INFRARED DOUBLE-RESONANCE SPECTROSCOPY OF V-T,R RELAXATION OF HF(v=1) USING AN F-CENTER LASER

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Abstract

Infrared double resonance studies of the V-T,R relaxation of HF(v=1) by HF are performed using a tunable F-center laser. A substantial fraction of the total vibrational relaxation occurs through the high-lying rotational levels of v=0. The results indicate that J = 10-14 comprise ~20-40% of the population in the total relaxation, with the distribution increasing rapidly with decreasing J in this range. The observed signals, corrected for cascade, correspond to the fractions: J=10, ~10-40%; J=11, ~4-10%; J=12, ~2-6%; J=13, ~1-2%; J=14, ~0.05-0.35%. In addition, the V-T,R rate determined here, k = 1.46 ± 0.15 x 10^{-12} cm^3 molecule^{-1} s^{-1}, reconfirms previous double resonance results. Also, studies involving buffer gas addition (Ar) give no indication of "bottleneck" effects on the high-J's. In fact, the R-R,T rates (~10^{-10} cm^3 molecule^{-1} s^{-1}) always exceed the V-T,R rate by one to two orders of magnitude.

Introduction

A long-standing problem in the field of energy transfer concerns the rotational level distribution produced in the V-T,R relaxation of HF(v) colliding with HF. In particular, interest focuses on the high-lying rotational levels, which are in near-energy resonance with higher vibrational manifolds. The significance of the role played by the high-J's of v=1 in the V-T,R relaxation of level v has often been speculated, but it has never been measured directly, nor has it been adequately determined indirectly from the many earlier relaxation studies. The present work represents a major step toward resolving this issue; here we report direct measurements of the population transfer to each of the high-J's of HF(v=0) upon relaxation of v=1. In this first case, only V,T,R relaxation of HF(v=1) with HF is considered. The results show that a significant fraction of the v=1 molecules do relax to the high rotational levels. A more detailed account of the study will be published in the near future.\(^1\)

The interest in V-T,R relaxation to high-lying rotational levels is several-fold. Firstly, from a purely fundamental point of view, V-R transfer is a dynamical problem of considerable interest. However, even recent theoretical work in this area\(^2\) has not in general addressed the J-level specificity of the V-T,R relaxation. A notable exception is the work of Thompson,\(^3\) who used quasiclassical trajectory calculations to study quantum-state-specific energy transfer in Ar + HF collisions. Secondly, in the past few years, novel rotational laser experiments have been performed by Sirkin and Pimentel\(^4\) and Smith and Robinson.\(^5\) Lasing is observed between rotational levels which lie in near-energy resonance with higher vibrational manifolds. A V-R energy transfer mechanism is invoked to explain the population in the high-J levels. Finally, the efficiency of chemical lasers may depend critically on the rotational population distribution. Since little is known concerning rotational relaxation for very high-J's, it has been speculated that these rates may turn out to be very slow. If such "metastability" for high-J's born via V-T,R relaxation does exist and is not accounted for in laser kinetic modeling, it might result in a misinterpretation of chemical laser efficiency.

Experimental Technique

In the present experiments, time-resolved infrared double resonance spectroscopy is used to investigate V-T,R relaxation of HF. In this dynamical study, a four-level double resonance approach is utilized, where the two radiation fields only "communicate" with one another through collisional phenomena. An overview of the energy levels and relaxation pathways is shown in Fig. 1. A typical pump transition, P(7), excites molecules to v=1, J=6. Transient absorption of the probe laser, which is tuned to a high-J level (R(14)

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Figure 1. Energy level diagram of the lowest two vibrational manifolds of HF. Following pulse excitation, the \( v=1 \) manifold relaxes by collisional \( V-T, R \) transfer to \( v=0 \). Typical pump and probe transitions are indicated.

Figure 2. Schematic drawing of the experimental apparatus showing the double resonance cell, high-temperature cell, pulse and probe lasers, and signal processing equipment.

shown in Fig. 1), contains the information on relevant rates and nascent population fractions. The apparatus employed is shown in Fig. 2. The probe laser is a continuously tunable F-center laser, pumped by a Kr\(^+\) laser and tuned to high-lying R-branch transitions in HF, \( v = 0 \rightarrow 1 \) in absorption. The pump laser is a pulsed transverse-discharge chemical laser operating on P-lines, \( v = 1 \rightarrow 0 \). The pump and probe lasers overlap with a counter-propagating geometry in a 65-cm-long stainless steel double resonance cell, which is equipped with sapphire windows. The transient absorption signal on the F-center probe is detected by an InSb (~1 MHz) or Au:Ge (~50 MHz) detector. After suitable amplification, the time-resolved signals are captured by a transient digitizer and summed in a signal averager.
Results

An example of a transient absorption signal on the F-center probe, which is tuned to the R(12) 0→1 transition, following excitation of HF to v=1, is shown in Fig. 3. The signal exhibits a very fast rise and single exponential decay, typical of all the high-J signals observed here. It turns out that the fast risetime of the transient absorption signals is determined by the R-R,T relaxation of the level, while the decay of the transient absorption actually reflects the V-T,R feeding mechanism. In all cases, the relation kv-T,R ≪ kR-R,T holds, which has an enormous significance in the quantitative analysis. The essential features of the kinetics are illustrated by considering the highest possible level, J=14, where cascade can be neglected. The system is represented by

\[ f_{14} N_{v=1} \frac{k_{V-T,R}}{k_{R-R,T}} N_{14} \cdot \frac{k_{R-R,T}}{N_{13}} \]  

