Relaxation of conformers and isomers in seeded supersonic jets of inert gases

R. S. Ruoff, a) T. D. Klots, b) T. Emilsson, and H. S. Gutowsky
Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 16 June 1989; accepted 24 May 1990)

We have studied the relaxation of conformers and the formation/relaxation of isomeric, weakly bonded dimers in pulsed supersonic expansions of seeded inert gases (He, Ne, Ar, Kr). The relaxation was determined from the intensity of a rotational transition for the higher energy species as a function of carrier gas composition, using the Balle/Flygare Fourier transform microwave spectrometer. Of thirteen molecules with rotational conformers which we examined, those with barriers to internal rotation greater than 400 cm$^{-1}$ did not relax significantly in any of the carriers. The higher energy forms of ethyl formate, ethanol, and isopropanol, with smaller barriers, were not relaxed by He; those of ethanol and isopropanol were somewhat relaxed by Ne; and all were completely relaxed by as little as 5 to 20 mole percent of Ar or Kr in He or Ne. The relaxation in He or Ne is first order in the concentration of added Ne, Ar, or Kr as well as in the concentration of the high energy conformer. The pseudo first-order rate constants (larger in Ne than in He) increase sharply with Z of the rare gas, roughly in a 0:1:2:4 progression for He, Ne, Ar, and Kr, suggesting that the relaxation involves relatively long-range polarization effects. Similar behavior was found in the formation/relaxation of the weakly bonded dimer pairs: linear OCO–HCN, T-shaped HCN–CO$_2$; linear FH–NNO and bent NNO–HF; and bent HF–DF and DF–HF. The case of the HCN/CO$_2$ dimers is particularly striking. The T-shaped dimer was found first, using Ar as the carrier gas. Five years later the linear form was found with first run neon as carrier, but it could not be detected at all with Ar as the carrier. These results show that in favorable cases high energy species can be studied in supersonic expansions by freezing out a “high-temperature” concentration with a nonrelaxing carrier gas.

INTRODUCTION

The use of supersonic jets for spectroscopic experiments has increased rapidly in recent years. Relaxation in a free-jet expansion among rotational and vibrational modes of molecules has been studied in considerable detail. However, much less attention has been given to interconversion of conformational isomers in the expansion. An early study of this sort by Felder and Günthard found that conformational interconversions occur in supersonic expansions only for molecules with relatively low barriers to internal rotation. This result was obtained by cryogenic trapping of the conformers from an expanded beam in an argon matrix and determining their ratio from infrared absorption intensities. Comparison of the ratios for effusive and supersonic jets established whether or not relaxation to the more stable conformer occurred during the expansion.

Three molecules were investigated, 1,2-difluoroethane, 1,2-dichloroethane, and methyl nitrite. They have a range of barriers to interconversion, 700, 1200, and 2800 cm$^{-1}$, respectively, and conformers differing in energy by 200, 360, and 220 cm$^{-1}$. Jet expansion of the pure gases caused considerable relaxation to the more stable (gauche) form of 1,2-difluoroethane (DFE), but not for the other two molecules. In seeded argon beams the relaxation of trans DFE was much weaker, while with helium as carrier there was no apparent relaxation. This dependence of conformer relaxation on the carrier gas is the object of our study. We have made a more systematic determination of it and report several instances in which the differences are quite remarkable.

Our experiments employed the Flygare/Balle Fourier transform microwave spectrometer, which incorporates a pulsed supersonic nozzle. A seeded jet of rare gas is customarily used to generate weak dimers and small clusters. The expanded jet passes through a Fabry–Perot cavity where the pulsed microwave spectrometer detects rotational transitions of the polar species. This arrangement lends itself to the study of conformational relaxation. The rotational temperature of a species in the expanded jet with a rare gas as carrier is typically 3 K. Moreover, because of the fast rotational relaxation, the different species have the same rotational temperature. Therefore, changes in the intensity of a transition are directly proportional to species concentrations, which thereby are readily measured for different carrier gases and backing pressures.

Microwave spectra have been analyzed for about 75 molecular species with conformational isomers. Although many of these are difficult to work with for one reason or another there is no lack of species which are commercially

---

a) T. J. Watson Research Center, IBM, Yorktown Heights, New York 10598.

b) Argonne National Laboratory, Argonne, Illinois 60439.
available, inexpensive, stable, and have a range of barrier heights. Those which we have studied are: ethyl formate,\textsuperscript{5} ethanol,\textsuperscript{7} isopropanol,\textsuperscript{8} propanol,\textsuperscript{9} CH\textsubscript{3}DCHO,\textsuperscript{10} n-propanol,\textsuperscript{11} ethyl methyl sulfide,\textsuperscript{12} butyronitrile,\textsuperscript{13} 3-chloropropene,\textsuperscript{14} ethyl nitrite,\textsuperscript{15} 1-butene,\textsuperscript{16} acrolein,\textsuperscript{17} and Cl-cyclohexane.\textsuperscript{18} Barrier heights separating conformers range from about 350 cm\textsuperscript{-1} for trans and gauche ethanol to about 4000 cm\textsuperscript{-1} for equatorial and axial Cl-cyclohexane. Energy differences of conformers for a given molecule are from 16 to 660 cm\textsuperscript{-1}.

