VIBRATIONAL LIFETIMES AND INTRAMOLECULAR ENERGY RANDOMISATION OF POLYATOMIC MOLECULES IN LIQUIDS

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ABSTRACT

   Transient experiments with picosecond laser pulses give valuable
information on the dynamic properties of polyatomic molecules in
the electronic ground state. In small molecules the decay of vibra-
tional energy occurs via individual lower energy states; in large
molecules the experimental data support a statistical model.

   For a number of years we have been concerned with two elementary
questions: How long does a normal mode of a polyatomic molecule
vibrate after excitation and in which way and how fast is vibratio-
nal energy redistributed over the molecule? Our investigations were
made in liquids, since this phase is of paramount importance in
chemistry and biology. There are numerous reactions in chemistry
and biology, where excess energy first goes into vibrational energy
states and from there to the thermal bath. What are the relevant
time constants for these processes? Another topic of current inter-
est is the prospect of state-selected chemistry where new and
efficient reaction channels are predicted after excitation of indi-
vidual vibrational modes by infrared laser radiation. In this re-
spect, the population life times of vibrational modes are of rele-
vance. The data presented in this note shine new light on the
problem raised above.

   The main reason for the lack of information on vibrational life
times in liquids is the strong interaction of molecules in the
liquid phase. The expected time constants are very short, of the
order of 10^{-10} to 10^{-12} seconds. With the advent of ultrashort
laser pulses it becomes possible to start quantitative experiments
in this very short time domain /1-3/. In our experiments we excite
a well defined vibrational mode, e.g. a known CH-stretching mode,

by an ultrasnort (∿ 5 ps) infrared pulse of the appropriate fre-
quency and monitor the anti-Stokes Raman spectrum with a second
delayed visible pulse, again of a few picoseconds duration. In this
way we are able to investigate several vibrational energy states
of the same molecule. We may follow the redistribution of vibratio-
nal energy from the excited mode to lower lying states. In particu-
lar, we study for different vibrational modes (i) the rise and the
delayed maximum of the excess vibrational population, (ii) the
decay time of the mode, and - most recently - (iii) the absolute
cnange in population.

In a number of previous papers we investigated the population
life time of individual modes in <u>small molecules</u> /4-7/. CH-stretch-
ing modes were resonantly excited around 3000 cm^{-1} by tunable IR-
pulses. Of major interest are the following observations:

(i) There exists rapid vibrational energy exchange between similar
modes of nearby energy states. For instance, energy is rapidly
transferred from the primary excited CH-stretching modes to a neigh-
boring Raman active CH-stretching mode during the excitation time
of a few picoseconds.

(ii) Tne decay of vibrational energy proceeds via anharmonic coup-
ling with neighboring overtones and combination modes. As an
example we point to the favorable energy transfer in certain mole-
cules from the CH-stretching modes at ∿ 3000 cm^{-1} to the overtones
of the corresponding bending modes at approximately 1500 cm^{-1}.

(iii) The degree of interaction between the fundamentals and the
overtones and combination modes may be infered from an inspection
of the types of modes involved and from the investigation of the
Fermi resonance between the modes of interest. The quantitative
study of the infrared Raman spectra has allowed us to estimate
transfer rates for vibrational energy in fair agreement with expe-
rimental observations.

As an example we present data on CH_2CCl_2 and trans CHCl=CHCl,
where only two atoms exchange their positions while tne structure
and the number of atoms are preserved /6/. In Fig. 1a experimental
data of CH_2CCl_2 are depicted. The v_1 mode at 3036 cm^{-1} is resonant-
ly excited by an infrared pulse and the anti-Stokes signal of the
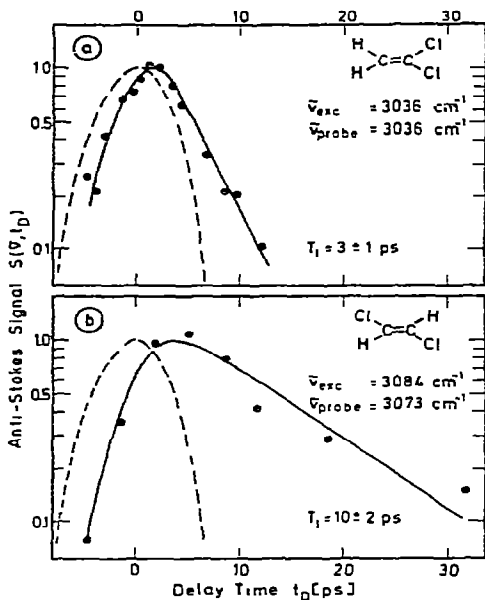same mode is observed. The Raman signal, i.e. the population of

Figure 1: Anti-Stokes signal versus delay time of the probing pulse. (a) CH_2CCl_2 in CCl_4 (c = 0.35 m.f.). The decay of the CH_2-stretching mode at 3036 cm^{-1} is shown. (b) trans CHClCHCl in CCl_4 (c = 0.35 m.f.). The CH-stretching mode at 3084 cm^{-1} is excited and the mode at 3073 cm^{-1} is monitored. The broken curves are the cross-correlation functions of the IR exciting and green probing pulse.

