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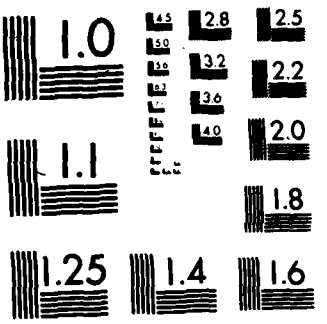

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FINAL SCIENTIFIC REPORT

GRANT: AFOSR-79-0086

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"Rates of Relaxation in the Upper Vibrational Levels of HF and DF"

STATEMENT OF PURPOSE

The goal of this work was to design and carry out experiments which would measure the rates of various relaxation processes from the highly excited vibrational levels of HF and/or DF which were produced by direct pumping into states v>3. A thorough knowledge of these rates is essential for development of completes descriptions of the HF and DF chemical laser systems. This report briefly describes the experiments that were performed and summarizes the results and conclusions. Details of the experiments and a complete set of data are contained in Yolanda Jones's PhD thesis (Y.D.Jones, "The Rates of Relaxation in the Upper Vibrational Levels of Hydrogen Fluoride and Deuterium Fluoride", The University of New Mexico, 1981)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This program has the aim of measuring various relaxation processes from highly excited vibrational levels of HF and/or DF. These rates are important for complete understanding of the HF and DF chemical laser.

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EXPERIMENTAL DESIGN

Figures 1 - 3 show schematically the approach used to measure the rates. In figure 1 is the first experiment that demonstrated the feasibility of pumping a measurable quantity of HF molecules from the v=Ø state to an upper vibrational level. In this experiment a flashlamp pumped dye laser (.4J per pulse of 25Ønsec) excites the sample at v=4 (673.684nm .ØØ5nm bandwidth) and a HF laser probes the intensity of the v=Ø to v=1 transition of the HF sample. A change in the absorbance was observed which corresponded to an approximate 1Ø% change in the population of v=Ø. Similar results were obtained for pumping into other overtones of HF and DF. A high resolution spectrograph is used to accurately mointer the laser wavelength. In this experiment an gold doped germanium detector contained in a Laser Analytics Diode Laser Spectrometer was used as the detector. In Figure 2 the HF sample is pumped from v=Ø to v=1 with a chopped tuned HF laser and the rate at which energy flows into and out of specific rotational states of v=Ø and v=1 is probed using the tunable diode laser. The changes in intensity of the resonant (with a given vJ state) energy from the diode laser, as a function of time was captured on a waveform recorder and then displayed on an oscilloscope or on a strip chart recorder. One of the next improvements to be made in this experiment is to incorporate a transient digitizer into the system so that data does not need to be digitized by hand from oscilloscope photographs or from strip chart recordings. As a example of the course of the experiment consider the case of the pump laser tuned to the P(13) transition of the v=Ø to v=5 vibrational transition.

If the diode laser is then tuned to the P(2) transition of v=2 to v=3 there will initially be no attenuation of the diode laser signal, other than the optical losses in the spectrometer and in the multipass sample cell. As the system in the v=5 state relaxes via v-J and v-v transfer processes some of the energy transfer processes will eventually result in the formation of states involved in the diode laser transition and a transient absorption will be observed. This signal will appear at a rate that is characteristic of the rates leading to the ground state of the diode laser transition and will disappear at a rate characteristice of the depopulation of the states involved in the diode laser transition.

RESULTS

Figure 4 shows a typical plot of the temporal dependence of the absorption of the probe laser. These data were treated by a simple two term model in order to obtain what can be characterized as fill rates and relaxation rates. Tables 1 and 2 summarize these results for a variety of experiments. One difficulty with these experiments is immediately apparant from the data in these tables and that relates to the inability to mount a truely systematic attack on the relaxation rates. This limitation arises from the fact that the number of different (and adjacent) states which can be accessed with the probe laser is limited by the availability of diodes for the probe system. A given diode covers a range of 25-40 cm-1 which usually contains at most 2 or 3 useful HF or DF transitions. A plan is currently underway to incorporate a krypton pumped F-centered laser as the probe laser.