For conformers separated by a barrier of about 350 cm\textsuperscript{-1} or less there is a remarkable dependence on the carrier gas of signal intensity for the less stable conformer. Parallel study of the signal from the more stable conformer shows that this dependence is not due to competitive clustering or differences in beam temperature. Rather it is a result of the high energy conformer relaxing to the low energy form in the presence of heavier carrier gases. However, with the light carrier gas He there is no apparent change in the proportions of the conformers in spite of the very low translational and rotational temperatures attained in the supersonic expansion. We have also observed similar effects for isomeric pairs of weakly bonded dimers found in an expanding jet of seeded carrier gas.\textsuperscript{19} The CO\textsubscript{2}/HCN dimer is a striking example. Only the $T$-shaped HCN$\cdots$CO\textsubscript{2} is found with argon as the carrier, while both the $T$-shaped and linear OCO$\cdots$HCN forms are found with helium as the carrier. Details of our results for both types of system are given and compared in this account. The nature of the mechanism for the relaxation is considered.

**EXPERIMENT**

The supersonic nozzle used in our experiments is a pulsed, solenoid-activated valve (General Valve) with a 1 mm circular orifice. Backing pressures were between 1/2 and 2 atm. Carrier gases were He, first run neon (70\% Ne, 30\% He), Ne, Ar, Kr, and various mixtures of them. Except for 1-butene, which is a gas, the conformers studied are liquids at room temperature. For them the carrier gas was passed through a glass bubbler containing the liquid. The vapor pressures of ethanol and ethyl formate are relatively high so the liquids were cooled by placing the bubbler in ice water or an acetone/dry ice bath at $-15$ °C. The 1-butene was premixed with helium in a 15/85 ratio and then blended with the carrier gas.

For the weakly bonded dimers, the component species were premixed with helium: CO\textsubscript{2} in a 10/90 ratio, HF(DF) at 3/97, and HCN at 3/97. The final composition of the seeded carrier was determined by a secondary mixing in a flow system with adjustable individual flows and flow gauges calibrated for the different, unmixed carrier gases. Final concentrations at the valve were about 2\% CO\textsubscript{2} and 0.2\% HCN for the CO\textsubscript{2}/HCN studies and 0.05\% HF and 0.05\% DF for HF/DF, the rest being the carrier gas.

The conformers, except for CH\textsubscript{3}DCHO, were obtained from standard commercial sources and used without further purification. The partially deuterated acetaldehyde was prepared by adding equal volumes of D\textsubscript{2}O and acetaldehyde to a Carius tube and heating at 700 °C for 24 hours.\textsuperscript{20} The CO\textsubscript{2}, HF, and HCN were from commercial sources as were the carrier gases. The DF was synthesized by reacting D\textsubscript{2} with F\textsubscript{2}.

The mixtures of carrier gases were made by using flow gauges to monitor the flow of each gas, and converting the flow rates to volumes. The flow gauges were Matheson Models 7261 and 7262, calibrated for each carrier gas at both 8 and 16 psig, which were used as backing pressures. The accuracy of the measured concentrations is estimated to be 0.3\% for the 0 to 15\% range and 2\% for 15 to 100\%.

It is difficult to determine accurately the relative concentrations of two different species in the expanded jet by observing the relative intensities of their rotational transitions.\textsuperscript{21} The signal strengths are affected not only by the inherent differences in the species but also by conditions of the expansion and the instrumental adjustments necessary in changing from one species and transition to another. As a test of spectrometer capability we observed the J = 0$\rightarrow$1 transition for several of the isotopic species of OCS at natural abundance in the same pulsed nozzle conditions. Spectrometer settings were held constant except for those dependent on frequency, which was changed by a relatively small amount (11.4 to 12 GHz). The relative intensities obtained as described below were close (±10\%) to the isotopic abundances. With allowance for differences in transition moments we have used this approach to obtain semiquantitative estimates of relative concentrations of different species.