the ν_1 mode, decays with a life time of T_1 = 3±1 ps. Quite different is the time dependence of the CH-stretching modes in trans CHCl=CHCl (see Fig. 1b). The molecule is excited via the ν_9 mode at 3084 cm^{-1} and the population of the ν_1 mode at 3073 cm^{-1} is monitored. Now we find a longer time constant of T_1 = 10±2 ps. In Fig. 2 we show the IR absorption and Raman spectra between 2950 and 3250 cm^{-1} of both molecules. We point to the strong Fermi resonances in the IR spectrum of CH_2CCl_2 with combination modes and overtones. This strong anharmonic coupling is responsible for the short life time of the molecule. Vibrational energy is rapidly transferred to combination modes and overtones and thus to lower energy states. The smaller Fermi resonances of trans CHCl=CHCl give rise to the longer life time discussed above.

(iv) Very small molecules have only a few normal modes and thus a limited number of decay routes. The individual population life times may vary drastically within the same molecule. Acetylene re-
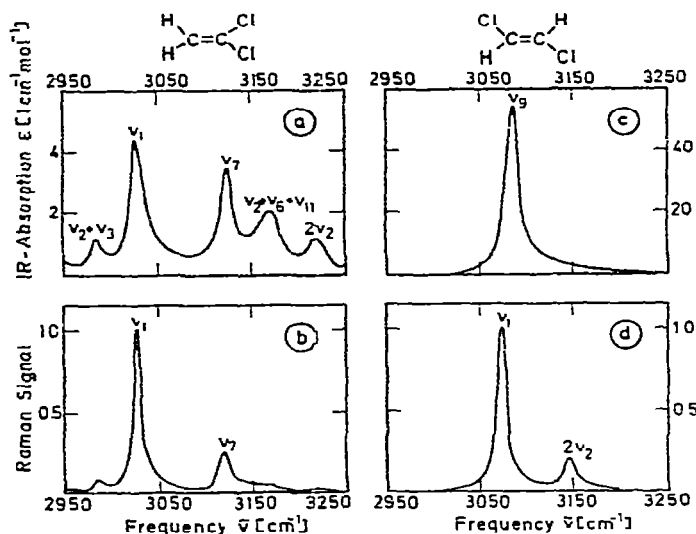
Figure 2: Infrared absorption (a) and Raman (b) spectrum of CH_2CCl_2 between 2950 and 3250 cm^{-1}. Two combination tones are in strong Fermi resonance with the two CH-stretching modes at ν_1 and ν_7. Infrared absorption (c) and Raman (d) spectrum of trans CHClCHCl There is less Fermi resonance mixing than in CH_2CCl_2.

presents a particularly interesting example /7/. The CH-stretching modes couple quite effectively to combination modes in the frequency range of 3200 cm^{-1} making the life time of the CH-stretching modes short, approximately 2 ps. We note that all combination modes contain the C≡C-stretching mode at ν_2 = 1968 cm^{-1}. What is the life time of this lower vibrational state? Inspection of the energy levels in acetylene suggests that the transfer of energy to neighboring combination modes is very unfavorable on account of symmetry selection rules. One expects a long life time of the ν_2 mode. Indeed, we found an exceptionally long life time. In Fig. 3 we show
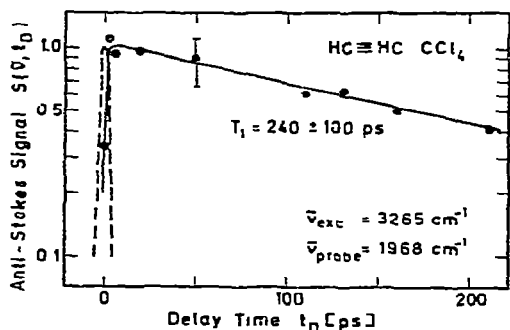

Figure 3: Time dependence of the population of the C≡C mode of acetylene in liquid CCl_4 following excitation of the ν_3 CH-stretching mode at 3265 cm^{-1}. After a rapid rise the population decays slowly with a decay time of 240 ps.

the experimental data. The ν_2 mode is very rapidly populated after excitation of the infrared active CH-stretching mode and it decays very slowly with a life time of T_1 = 240 ps. This life time is the longest found so far for a vibrational mode of a polyatomic molecule at room temperature.

We now turn to the discussion of <u>medium size molecules</u>, where the mode density is quite large around the primarily excited mode. As an example we present data on naphthalene ($C_{10}H_8$), where infrared active CH-stretching modes are excited by IR pulses of $\tilde{\nu}$ = 3055 cm^{-1} /8/. The transient change of the population of the three strong Raman transitions at $\tilde{\nu}_1$ = 3050 cm^{-1} (CH-stretching mode), $\tilde{\nu}_3$ = 1380 cm^{-1} (ring deformation mode), and $\tilde{\nu}_8$ = 765 cm^{-1} (skeleton mode) is depicted in Fig. 4 a to c. The three figures show quite vividly the build-up and decay of the different vibrational levels. The ν_1 mode is rapidly populated, i.e., energy is quickly transferred from the excited modes, ν_1 decays quite fast with a time constant of 2 ps. The ν_5 mode rises more slowly and decays with a time constant of 9 ps. Model calculations suggest that the ν_5 mode was populated by the decay of the CH-stretching modes. Also the ν_8 mode shows a delayed maximum of excess population and a decay with a similar time constant of 7 ps.