(1a)

where \( f_{14} \) is the fraction of molecules in \( v=1 \) which relaxes through the \( J=14 \) channel. The \( v=1 \) population decays by a single exponential,

\[ N_{v=1} = N_{v=1}(t=0) e^{-k_{V-T,R}[HF]t} \]  

(1b)

where [HF] is the molecular concentration (molecules/cm\(^3\)). The time behavior of the \( J=14 \) population is given by

\[ N_{14} = \frac{f_{14} N_{v=1}(t=0) k_{V-T,R}}{k_{R-R,T}} \left( e^{-k_{V-T,R}[HF]t} - e^{-k_{R-R,T}[HF]t} \right) \]  

(1c)

Since the R-R,T decay rate is much faster than the V-T,R feeding rate, the peak amplitude of the high-J population is small, being "attenuated" by a factor \( \frac{k_{V-T,R}}{k_{R-R,T}} \). Finally, in general, cascade effects must be considered in the kinetic scheme. This is taken into account through a simple computer simulation.

The time variation of the transient absorption signals yields the V-T,R relaxation rate constant, determined here to be \( k_{V-T,R} = 1.46 \pm 0.15 \times 10^{-12} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). This is in excellent agreement with an earlier independent study of the vibrational relaxation of HF.\(^9\) The rotational relaxation rate constants had previously been unknown for the high-J's of HF. At least for HF-HF interactions, we find that they are still very rapid for \( J=10-14 \), and of \( \sim 10^{-10} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). In principle, knowledge of the kinetics, together with known pulse energies, overlap geometry, diffusion contributions and so on, allow calculation of the branching ratios from the observed signals. However, estimating all these latter quantities could introduce significant systematic errors. Instead, we make an internal normalization where most of the uncertainties embodied in these various experimental factors will largely cancel. To do the absolute calibration, another set of

Figure 3. Transient absorption on the F-center beam, tuned to J=12 of \( v=0 \), following pulsed excitation of HF to \( v=1 \). The rapid rise reflects the R-R,T decay of the level, while the signal decay is indicative of the V-T,R feeding mechanism.

Figure 4. Transient absorption on the F-center beam tuned to J=4 of \( v=1 \). The relative amplitude of the signal may be qualitatively compared with Fig. 3.
probe transitions, \( v = 1+2 \) in absorption is measured. An example of one such transient absorption signal is shown in Fig. 4. During the course of the study, \( R(J) \), \( J = 4-7 \) transitions are utilized for the normalization, depending on the specific pressure regime. Since the \( v=1 \) population follows from the kinetics of Eq. (1b), the amplitude can be related through Boltzmann statistics to the total number of molecules pumped to \( v=1 \).

The results obtained for the branching fractions to each of the high-\( J \)'s of \( v=0 \), following pulse excitation to \( v=1 \), are shown in Fig. 5. This initial study is restricted to \( J = 10-14 \) inclusive, due to a number of complications (e.g. gross heating and cascade) which arise for the lower levels. The levels closest in energy to \( v=1 \), namely \( J=13 \) and 14, do not obtain most of the population. Nevertheless, the role of \( V-R \) transfer is clearly significant. The results are very suggestive of a peak in the distribution in the range \( J \sim 8-10 \). It should be noted that the present experiment cannot determine which of the colliding HF molecules (i.e. \( HF(v=0) \) or \( HF(v=1) \)) ends up in the high-\( J \)'s. The results reflect the contribution of all molecules whose final state coincides with the probed level. In particular, it is possible that the \( v=0 \) collision partner becomes sufficiently rotationally excited to provide overall near-energy-resonance. Future experiments with HF/DF mixtures may serve to clarify this point.

**Conclusions**

The study has both important fundamental and practical implications. Explicit calculations on the final rotational level populations have generally been lacking, due both to the intrinsic theoretical complexity and lack of experimental input. The \( V,T,R \) relaxation to high-\( J \)'s measured here should stimulate future theoretical work on state-to-state cross sections. Direct applications include both HF-rotational and HF-vibrational lasers. Although an inverted population distribution is not found in the present work, even the highest-\( J \)'s obtain a non-negligible fraction of the total relaxation. Under real operating conditions in an HF-rotational laser, inversions may develop through a multitude of collisional processes. Hence the present work lends support to the proposed \( V,R \) pumping mechanisms\(^6,7\) in those systems. In addition, the normal assumption of rotational thermodynamic equilibrium in HF-vibrational lasers seems to be well justified, at least for \( \Delta v = -1 \) relaxation. Due to the large \( E,R,T \) relaxation rate constants on the high-\( J \)'s, no "bottleneck" effects can develop. However, possible formation of "metastable" rotational states resulting from multiquantum vibrational relaxation with \( v=2 \) remains an open question. Future experiments involving overtone excitation will largely focus on these relaxation processes, which can produce final rotational states \( J > 20 \).

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