Fortunately our main concern was to determine the concentration of a given conformer or isomer as a function of the composition of the carrier gas. This we did at fixed frequency by observing the dependence on composition of the signal strength for a given rotational transition, with all other aspects of the system held constant. Under these conditions the detected voltage is directly proportional to the number of emitters. The signal strengths were measured by combining calibrated attenuation (amplitude) with the number N of digitized free induction decays (FID's) needed to fill the dynamic range of the averager. The attenuation was adjusted so that the number of FID's filling the averager was about 1600. This corresponds to a data-acquisition time of 20 s at the usual 10 gas pulses per s and 8 microwave pulses per gas pulse in these experiments. Each such signal strength for a particular set of carrier gases was normalized by assigning 10 to the composition with the strongest signals.

A basic assumption of our approach is that the concentration of the detected species is directly proportional to the signal strength $S$ defined as 1/N. It was checked by observing $N$ as a function of isobutylene concentration in first run neon for the $2_{11} \rightarrow 2_{00}$ transition at 5370.5 MHz.\textsuperscript{22} The dependence of $S$ found over a five-fold range in isobutylene concentration is linear with an rms deviation of $\sim 2\%$.

Another critical point, discussed later, is that changing the composition of the carrier gas affects the signal strength of conformers and isomers primarily by their interconversion. Differences in jet temperatures and rota-
TABLE I. Rotational transitions observed for the different conformers. a

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Low energy form</th>
<th>High energy form</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Transition</td>
<td>MHZ</td>
</tr>
<tr>
<td>ethyl formate</td>
<td>0_00 – 1_01</td>
<td>5 483.9</td>
</tr>
<tr>
<td>ethanol</td>
<td>0_00 – 1_01</td>
<td>17 288.4</td>
</tr>
<tr>
<td>isopropanol</td>
<td>0_00 – 1_11</td>
<td>13 406.8</td>
</tr>
<tr>
<td>propanol</td>
<td>0_00 – 1_01</td>
<td>10 492.5</td>
</tr>
<tr>
<td>CH_3CH=CHO</td>
<td>0_00 – 1_01</td>
<td>18 501.8</td>
</tr>
<tr>
<td>n-propanol</td>
<td>0_00 – 1_01</td>
<td>9 443.7</td>
</tr>
<tr>
<td>butyronitrile</td>
<td>0_00 – 1_01</td>
<td>7 119.3</td>
</tr>
<tr>
<td>3-chloropropene</td>
<td>0_00 – 1_01</td>
<td>5 541.4</td>
</tr>
<tr>
<td>ethyl nitrite</td>
<td>0_00 – 1_01</td>
<td>5 695.5</td>
</tr>
<tr>
<td>1-butene</td>
<td>0_00 – 1_01</td>
<td>9 878.1</td>
</tr>
<tr>
<td>acrolein</td>
<td>0_00 – 1_01</td>
<td>8 902.2</td>
</tr>
<tr>
<td>Cl-cyclohexane</td>
<td>1_00 – 2_11</td>
<td>5 318.3</td>
</tr>
</tbody>
</table>

*a* Conformer names are given in Table II, and references in the Introduction.

*The gauche conformer is listed first and the trans second. See Table II.

*Line centers given for HCl species. Several hyperfine components were observed for each transition.

*This molecule has three conformers as listed in Table II. The 0_00 – 1_01 transition was observed for the middle energy trans-gauche form at 5365.9 MHz.

Rotational relaxation, while apparent with widely different carrier gases, are of secondary importance.

RESULTS

Conformers

Search for conformation relaxation

Table I lists the various molecules studied and the rotational transitions observed for two conformers of each molecule. Most pairs of transitions are for \( J = 0 \rightarrow 1 \), relatively close in frequency and with comparable rotational Boltzmann factors. The types of conformer and the energy differences and barrier heights between the conformers are given in Table II.

When helium was used as the carrier gas all of the conformers showed little if any evidence of conformer relaxation. The relative concentrations for each conformer pair, as estimated from the signal intensities after the jet expansion, were as predicted for the gas at ambient temperature before the expansion. That is, the signal intensities were consistent with the equilibrium ratio of concentrations (\( K_{eq} \)) predicted by the energy difference (\( \Delta E \)) between conformers at \( T \approx 298 \) K, 

\[
K_{eq} = f \exp\left( -\frac{\Delta E}{RT} \right),
\]

(1)

where \( f \) is the ratio of the numbers of equivalent forms for each conformer, e.g. 2 gauche and 1 trans (Fig. 1). This total absence of conformer relaxation with He contrasts with the results for Ar.