This laser is "continuously tunable" over a wide range in the region of interest and would enable a more systematic study to be undertaken.

With several exceptions all of the data we have obtained indicate:

1. In the case of high J states (where data is not available from other experiments) the rates of relaxation are significantly slower than the relaxation of low J states in the same v state.

2. As the number of states separating the pump and probe levels increases the fill rate of the probe states decreases.

3. The sparse data indicate that relaxation rate decreases with increasing J. This is supportive of models in which the rotational contribution to relaxation goes as exp(-BJ(J+1)).

4. In the case of low J work (R4(Ø)) the relaxation rate that is obtained is quite comparable to rates obtained by other techniques for the deactivation of v=4. This is supportive evidence that these experiments are indeed measuring what they are intended to measure.

5. For DF the relaxation rate is slower than that for probing similar levels in HF. In modelling studies the most commonly used form of the DF/HF relative rates is HF rate = 2.5 DF rate and our few DF data indicate that this is an appropriate scaling factor but more DF rates are needed in order to refine this value.

6. Our data are also supportive of an exponential factor in the vibrational dependence of the total rate. The factor currently used in many calculations is v^2.5. More data are needed, particularily at higher v values where there is some indication that the exponent is <2.5.

Because the data at low levels compare well with the results of other experiments and because there are no other available data at high v and J values, these results are important and such experiments should be continued.

A number of problems have arisen in this work which should be explored in the future. Several of these relate to the experiment itself and have been mentioned in this and previous reports. There are also a variety of problems relating to the data analysis and interpretation. There are a large number of pathways by which any given lower level can be populated from an upper level and this number increases dramatically as the number of intervening levels increases. This points out the need for studying a number of states both close to and removed from the pumped state. Secondly, absorption depends on a population difference between the two levels involved in a transition and therefore the temporal behavior of the transient signal depends on the rate at which both of the levels involved in the probe transition and populated and depopulated. This needs to be considered in the extraction of rate constants from the transient behavior. In addition the possibility of rotational lasing as a depopulation mode needs to be considered and approached experimentally.