Of special interest for the elucidation of the energy transfer processes are the transient peak occupation numbers of the various monitored modes. For the ν_5 and ν_8 modes we find n = 0 01 and n = 0.1, respectively. Since the density of vibrational states in the energy range of the CH-stretching modes is quite large, namely 500/cm^{-1}, we considered an intramolecular energy relaxation process in terms of a statistical energy randomisation. When E (300 K) represents the ensemble average of the vibrational energy at room temperature, we may formally evaluate a vibrational temperature T^* for these molecules which have absorbed one quantum of 3050 cm^{-1}. From $E(T^*)$ = E(300 K) + hc 3050 we estimate T^* = 537 K for naphthalene. The occupation numbers calculated for T^* are in good agreement with the values found experimentally giving support to the statistical model.
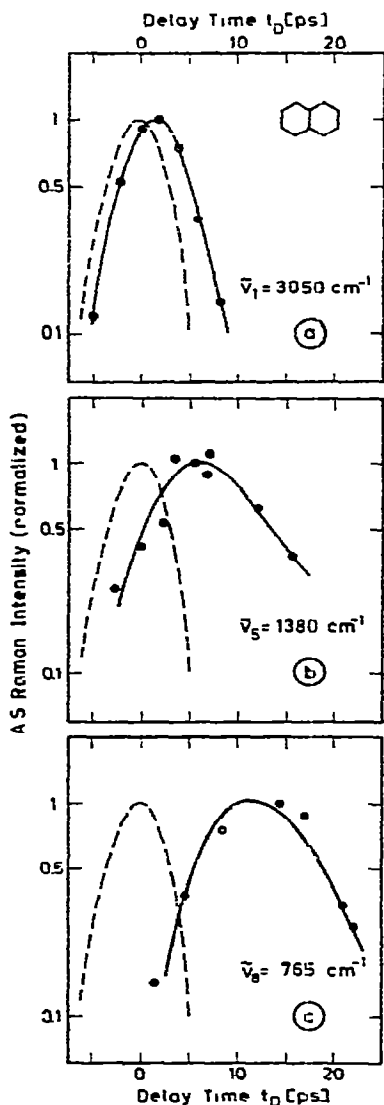
Figure 4: Redistribution of vibrational energy in naphthalene. (a) Anti-Stokes Raman signal of the mode ν_1 (3050 cm^{-1}). Rapid transfer of vibrational energy from the initially pumped IR-active CH-stretching mode to the monitored Raman active CH-stretching mode. The correlation curve between IR and green pulse is shown for comparison (broken line). (b) Anti-Stokes Raman signal of ν_5 (1380 cm^{-1}). This ring deformation mode is populated by the relaxation of the CH-stretching modes. (c) Anti-Stokes Raman signal of ν_8 (765 cm^{-1}).

It appears from our data that the vibrational excess energy is rapidly transferred from the set of CH-stretching modes to the many neighboring combination modes. The coupling between the latter modes tends to randomize the vibrational energy within the very short time of 5 to 10 ps. More recent data of even larger molecules confirm the picture of rapid intramolecular energy randomisation. Our investigations suggest that state-selected chemistry in liquids will be highly restricted on account of the extremely short vibra-

tional life times and the rapid randomisation of vibrational energy in large polyatomic molecules.

REFERENCES

1   A. Laubereau and W. Kaiser, Rev. Mod. Phys. 50 (1978) 607
2   A. Laubereau, D. von der Linde, and W. Kaiser, Phys. Rev. Lett. 28 (1972) 1162
3   R.R. Alfano and S.L. Shapiro, Phys. Rev. Lett. 29 (1972) 1655 ; E.J. Heilweil, F.E. Doany, R. Moore, and R.M. Hochstrasser, J. Chem. Phys. 76 (1982) 5632 ; H. Graener and A. Laubereau, Appl. Phys. B29 (1982) 213
4   A. Fendt, S.F. Fischer, and W. Kaiser, Chem. Phys. 57 (1981) 55
5   A. Fendt, S.F. Fischer, and W. Kaiser, Chem. Phys. Lett. 82 (1981) 350
6   C. Kolmeder, W. Zinth, and W. Kaiser, Chem. Phys. Lett. 91 (1982) 323
7   W. Zinth, C. Kolmeder, B. Benna, A. Irgens-Defregger, S.F. Fischer, and W. Kaiser, J. Chem. Phys. 78 (1983) 3916
8   N.H. Gottfried and W. Kaiser, in press, Chem. Phys. Lett.(1983)