With argon as the carrier gas the signals in most cases were appreciably weaker for both forms, but no signal was detected for the higher energy form of ethyl formate, ethanol, and isopropanol. For them, effectively all of the high energy form was removed from the expanded jet by the Ar. The conformations of these three molecules are depicted by Newman projections in Fig. 1. Inspection of the data in Table II shows that ethyl formate and ethanol have the smallest barriers (\( \sim 350 \text{ cm}^{-1} \)) to conformer interconversion of those listed. The barrier for isopropanol has not been reported. On the other hand, none of the molecules with known barriers above \( 1000 \text{ cm}^{-1} \) exhibited a large, selective decrease in signal for its high energy conformer. Barrier heights have not yet been reported for four of the other nonrelaxed molecules in Table II, but our results lead us to suggest that their barriers are likely to be above 400

TABLE II. Molecules, types of conformer, energy differences, barrier heights, and extents of conformer relaxation.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Energy of conformer</th>
<th>Barrier</th>
<th>Relaxation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
<td>High</td>
<td>( \Delta E (\Delta H) )</td>
</tr>
<tr>
<td>ethyle formate</td>
<td>trans</td>
<td>gauche</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>ethanol</td>
<td>trans, gauche</td>
<td>41</td>
</tr>
<tr>
<td>isopropanol</td>
<td>gauche</td>
<td>trans</td>
<td>175</td>
</tr>
<tr>
<td>propanol</td>
<td>cis</td>
<td>gauche</td>
<td>315</td>
</tr>
<tr>
<td>CH_3CH=CHO</td>
<td>sym</td>
<td>asym</td>
<td>16</td>
</tr>
<tr>
<td>n-propanol</td>
<td>gauche</td>
<td>trans</td>
<td>100</td>
</tr>
<tr>
<td>CH_3H∼S=CH_3</td>
<td>gauche</td>
<td>trans</td>
<td>3</td>
</tr>
<tr>
<td>butyronitrile</td>
<td>gauche or trans</td>
<td>231</td>
<td>c</td>
</tr>
<tr>
<td>3-chloropropene</td>
<td>gauche</td>
<td>cis</td>
<td>231</td>
</tr>
<tr>
<td>ethyl nitrite</td>
<td>c.t gc</td>
<td>c, g</td>
<td>8,128</td>
</tr>
<tr>
<td>1-butene</td>
<td>cis</td>
<td>gauche</td>
<td>16(16)</td>
</tr>
<tr>
<td>acrolein</td>
<td>trans</td>
<td>s cis</td>
<td>660</td>
</tr>
<tr>
<td>Cl-cyclohexane</td>
<td>eq</td>
<td>axial</td>
<td>180</td>
</tr>
</tbody>
</table>

*a* The references citing the original microwave studies are given in the Introduction.

*b* Energy differences and barrier heights in \( \text{cm}^{-1} \).

*b* Not available.

*b* Different values reported for the barrier.

*b* The low energy conformer has not been determined.

*b* Three conformers present: cis-trans; trans-gauche; cis-gauche.

J. Chem. Phys., Vol. 93, No. 5, 1 September 1990
cm$^{-1}$. In the case of cis and gauche propanol two different values have been reported for the barrier height, 360 and 800 cm$^{-1}$. There was evidence for only some weak relaxation in argon of its high energy gauche conformer, and also in krypton and first run neon, so the 800 cm$^{-1}$ barrier is perhaps more reasonable.

Differential clustering of the conformers seems unlikely to be the primary cause of the apparent strong relaxation of ethyl formate, ethanol, and isopropanol. Undoubtedly, heterodimers of Ar/conformer are formed, the extent depending upon the properties of the conformer as noted in the following section. However, the relative signal strengths of high and low energy conformers, which do not relax, were about the same with different carrier gases. For example, with 1-butene the signal strengths of the low-energy, cis conformer were in a ratio of 15:5:1 for expansions with He, Ar, and pure 1-butene. The intensity ratios for the high-energy gauche conformer were 13.5:4.5:1. The differences between conformers are small compared with the differences between carrier gases. The carrier gas does affect the rotational temperature reached in the expansion and the types and extent of clustering. But these effects are usually comparable for both conformers.

**Dependence of interactions on carrier gas**

A more detailed study was made of conformer inter-conversion for the three molecules exhibiting strong relaxation in the jet expansions with argon. Results for them are shown in Figs. 2–4, respectively. Carrier gases used include Ne, first run Ne, and Kr as well as He and Ar, depending on the circumstances. Both conformers were studied for ethyl formate and ethanol. In the case of isopropanol, results are given for the less stable trans conformer. In addition, the more stable gauche form was observed to maintain the same signal level at several [Ne] in He.

The signal of the less stable gauche ethyl formate increased by a factor of 2 in first run neon compared with He. Therefore, we used first run neon as well as He as the
primary carriers and studied the concentration dependence for added Ar or Kr. The results for both conformers in first run neon are plotted in Fig. 2. Note that the measured signal intensities have been normalized to 10 for the largest signal from each conformer as we are interested in reduction of the signal as a function of carrier gas composition.

