The reflected beam (about 30% of the intensity of the incident beam) is focused at the entrance slit of the Digikrom monochromator M1 (equipped with the Spivicon 34-diode array detector D1) used to control the peak wavelength, \( \lambda \), and width, \( \delta \lambda \), of the laser emission. The wavelength jitter is reduced by correcting the electron-accelerating potential by an electric signal proportional to the deviation of \( \lambda \) from its central value, \( \lambda_0 \) (for details cf. Ref. [7]).

- The transmitted beam is then separated by a CaF\(_2\) plate into the pump beam (ca. 90% of the remaining power) and two beams reflected at both surfaces of the window. One of them is directly sent to the entrance slit of monochromator M2 equipped with the MCT infrared detector D2. The second one — delayed by an optical delay line L — inducing a variable (\( \sim 50 \) to 250 ps) delay with respect to the pump beam — is used as the probe beam. The pump and probe beams are then crossed at the sample S, the probe beam being focused at the entrance slit of the monochromator M3 with the D3 detector identical with the D2 one. The intensity of the pump beam is measured by a pyroelectric detector D4; this beam can be periodically blocked.

- The response times of the D2 and D3 detectors are long as compared to the interval between micropulses: the integrated intensities of electric pulses \( S(D2) \) and \( S(D3) \) correspond to the average fluences of the incident, \( I_0 = S(D2) \), and transmitted, \( I = S(D3) \), probe beams. The signals are integrated by two identical boxcar integrators and recorded by a micro-computer recording also the response of the D4 detector monitoring the intensity of the pump, \( I_0 \). One can measure the \( I/I_0 \) ratio either at a constant optical delay in presence, \( (I/I_0)_p \), and in absence, \( (I/I_0)_a \), of the pump beam or by continuous scanning the delay.

For room-temperature measurements we used liquid solutions contained in a cell with adjustable thickness equipped with KBr windows, while for low-temperature experiments, argon matrices were deposited on the CsBr window of a liquid-helium cryostat cooled to \( \sim 6 \) K.

The absorption spectra of samples were recorded using a conventional light source (Nernststift), a chopper and a lock-in amplifier.

4. Results and data treatment

The measurements were carried out in the 2100–2300 cm\(^{-1}\) spectral range, free of H\(_2\)O vapor and CO\(_2\) absorption. Two types of systems were investigated:

(i) Medium-size molecules: acetonitrile (CH\(_3\)CN) and benzonitrile (C\(_6\)H\(_5\)CN) in dilute (\( 10^{-3} \) to \( 10^{-2} \) mole/l) room-temperature CCl\(_4\) solutions, for which the relaxation at the picosecond scale is expected upon the excitation of one quantum of the C=\( \equiv \)N stretching mode at 2250 and 2210 cm\(^{-1}\), respectively.

(ii) Small molecules dispersed (\( M:A = 1:2000 \)) in low-temperature argon matrices (\( T \approx 6 \) K): CO excited to the \( \nu = 1 \) level (2138.6 cm\(^{-1}\)) with the relaxation time of 20 ms [8], and \(^1\)CO\(_2\) excited to the \( \nu_3 = 1 \) level (2273.5 and 2280.7 cm\(^{-1}\) for two different sites) for which one can expect relaxation in the microsecond range. In the last case, the heavy isotopomer was used
in order to avoid absorption of the laser radiation by atmospheric CO$_2$.

4.1. Rapid relaxation of $R$--$C$=N molecules in CCl$_4$ solutions

The time dependence of the sample absorption is similar for both solutes. The absorption bands are relatively broad ($\delta \nu \approx 5$ cm$^{-1}$), so that the major part of the (spectrally unresolved) pump laser pulse is absorbed. On the other hand, we are probing through a narrow slit of the M3 monochromator a ca. 1 cm$^{-1}$ region coinciding either with the peak or with the wing of the absorption band.

In presence of the pump beam, we observe two distinct effects:

(i) A short-lived absorption dip (transient bleaching) when probing in the absorption peak (Fig. 3).  This effect is strongly attenuated in the wings of the absorption band or when the concentration of the solute is reduced. Its duration seems to be limited by the time resolution of our experiment -- reduced to ca. 6 ps by use of narrow spectral slits. In the peak, the intensity of the transmitted radiation is increased by a factor of $\sim 2$, this effect corresponding to the $\vert 0 \rangle \rightarrow \vert x \rangle$ transfer of the important fraction of the initial ground state population by the pump beam.

