

## Pathways of relaxation of the N–H stretching vibration of pyrrole in liquids

J. R. Ambroseo and R. M. Hochstrasser

Citation: *The Journal of Chemical Physics* **89**, 5956 (1988); doi: 10.1063/1.455547

View online: <http://dx.doi.org/10.1063/1.455547>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/89/9?ver=pdfcov>

Published by the **AIP Publishing**

---

### Articles you may be interested in

[Vibrational overtone spectroscopy and intramolecular dynamics of C–H stretches in pyrrole](#)

*J. Chem. Phys.* **138**, 194310 (2013); 10.1063/1.4804540

[NH stretching vibrations of pyrrole clusters studied by infrared cavity ringdown spectroscopy](#)

*J. Chem. Phys.* **127**, 184310 (2007); 10.1063/1.2790894

[Vibrationally mediated photodissociation of ammonia: The influence of N–H stretching vibrations on passage through conical intersections](#)

*J. Chem. Phys.* **125**, 174309 (2006); 10.1063/1.2363192

[Vibrational spectroscopy of CH/NH stretches in pyrrole: An algebraic approach](#)

*J. Chem. Phys.* **106**, 5379 (1997); 10.1063/1.473564

[On the Complexity of the N–H Stretching Vibration Band in Pyrrole and Indole](#)

*J. Chem. Phys.* **20**, 1043 (1952); 10.1063/1.1700630

---



The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments, and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 July 1988 for a fuller description of Letters to the Editor.

## COMMUNICATIONS

## Pathways of relaxation of the N-H stretching vibration of pyrrole in liquids<sup>a)</sup>

J. R. Ambroseo and R. M. Hochstrasser

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 22 June 1988; accepted 18 August 1988)

This paper reports experimental observations of vibrational energy flow in liquid and solution phase pyrrole. In addition, the lifetimes of the  $v = 1$  level of the N-H stretch (at  $3400\text{ cm}^{-1}$ ) are sufficiently long that vibrational energy transfer, involving bimolecular collisions, was observed, allowing the intermolecular and intramolecular contributions to the vibrational relaxation to be separated.

The elucidation of pathways of vibrational energy relaxation in molecules and the manner by which these pathways are influenced by the surrounding medium are important issues for understanding chemical dynamics of condensed matter. The pioneering work by Kaiser and co-workers<sup>1</sup> generated a wealth of information particularly on the  $T_1$  relaxation of the C-H stretch excitations and their coupling to the C-H bends. However, there is still little information on relaxation pathways even though there were various reports of  $T_1$  measurements in liquids<sup>1,2</sup> and solids.<sup>3</sup> A feature from recent work on  $T_1$  relaxation times of large molecules in solids<sup>4</sup> and liquids,<sup>2(b)</sup> further evidenced in this study, is that far from being picosecond time scale processes they often lie in the 100's ps or even ns<sup>4</sup> regime. In addition, experiments that distinguish intramolecular from intermolecular relaxation or that evaluate the effects of different media on the vibrational relaxation are scarce. Distinct solvent effects on the  $T_1$  relaxation are reported here.

In the experiment the N-H stretching motion of pyrrole is populated by  $\sim 4$  ps infrared pulses obtained by difference frequency mixing (in  $\text{LiIO}_3$ ) pulses at 1054 nm from a Nd:phosphate-glass laser and at 775 nm from an amplified "continuum." The resulting populations of other vibrational levels and their time evolution were determined by spontaneous anti-Stokes Raman scattering<sup>1</sup> with a 527 nm pulse. The signal/noise was adequate to enable studies of dilute solutions of pyrrole in ethers and benzene.

The vibrational relaxation time of the N-H stretch (see Fig. 1) was found to be solvent dependent increasing from  $42 \pm 3$  ps for neat pyrrole to  $220 \pm 20$  ps for  $10^{-2}$  molar pyrrole in diethylether. The relaxation pathway was studied by measuring the population in the four C-H stretches

around  $3000\text{ cm}^{-1}$  and the ring stretch ( $1144\text{ cm}^{-1}$ ) regions following the pumping of the N-H stretch. In neat pyrrole less than 1% of the N-H population flows into C-H modes whereas  $\sim 32\%$  of this population is transferred to the ring stretch ( $T_1 \approx 4$  ps). The system has a remarkable propensity for coupling N-H stretch and ring stretch motions.