It is seen that the gauche conformer essentially disappears with only 6 mole percent of Ar while Kr is even more effective in removing the gauche form, which disappears at 4 mole percent Kr. On the other hand, the more stable trans form is virtually unaffected by Ar. The trans signal decreased with the addition of Kr, but not nearly as much as the gauche. In the study made of the gauche form with pure He as the primary carrier gas the He–Ar or He–Kr combinations were only about half as effective as first run Ne–Ar or Ne–Kr at reducing the gauche signal.

The results for ethanol and isopropanol are given in Figs. 3 and 4 for helium as the primary carrier gas. In both cases the signal from the high energy form was reduced sharply by krypton, virtually to zero by 5 mole percent. However, ethanol was affected more strongly by neon than was the isopropanol. The effect of argon on ethanol was also tested, with results intermediate between those given for Ne and Kr. Particularly noteworthy are the findings for the low energy, trans form of ethanol. The addition of Ne, as shown in Fig. 3, increased the trans signal substantially while reducing that of the high energy gauche conformer. This could be due to conversion of the gauche form to the trans. However, the results differ for ethyl formate. Argon and krypton decrease the signal of the high energy form sharply, but also decrease the low energy form somewhat, particularly krypton. It is apparent that the relaxants added to the primary carrier can do more to the conformers than simply convert the high to the low energy form.

**Velocity slippage**

In the course of measurements on mixtures of light and heavy carrier gases transient effects were noticed at the front of the jet expansion. The duration of the gas pulse is typically 4 ms in our experiments, while the time required to detect and digitize a single FID is \( \sim 100 \mu s \). Therefore, a number of successive FID’s can be observed for a single gas pulse as it transits the Fabry–Perot cavity which is 20 cm from the nozzle. With recent modifications the apparatus has an upper limit of 32 FID’s per gas pulse, the usual number being 8. This enables us to monitor signals from separate time “slices” of the jet expansion.

The FID at the forefront of the jet often differs from those following. In the present context, for example when ethyl formate is observed in helium with 4% argon as the carrier gas, the first FID for the (less stable) gauche conformer is quite strong in spite of the fact that the subsequent FID’s are a good deal weaker (Fig. 2). This is consistent with velocity slippage which makes the front of the jet less concentrated in argon than the trailing, steady-state jet. Presumably the heavy ethyl formate also is even less concentrated, but the gauche conformer gives a stronger signal in the first slice because there’s less argon there to relax it. The signal decrease by slippage is more than restored by signal increase due to nonrelaxation. Because of the transient effects only the central portion of the gas pulse was used in gathering data for our comparisons of conformers and isomers. However, the effects could be used to study some aspects of the dynamics of jet expansions.

### Nature of the conformer–carrier gas interactions

From the results presented above it is apparent that the interactions of the heavier rare gases with the conformers are complex. However, when the barrier to interconversion is “low enough,” the concentration of the high energy conformer \((H)\) is governed largely by its relaxation to the low energy form. On this basis we make a kinetics analysis of the decrease in signal from \(H\) with mole fraction of added heavy rare gas \((R_g)\). The relaxation should be first order in \(H\) and in \(R_g\). However, in some of the collisions, \(H\) may combine with \(R_g\), forming heterodimers in a process also first order in \(H\) and in \(R_g\); that is:

\[
H + R_g \rightarrow L^* + R_g \quad \text{relaxation,} \quad (1a)
\]

\[
H + R_g \rightarrow H-R_g^* \quad \text{dimer formation,} \quad (1b)
\]

where \(L\) is the low energy form. Energy released by dimer formation and the relaxation (*) would be absorbed in collisions with the helium or other light carrier gas present at high concentration.

Combining the two parts of Eq. (1) with the condition that \([R_g] > [H]\), we have

\[
d[H]/dt = -k[H][R_g], \quad (2)
\]

with \([R_g]\) effectively constant by experimental design. Integration over the interactive part of the pulsed jet expansion, under constant conditions except for \([H]\), and neglecting the back reaction, gives

\[
\log(S/S_0) \approx -k[R_g]t = -k_1[R_g], \quad (3)
\]

where \(k_1\) is a pseudo first-order rate constant averaged over the expansion and \([H]\) has been replaced by \(S\), the signal observed for \([H]\). This result predicts that semilog plots of the decreased signal for the high energy conformer should be linear in the concentration of added heavy rare gas. However, if either process in Eq. (3) involves \([R_g]^2\) the results could be nonlinear.