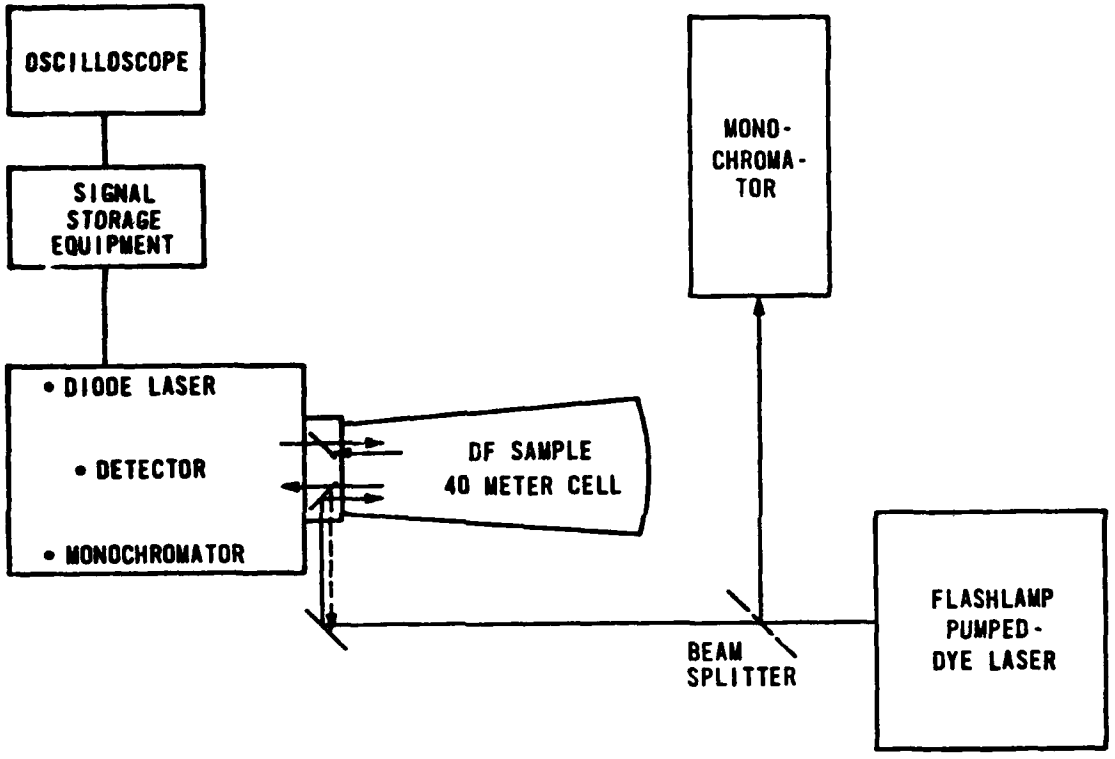


FIGURE 1: **PRIMARY EXPERIMENT: PUMP DF SAMPLE TO V ≥ 4 OBSERVE ADJACENT V'J' ABSORPTION**

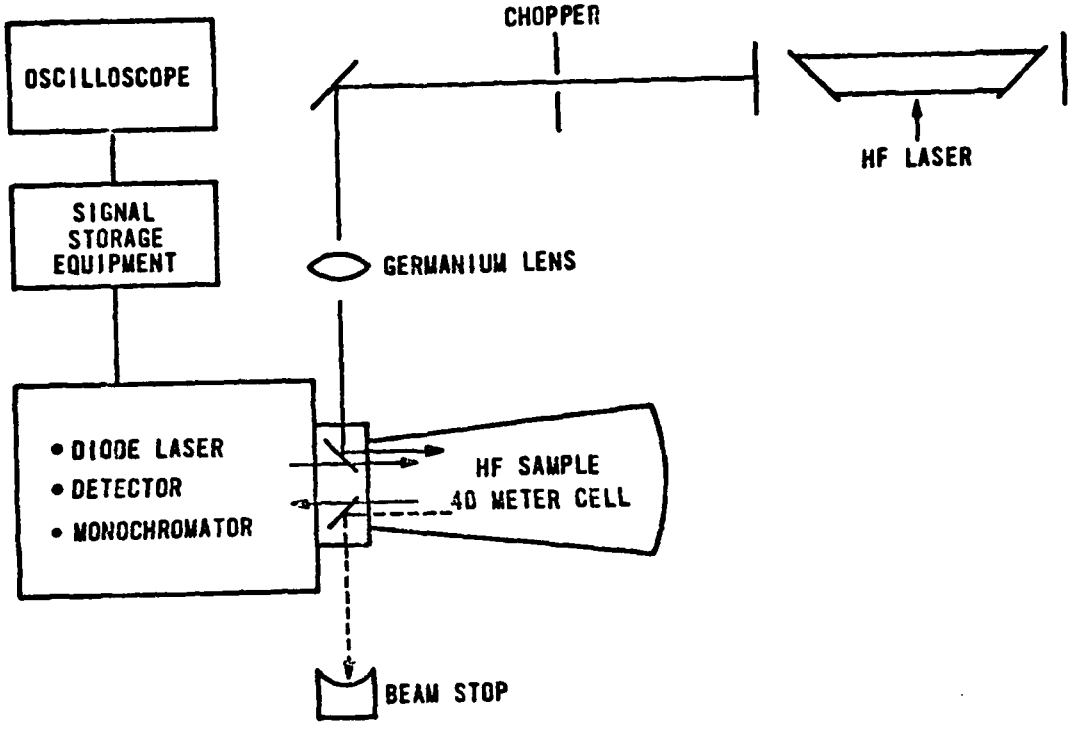


FIGURE 2: **EXPERIMENT: PUMP HF SAMPLE WITH HF LASER MEASURE (V, J) POPULATION CHANGE**

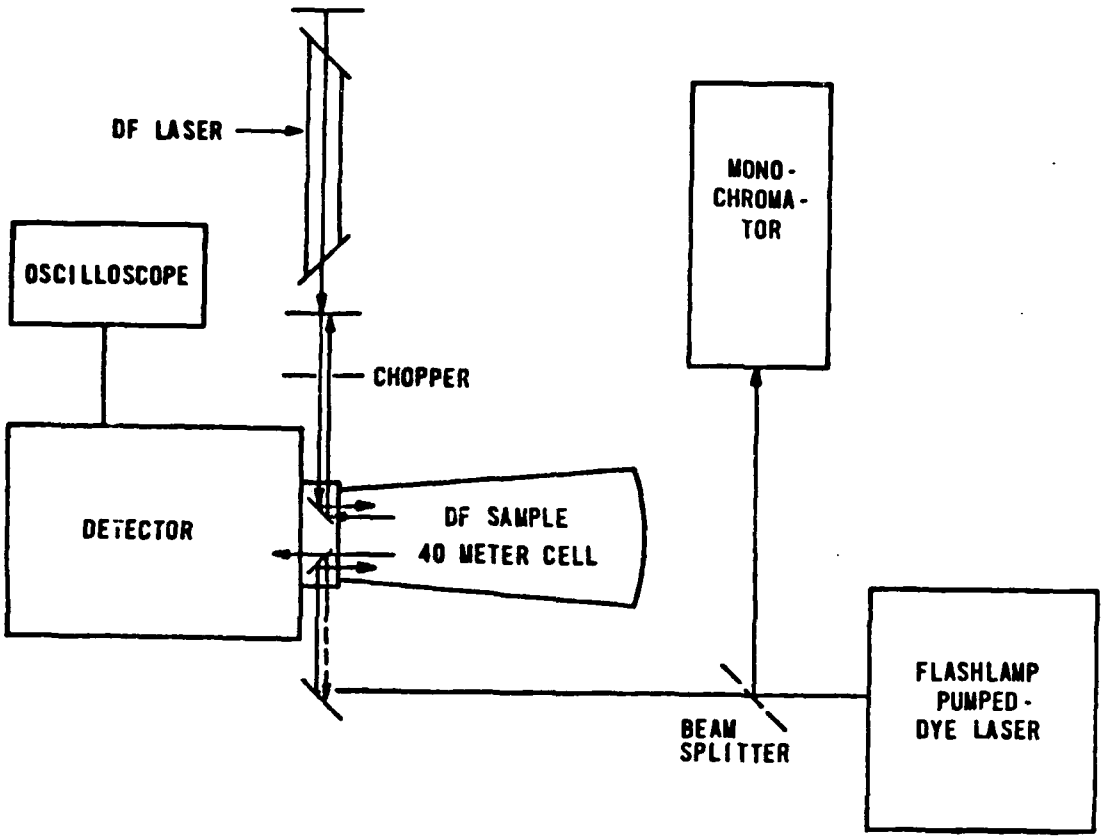


FIGURE 3: **EXPERIMENT: PUMP DF SAMPLE TO V ≥ 4**