The experiments with diluted samples show that the flow of energy from the N-H to the ring is an intermolecular process. On dilution with ether no  $1144\text{ cm}^{-1}$  population could be detected. The intermolecular character was further dramatized by the observation that when the diluent was benzene about 5% of the N-H population ( $T_1 = 79 \pm 9$  ps) of pyrrole was transferred into the  $991\text{ cm}^{-1}$  C=C stretch mode of benzene ( $T_1 \approx 12$  ps). These results suggest that the N-H motion of pyrrole is coupled to C=C bonds through

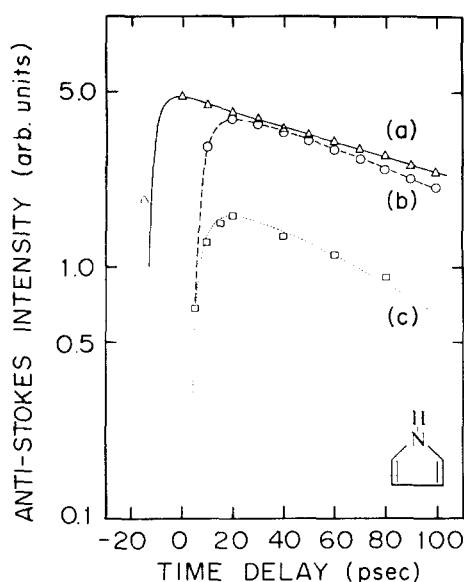


FIG. 1. Population of the NH stretch (a) in neat pyrrole following direct IR pumping,  $T_1 = 42 \pm 3$  ps. Energy flow into the ring-breathing mode (b) in neat pyrrole and into benzene's ring mode (c) in a benzene solution. (The rise times give the ring breathing decay, the fall times give the NH decay.)

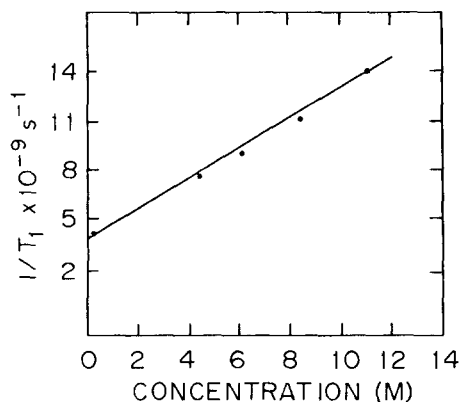


FIG. 2. Concentration dependence of the  $T_1$  relaxation of the NH stretch of pyrrole in ether solutions.

the  $\pi$ -electron system of neighboring pyrrole or benzene molecules in the solution.

As a further evidence of these conclusions the concentration dependence of  $T_1$  for the N–H stretch (see Fig. 2) was found to obey kinetics of the form

$$1/T_1 = 1/T_1^{(i)} + \gamma_{01}n_0$$

which suggests a Stern–Volmer process where  $T_1^{(i)}$  is an intramolecular relaxation time,  $n_0$  is the population of pyrrole molecules in the  $v = 0$  level of the N–H stretch, and  $\gamma_{01}$  is a bimolecular rate constant governing the relaxation of solvated molecules excited in  $v = 1$  during collisions with those in  $v = 0$ . The values are  $T_1^{(i)} = 240$  ps and  $\gamma_{01} = 8.2 \times 10^8 \text{ } \ell \text{ mol}^{-1} \text{ s}^{-1}$ . The latter is in the range expected for a diffusion controlled reaction. Thus, for neat pyrrole the intramolecular relaxation is almost entirely suppressed in favor of an

intermolecular process while in the dilute solutions the opposite situation prevails. To the best of our knowledge these are the first experiments of this nature in solutions.

The results are consistent with structures of neat pyrrole solutions based on infrared,<sup>5</sup> Raman,<sup>6</sup> and NMR spectroscopy.<sup>7</sup> Of the structures proposed for pyrrole–pyrrole interactions<sup>8</sup> the one in which the N–H bond is perpendicular to the plane of another pyrrole with the proton imbedded in the  $\pi$  system, is most consistent with our results. In that configuration the carbon–carbon bonds of one molecule would be expected to respond to motion of the proton of another.