Semilog plots are given in Figs. 5 and 6 for gauche ethyl formate and ethanol in helium as the primary carrier. The plots for ethyl formate are with added Ar and Kr and those for ethanol with Ne and Kr. The measurements are not of high precision, but it is seen that the dependence is indeed linear. The data in Fig. 5 for argon added to ethyl formate in He are also plotted there against \([Ar]\), giving a strongly curved dependence verifying the first-order fit. The slopes of the lines are the rate constant \(k_1\), in units of (gas-pulse-mole percent\(^{-1}\)). The values are a measure of the conformer, rare-gas interaction. For ethyl formate the values of \(k_1\) are 0.15 and 0.4 with Ar and Kr, respectively. The results for ethanol are smaller, 0.06 and 0.2, with Ne and Kr, about half those for ethyl formate.
Not surprisingly the interactions depend on both the conformer and the added rare gas. At least part of the larger $k_s$'s for ethyl formate is attributable to its greater tendency to form a dimer with the rare gas. Also, all of the $k_s$'s contain a generally small contribution from the effect of carrier gas composition on beam temperature, as discussed later. The extent of the dependence of $k_1$ on the rare gas is surprising. The $k_1$ for Kr with ethyl formate is nearly triple that of Ar (0.4/0.15). With ethanol, the $k_1$ for Kr is more than triple that of Ne (0.2/0.06). Thus, the effectiveness of a rare-gas atom increases sharply with atomic number, the results indicating roughly a 0:1:2:4 progression for He, Ne, Ar, and Kr. This strong dependence on the rare gas atom of the interaction suggests that it involves relatively long range polarization effects.

The nature of the primary carrier gas also can have a major effect on the relaxation. This is shown in Fig. 7 by semilog plots for the relaxation of gauche ethyl formate upon addition of Ar and Kr to first run neon. Comparison of this figure with the analogous results in Fig. 5 for He as the carrier shows that the relaxation by Ar and Kr in first run neon is about 1.5 times that in He. The $k_s$ for first run neon are 0.25 and 0.6 with Ar and Kr, respectively, compared with 0.15 and 0.4 for He. This result is readily accommodated by the model introduced above.

In principle the neon itself may affect the concentration of the high energy conformer [H]. This would add a term $k_1[Ne][H]$ to Eq. (2). However, since [Ne] is effectively constant throughout a set of measurements at different [Rg], it does not affect the form of the final result; it simply has a constant effect, changing $S_e$ in Eq. (3) to $S'_e$. Therefore, the difference in the $k_s$ for He and first run neon as carrier is attributed to differences in the interactive part of the pulsed jet expansion, i.e., to $k[Rg][H]$ in Eq. (3). The Ne jet moves more slowly than that of He, requiring more time to develop into a noninteracting beam, during which the added Ar or Kr can relax more of the [H], as observed. The relative velocities of He and first run neon are about 2:1 compared to relaxation rates of 1:1.5 in their jet expansion.

### Isomers of weakly bonded dimers

#### Studies of three isomer pairs

HCN/CO$_2$—Paralleling our study of conformer relaxation, observations were made of similar behavior for several isomeric pairs of weakly bonded dimers. The most striking case is that of the $T$-shaped and linear heterodimers HCN–CO$_2$ and OCO–HCN. The $T$-shaped form has $C_{2v}$ symmetry with the N of the HCN attracted to the C of the CO$_2$. It was found by the Klemperer group several years ago in an unsuccessful search for the linear dimer in a nozzle expansion using argon as the carrier gas. Recently we discovered the hydrogen bonded, linear isomer while searching for additional transitions of HCN–(CO$_2$)$_2$; a trimer whose signal is a factor of 6 to 10 times stronger in first run neon than in argon. After finding the $J = 1 \rightarrow 2$ transition of the linear OCO–HCN in first run neon, we were unable to detect it with argon as the carrier gas.
On the other hand, the $T$-shaped form is readily observed in either argon, first run neon, or helium. Signal strengths of each isomer were about the same in helium and first run neon, with the ratio for $T$-shaped to linear isomers roughly 15/1, indicating that the $T$-shaped form is more stable. The dependence of normalized signal strength on composition of the carrier gas was determined as for the conformers. Figure 8 gives the results as a function of Ar concentration in first run neon. It is seen that as the $[\text{Ar}]$ increases, the signal from the linear species falls off sharply while that for the $T$-shaped isomer increases more gently to a maximum at about 10% Ar and then decreases. The plots go to an Ar mole percent of 21; with pure Ar, the linear isomer was not detected. A semilog plot (not shown) of the signal from the linear form is linear through $[\text{Ar}] = 7\%$ but then diverges. The slope gives a $k_1$ of 0.1.