(ii) An increase or decrease of the transmitted signal (the sign of the effect depends on the position of the pump--probe crossing point either within the liquid or at the liquid/window interface) building up with a rise time of ca. 50 ps (Fig. 4). The intensity of this effect remains nearly unchanged when the frequency of the probe beam is displaced from the absorption peak to its wing, as long as the pump beam is strongly absorbed. It disappears when the pump is shifted out of the absorption region. It seems thus to be related to macroscopic (or mesoscopic) effects resulting from the transfer of a large amount of energy to the solvent: diffraction of re-focalization of the probe beam by a thermal or density lens. The buildup time of the effect is similar to that observed in the case of the strong absorption of the visible light in concentrated dye solutions [9].

4.2. Slow relaxation in low-temperature, rare-gas matrices

In presence of the pump beam, the transmission of the sample is increased by a factor of 2, this ratio being constant when the pump--probe delay is varied between $\sim 50$ and 250 ps. Such a behavior corresponds obviously to the $\tau \gg T$ limit. This result is not surprising: the purely radiative deactivation of the $\sigma = 1$ level of CO in the Ar matrix at $T \sim 10$ K (a single-step process) takes place with $k_{\text{eff}} = 50$ s$^{-1}$ (this value is consistent with the ca. 20 ns decay time of the IR fluorescence observed in this work in a good agreement with previous experiments [8]).

The same behavior — a strong bleaching independent of the pump--probe delay — was observed for CO$_2$ in the argon matrix (Fig. 5). This corresponds to the $\tau \gg T$ limit, i.e. to $k \ll 10^7$ s$^{-1}$. In view of such an inefficient non-radiative process it seems possible to observe the infrared fluorescence corresponding to one or several bottleneck steps in the $\vert x \rangle \rightarrow \{ l \} \rightarrow \vert 0 \rangle$ cascading.
We attempted to detect such a fluorescence in the 600 to 700 cm\(^{-1}\) spectral range, i.e., for the \(\Delta v = -1\) transitions. As a matter of fact, a weak fluorescence signal with a decay time of 3 \(\mu s\) \((k \approx 3 \times 10^5 \text{ s}^{-1})\) and a spectrum consisting of a single line centered at 16.3 \(\mu m\) \((613 \text{ cm}^{-1})\) was observed for one of the samples but could not be observed for other ones. This emission may be assigned to the \(v_2 = 2 \rightarrow v_2 = 1\) transition in \(^{13}\text{CO}_2\) trapped in a metastable site with a long vibrational lifetime. As evidenced by the high-resolution FTIR spectroscopy, this site, stable only for \(T \leq 10\ \text{K}\), is characterized by an extremely narrow absorption

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**Fig. 4.** Induced transparency: \[
\frac{(I/I_0)_p - (I/I_0)_b}{(I/I_0)_b}\]
of the acetonitrile/CCl\(_4\) solution measured out of the CH\(_3\)CN absorption maximum: points — experiments, solid line — best fit by \(1 - e^{-kt}\) with \(k = 2 \times 10^{10} \text{ s}^{-1}\).

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**Fig. 5.** Transmission of the probe beam in presence \((I/I_0)_p\) and absence \((I/I_0)_b\) of the pump beam \((\nu = 2275 \text{ cm}^{-1})\) in the argon matrix containing \(5 \times 10^{-4} \text{^{13}CO}_2\). The modulation depth is independent of the pump–probe delay.
band [10]. If this assignment is confirmed, the decay rates for other sites of the $^{13}$CO$_2$/Ar system must be contained in the $10^6$–$10^7$ s$^{-1}$ limits, their fluorescence being too short or too weak to be detected in our experimental conditions.

5. Conclusions

The preliminary results were obtained for two limiting cases corresponding to decay rates too high and too low for direct determination of $k_1$ and $k_2$. Nevertheless, they show that: (i) the laser energy is high enough to induce in a single pulse a population transfer which is easily detectable even in the case of very rapid decays, (ii) for slowly decaying systems, we closely approach the saturation of transitions.

This work is continued, the attention being focused on larger molecules in rare-gas matrices.

References