OBSERVE CHANGE IN 0 — 1 ABSORPTION

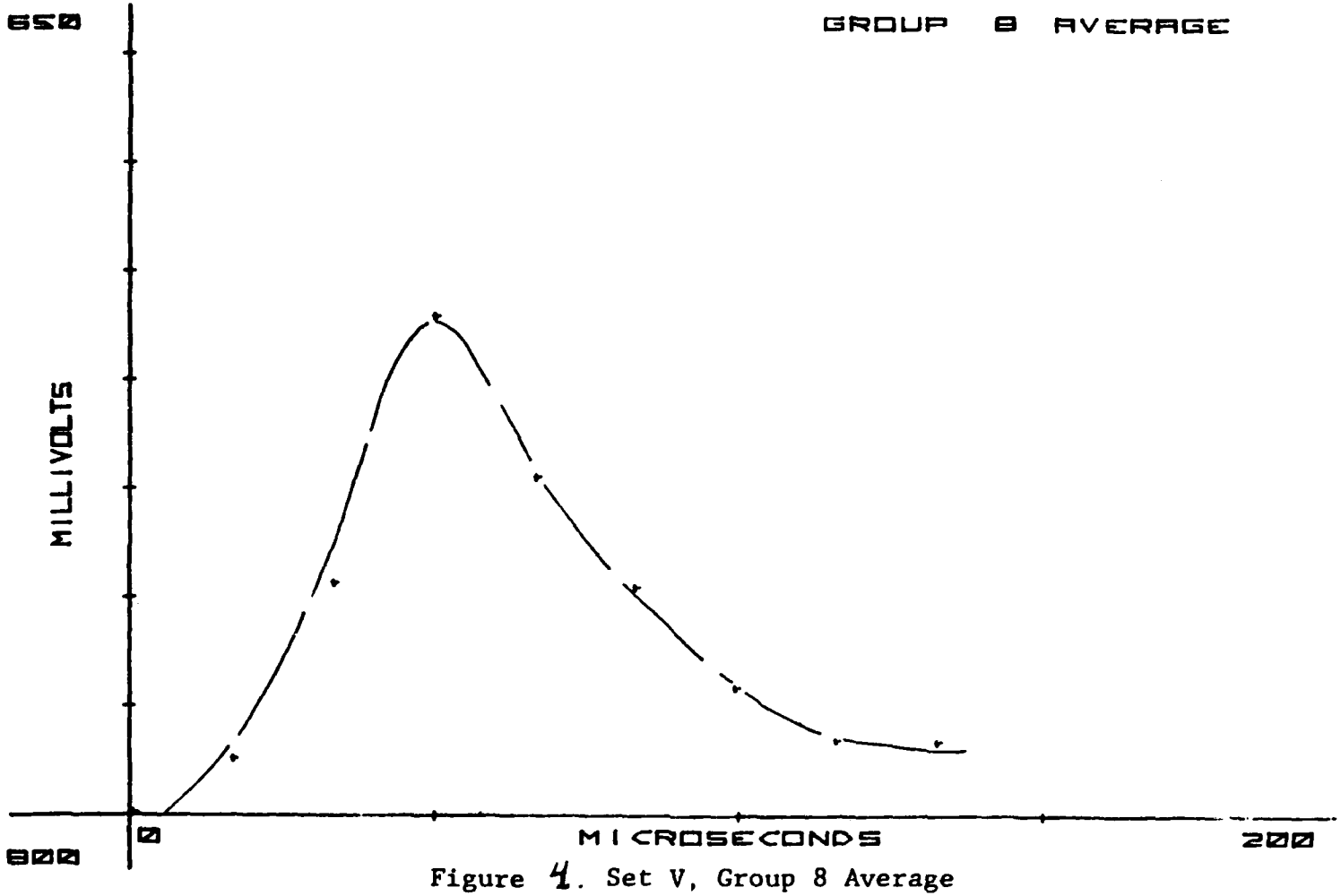


Figure 4. Set V, Group 8 Average

V	Pump J	Probe	Fill Rate ($1/p\tau$) ($\times 10^4$ $sec^{-1}Torr^{-1}$ units)	Set
	HF			
2	11	$P_1(22)$	8.6 ± 1.8	I
2	11	$P_1(10)$	250.0 ± 20. (sec^{-1})	II
4	2 to 1	$P_2(18)$	2.5 ± 0.5	III
5	2 to 1	$P_4(12)$	5.7 ± 1.1	IV
5	2 to 3	$P_4(13)$	8.5 ± 1.7	X
5	3 to 4	$P_4(13)$	6.0 ± 1.2	V
5	5 to 4	$P_4(13)$	17.0 ± 3.4	VI
5	12 to 13	$P_4(13)$	33.0 ± 6.6	IX
4	13 to 14	$P_3(15)$	4.0 ± 0.8	VIII
4	2 to 1	$P_3(15)$	1.6 ± 0.3	XI
4	8 to 9	$P_3(13)$	5.6 ± 1.1	XII
4	12 to 13	$P_3(13)$	91.0 ± 18.2	VII
4	4 to 5	$R_4(0)$	700.0 ± 140.0	XV
	DF			
6	4 to 3	$R_4(17)$	5.4 ± 1.1	XIII
6	2 to 3	$P_2(2)$	7.5 ± 1.5	XIV