HF/DF—The next case we consider is that of the bent, hydrogen-bonded dimers HF–DF and DF–HF. Because of differences in zero-point energy, DF–HF is calculated to be about 163 cm$^{-1}$ higher in energy than HF–DF. The HF–DF isomer was the first to be observed. It was found by Klemperer in his classic study of the HF/DF dimers, with argon as the carrier gas, but the DF–HF isomer could not be detected. It was not reported until a decade later when its much weaker signal was found, again in argon.

In the present study the use of first run neon or helium as carrier increased the signal for DF–HF tenfold. The results of systematic measurements of normalized intensities for both isomers are given in Fig. 9 as a function of argon concentration in first run neon. They differ from the other cases in that the signals from both isomers go through maxima as argon is added. However, the maximum for the high energy DF–HF isomer occurs at a much smaller [Ar] than that for the more stable HF–DF. Very similar results (not shown) were obtained when Kr was added to the carrier gas rather than Ar. The main difference is that the maxima are at much lower [Kr], 0 and 6%, than for [Ar], 7 and 50%.

We also determined the optimum signal strength for each of the two isomers obtainable in the different carrier gases by adjusting the backing pressure and the concentration of the 50–50 HF/DF mixture. The optimum signal was about the same for HF–DF in all five carriers tried. However, that of DF–HF was generally a good deal smaller and varied greatly with carrier. The ratio of DF–HF to HF–DF signal was about 0.3 to 1 in He and first run Ne, 0.017 in Ar, and 0.009 in Kr. The best signal found for DF–HF was 1 to 1 in first run neon with 6% Ar present.

$N_2O/\text{HF}$—The isomers of this dimer are both hydrogen bonded. One is the linear NNO–HF, while the other is bent, NNO–HF. As reported previously, both forms gave stronger signals by a factor of ~2 in pure neon than in argon carrier. But we found no appreciable differences between the isomers in different carriers, which included Kr and He as well as Ne first run and Ar.

**Isomer formation and relaxation**

The results for the three pairs of isomers are quite similar to those for conformer relaxation even though the dimers must be formed in the early stages of the jet expansion. Actually the data for the CO$_2$/HCN system (Fig. 8) are indistinguishable from conformer relaxation, with the linear dimer being the most stable form and there being a barrier of say ~ 300 cm$^{-1}$ between the forms. Theoretical calculations of the potential surface for the system are needed to test this interpretation.

The case of HF/DF is more complex (Fig. 9). The signal increases for both isomers as Ar is first added to the first run neon carrier. This may reflect formation of mixed Ar/HF and Ar/DF clusters which keep larger HF/DF clusters from forming. The subsequent drop in signal is more abrupt for the DF–HF isomer. This could be caused by its relaxation to the HF–DF form which is 100 to 165 cm$^{-1}$ more stable. Also, formation of higher clusters such as HFDF–Ar could contribute to the drop in signal for both isomers. The potential surface has been studied in detail for the HF dimer. The barrier for interconversion...
of the dimers is $385^{-1}$, which is consistent with a relaxation mechanism for the main drop in signal for the DF-HF isomer. Moreover, the unrelaxed ratio of DF-HF to HF-DF in helium or first run neon is about $1:3$. The equilibrium ratio predicted from their energy difference is about $1:2$, indicating that the proportions of the isomers get frozen in quite early in the jet expansion.\textsuperscript{21}

The insensitivity of the N$_2$O/HF dimers to carrier gas composition is the same as that of conformers with high barriers to interconversion. Theoretical estimates of the barrier between the two forms have been cited\textsuperscript{28} to be about $650$ cm$^{-1}$. Also, the proportions of the two isomers are characteristic of temperatures $\sim 200$ K, indicating they too get frozen in at an early stage of the expansion.

**Critique of the method**

It is noted in the Experimental section that changes in carrier gas composition affect the beam temperature and the rotational state populations in the expanded jet. These in turn modify the signal strength of the transitions observed, as do the conformer and isomer relaxation. However, the relaxation changes the relative intensities of the two forms while the carrier composition affects both forms more or less equally. Because of this, our experiments and analyses have favored differential effects. In addition the magnitude of the nonrelaxation effects of carrier gas composition was checked by experiments on isobutylene, an organic molecule somewhat like those of Table II, with internal rotation but without conformers, ($CH_3)_2 C = CH_2$.