These experiments also provide the indicated  $T_1$  relaxation times of the ring breathing motions of pyrrole and benzene. In the liquid benzene case the  $T_1$  is about one-fourth of that found in the solid at 1.6 K.<sup>3</sup>

<sup>a)</sup> This research was supported by NSF and NIH.

<sup>1</sup>A. Laubereau and W. Kaiser, *Rev. Mod. Phys.* **50**, 607 (1978).

<sup>2</sup>(a) R. R. Alfano and S. L. Shapiro, *Phys. Rev. Lett.* **29**, 1655 (1972); (b) E. J. Heilweil, M. P. Cassassa, R. R. Cavanagh, and J. C. Stephenson, *J. Vac. Sci. Technol. B* **3**, 1471 (1985); (c) A. Fendt, S. F. Fischer, and W. Kaiser, *Chem. Phys. Lett.* **82**, 350 (1981); (d) *Chem. Phys.* **57**, 55 (1981); (e) E. J. Heilweil, R. J. Moore, F. E. Doany, and R. M. Hochstrasser, *J. Chem. Phys.* **76**, 5632 (1982).

<sup>3</sup>(a) P. L. DeCola, R. M. Hochstrasser, and H. P. Trommsdorff, *Chem. Phys. Lett.* **72**, 1 (1980); (b) S. Velsko and R. M. Hochstrasser, *J. Phys. Chem.* **89**, 2240 (1985); (c) J. R. Hill, E. L. Chronister, T.-C. Chang, H. Kim, J. C. Postkwaite, and D. D. Dlott, *J. Chem. Phys.* **88**, 949 (1988).

<sup>4</sup>T. J. Trout, S. Velsko, R. Bozio, P. L. DeCola, and R. M. Hochstrasser, *J. Chem. Phys.* **81**, 4746 (1984).

<sup>5</sup>V. Lorenzelli and A. Alemagna, *Compt. Rend.* **257**, 2977 (1963).

<sup>6</sup>A. Lautie and A. Novak, *J. Chem. Phys.* **56**, 2479 (1972).

<sup>7</sup>J. A. Happe, *J. Phys. Chem.* **65**, 72 (1961).

<sup>8</sup>R. J. Jones and G. P. Bean, *The Chemistry of Pyrroles*, edited by A. T. Blomquist and H. H. Wasserman (Academic, New York, 1977), Vol. XXXIV, p. 439.

## Rotational analysis of the Herman infrared bands of nitrogen

K. P. Huber and M. Vervloet

*Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada*

(Received 21 July 1988; accepted 19 August 1988)

A recent theoretical study of the  $C''^5\Pi_u$  and  $A'^5\Sigma_g^+$  states of  $N_2$  by Partridge *et al.*<sup>1</sup> concludes that previous calculations<sup>2,3</sup> have seriously underestimated the depth of the potential wells in these two states. The authors review the implications of their results for an understanding of the role played by  $A'^5\Sigma_g^+$  in the mechanism of the Lewis–Rayleigh afterglow of nitrogen, and they provide convincing evidence for the assignment of the long-known, but previously unassigned, Herman infrared (HIR) bands<sup>4</sup> to the transition  $C''^5\Pi_u \rightarrow A'^5\Sigma_g^+$ .

Carroll and Sayers<sup>5</sup> gave a vibrational analysis of the HIR system which was later<sup>6</sup> confirmed by isotope studies. They noted that the bands were of complex structure with up to six close-lying heads and suggested that the spectrum

arises from a triplet, or possibly quintet, transition. In emission from most standard sources the complexity of the spectrum is made even worse by the proximity of the HIR bands to bands in the strong first positive group of  $N_2$ .

We have succeeded in largely avoiding the problem of overlapping structures by exciting the  $N_2$  emission in a supersonic jet discharge. This technique, combined with the advantages of high resolution and sensitivity offered by Fourier transform spectrometry, has previously been applied to the analysis of complex spectra of NO.<sup>7,8</sup> The new spectra of the HIR bands have rotational temperatures of around 30 K and originate in the lowest spin component of  $C''^5\Pi_u$ . They fully confirm the conclusions reached by Partridge *et al.*<sup>1</sup>