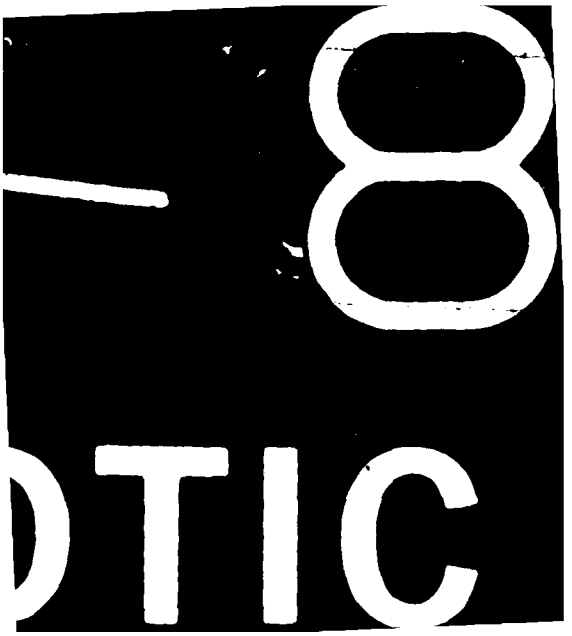
Table 1. Summary of Fill Rates

V	Pump J	Probe	Relaxation Rate ($1/p\tau$) ($\times 10^4$ $sec^{-1}Torr^{-1}$)	Set
	HF			
2	11	$P_1(22)$	1.0 ± 0.2	I
2	11	$P_1(10)$	140.0 ± 14.0 (sec^{-1})	II
4	2 to 1	$P_2(18)$	1.0 ± 0.2	III
5	2 to 1	$P_4(12)$	4.8 ± 1.0	IV
5	2 to 3	$P_4(13)$	4.4 ± 0.9	X
5	3 to 4	$P_4(13)$	3.9 ± 0.8	V
5	5 to 4	$P_4(13)$	3.5 ± 0.7	VI
5	12 to 13	$P_4(13)$	13.0 ± 2.6	IX
4	13 to 14	$P_3(15)$	3.2 ± 0.6	VIII
4	2 to 1	$P_3(15)$	1.0 ± 0.2	XI
4	8 to 9	$P_3(13)$	2.6 ± 0.5	XII
4	12 to 13	$P_3(13)$	7.0 ± 1.4	VII
4	4 to 5	R4(0)	205.0 ± 41.0	XV
	DF			
6	4 to 3	R4(17)	2.3 ± 0.5	XIII
6	2 to 3	$P_2(2)$	7.6 ± 1.5	XIV

Table 2. Summary of Relaxation Rates

V	Pump J	Probe	Relaxation Rate ($1/p\tau$) ($\times 10^4$ $sec^{-1}Torr^{-1}$)	Set
	HF			
2	11	$P_1(22)$	1.0 ± 0.2	I
2	11	$P_1(10)$	140.0 ± 14.0 (sec^{-1})	II
4	2 to 1	$P_2(18)$	1.0 ± 0.2	III
5	2 to 1	$P_4(12)$	4.8 ± 1.0	IV
5	2 to 3	$P_4(13)$	4.4 ± 0.9	X
5	3 to 4	$P_4(13)$	3.9 ± 0.8	V
5	5 to 4	$P_4(13)$	3.5 ± 0.7	VI
5	12 to 13	$P_4(13)$	13.0 ± 2.6	IX
4	13 to 14	$P_3(15)$	3.2 ± 0.6	VIII
4	2 to 1	$P_3(15)$	1.0 ± 0.2	XI
4	8 to 9	$P_3(13)$	2.6 ± 0.5	XII
4	12 to 13	$P_3(13)$	7.0 ± 1.4	VII
4	4 to 5	R4(0)	205.0 ± 41.0	XV
	DF			
6	4 to 3	R4(17)	2.3 ± 0.5	XIII
6	2 to 3	$P_2(2)$	7.6 ± 1.5	XIV

Table 2. Summary of Relaxation Rates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