The $2_{11} \rightarrow 2_{20}$ and $0_{00} \rightarrow 1_{11}$ transitions of isobutylene, at $5370.6$ and $13749.3$ MHz,\textsuperscript{22} were observed in a helium/argon carrier gas mixture as a function of its composition. The concentration of isobutylene was kept constant at 0.17 mole percent and the total backing pressure at 1 atm. On going from pure helium to a 50-50 He/Ar mixture, the signals from both transitions decreased, by a factor of three for $2_{11} \rightarrow 2_{20}$ and by a factor of two for $0_{00} \rightarrow 1_{11}$, almost linearly but with some upward curvature. Although substantial, these effects are small compared with the tenfold signal decrease caused by relaxation of a high energy conformer in 10 mole percent or less of Ar or Kr in He or Ne. Also, the nonrelaxation effects are relatively insensitive to the particular low-J transition of the isobutylene and to its frequency, indicating that the choice of transitions is not critical to a conformer or isomer pair for our purposes.

**DISCUSSION**

It is clear that the carrier gas can have a dramatic role in determining the relative concentrations of conformers and of isomers of weakly bonded dimers in supersonic expansions. Interpretation of the results is complicated by the dependence of beam temperature on carrier gas composition and by formation in the expansion of other species such as dimers and small clusters with and between the inert gases. However, the dominant factor is relaxation of the high energy conformer or isomer to the more stable form. The relaxation is caused by binary collisions of the high energy form with an inert gas atom, the heavier atoms (Ar,Kr) being much more effective than the lighter (He,Ne). But if the barrier to interconversion of the conformers or isomers is greater than about $350$ cm$^{-1}$, they are not relaxed, at least not in expansions with any of these four gases as carrier.

The similarity in behavior of the conformers and isomers is intriguing. It leads us to speculate that formation and relaxation of the weakly bonded dimers are a two step process in the expansion. That is, both isomers are formed in the initial, “high-temperature” part of the expansion. Then the high energy form gets relaxed by subsequent collisions with the heavy inert gas atoms, if any are present. This would be consistent with our observation that the proportions of isomers found in the light carrier gases are as predicted for temperatures somewhat below ambient rather than for the low rotational temperatures of $\sim 5$ K after the expansion. An alternative interpretation is for the heavy inert gas atom to participate directly in the formation mechanism, favoring the most stable form.

Another interesting aspect is the cutoff in relaxation for barriers larger than $\sim 350$ cm$^{-1}$. This probably is related to the strong dependence of the relaxation rate on the Z (or mass) of the inert gas atom employed. A detailed analysis of the collision mechanism\textsuperscript{31} is beyond the scope of this report, but we venture some qualitative comments. The fitting of the relaxation data by Eqs. (1)-(3) shows that the primary relaxation event is a bimolecular collision between the high energy conformer or isomer and a rare-gas atom. However, classical collision theory would predict the rare gases to have much more-nearly the same effects than observed. The differences should stem from the nature of the relaxation.

An important point is that the collisions inducing the relaxation need have only enough energy to surmount the small barrier (\textless; 350 cm$^{-1}$) of the conformer/isomer. Moreover, that amount of energy must be redistributed internally or given up by the conformer/isomer to stabilize it preferentially in the low energy form. In fact one would expect the extent of relaxation to be influenced not only by the barrier height but also by the energy difference between the conformers/isomers. The deuterated acetaldehdye was studied to test this point. Its conformers have an energy difference of only 16 cm$^{-1}$ and did not exhibit relaxation effects. However, it has a barrier of 400 cm$^{-1}$, somewhat above those of ethyl formate and ethanol (340 and 350 cm$^{-1}$), so it’s not clear whether the high barrier or the low energy difference inhibits the relaxation. Further study of the question is indicated; other partially deuterated molecules appear to be suitable for the purpose.

In any event, if both the barrier-surmounting and energy-loss steps in the relaxation were combined in a single collision it could be a weak, quasielastic interaction with a large effective cross section depending on the polarizability of the rare-gas atom. This would be more in keeping with the observed $k$’s. Modeling of the kinetics in the free jet suggests that such conformer converting collisions occur late in the expansion, where the local translational temperature is low enough to permit long-lived quasi-
resonant interactions between the rare gas atom relaxant and the conformers. A substantial part of the barrier-surmounting energy is likely to be provided by the weak attractive interaction energy of the collision pair. This energy scales roughly as the polarizability of the noble gas atom. On this basis, Kr should relax species with higher barriers than would Ar or Ne. Also, the use of a heated nozzle could enable relaxation over higher barriers. A final observation is that "weak" relaxants such as He and Ne do exist and can be employed to trap and study some types of excited species in supersonic expansions.

ACKNOWLEDGMENTS

We thank Don Secrest and Doug McDonald for helpful discussions and Phil Hajduk for assistance with some of the measurements. Our work was supported by NSF Grants CHE 85-20519 and CHE 88-20359. Also, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

33. Calculations modeling the free jet expansion under the conditions reported here are to be submitted by R. S. Ruoff.