

# Rotational spectrum and structure of the linear CO<sub>2</sub>-HCN dimer: Dependence of isomer formation on carrier gas

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A linear hydrogen-bonded dimer, OCO-HCN, has been identified and characterized *via* its microwave rotational spectrum. The study was made using the pulsed nozzle Fourier transform method with the Flygare/Balle Mark II spectrometer. A T-shaped HCN-CO<sub>2</sub> dimer was reported earlier by the Klemperer group. Rotational constants have been determined for all seven monoisotopically substituted species of the linear form.  $B_0$ ,  $D_J$ , and  $\chi_{aa}$  (<sup>14</sup>N) for the normal isotopic dimer are 1057.9397(2) MHz, 1.372(8) kHz, and -4.2466(5) MHz, respectively. The average torsional displacements of the OCO and HCN monomers about their center of mass (c.m.) are found to be 7.66° and 12.40°, based on the substitution O-C and C-N bond distances for the dimer. With these values for  $\alpha$  and  $\gamma$ , the  $B_0$  for the normal isotopic dimer corresponds to a c.m. to c.m. distance  $R = 5.035$  Å. Bending and stretching force constants and the well depth ( $\epsilon \sim 590$  cm<sup>-1</sup>) are estimated from the centrifugal distortion. The relative concentrations of the linear and T-shaped isomers are unusually sensitive to the carrier gas used in the supersonic jet expansion. The linear form could not be detected at all with argon as the carrier gas but gave a strong signal in neon first run (70% Ne, 30% He). In contrast, the T form gave strong signals in both carrier gases. However, a carrier-gas effect was not found for the N<sub>2</sub>O/HF dimer pair, which has a high barrier between the bent NNO-HF and linear FH-NNO isomers. Similar results were obtained for chlorocyclohexane (CCH) and ethyl formate (EF), which have two conformational isomers. In CCH which has a high barrier to *a*↔*e* interconversion, the two conformers gave strong signals in both Ar and He. In EF, with a low barrier, the *gauche* conformer could not be detected in Ar but gave a strong signal in He, while the *trans* form gave strong signals in both carrier gases.

## INTRODUCTION

Recently, the structure and dynamics of weakly bonded trimers and tetramers have been studied in microwave and infrared experiments.<sup>1-4</sup> Besides the added dimension of cluster size, we might expect such studies to find that conformational isomerism is more prevalent than in the dimers. Certainly it should be a common occurrence. Even a relatively simple complex, such as the Ar-HCl dimer, is best modeled as having more than one potential minimum.<sup>5,6</sup> Yet, as recently noted in a review<sup>4</sup> of van der Waals molecules, "there is almost a universal lack of multiple isomers detected" in supersonic expansions. Apparently only two cases have been found by rotational spectroscopy. One is the HCN trimer, for which both linear and cyclic structures have been observed.<sup>3,7</sup> The other is the linear FH-NNO<sup>8</sup> and its counterpart, bent NNO-HF.<sup>9</sup> We now report another case of geometrical isomerism in a weakly bonded system. It is the CO<sub>2</sub>/HCN dimer, for which we have characterized the linear OCO-HCN form.

The previously reported T-shaped HCN-CO<sub>2</sub> has  $C_{2v}$  symmetry with the N of HCN attracted to the C of CO<sub>2</sub>.<sup>10</sup> It was found in an unsuccessful search for the linear dimer. The newly discovered dimer is a classically hydrogen-bonded structure. The  $J = 1 \rightarrow 2$  transition was found while searching for transitions of the HCN-(CO<sub>2</sub>)<sub>2</sub> trimer.<sup>11</sup> Neon "first run" was being used as the carrier gas since with it the trimer signals are significantly better than in Ar. The signal

strength of the linear CO<sub>2</sub>-HCN dimer is quite good in Ne. But we could not detect it at all when argon was used as the carrier gas, which is why the Klemperer group missed it.<sup>10</sup> However, the T-shaped HCN-CO<sub>2</sub> is readily observed at comparable S/N with either Ar or Ne as the carrier gas. Such sensitivity of isomer detection to carrier gas seems unusual; at least we have not seen prior reports of it.

We have determined rotational constants for seven isotopic species of the linear CO<sub>2</sub>-HCN dimer, using pulsed nozzle, Fourier transform microwave spectroscopy. They give a full set of substitution positions in the dimer. Also, the <sup>14</sup>N nuclear quadrupole coupling hyperfine structure (hfs) has been analyzed. The average torsional oscillation of the HCN is of smaller amplitude in the linear dimer than in the T-shaped form. However, the weak-bond stretching force constant, determined from the observed centrifugal distortion, is smaller in the linear form. The simple Lennard-Jones, potential well depth is compared for the two structures. The sensitivity of isomer formation to carrier gas is considered. Measurements of it are given for the N<sub>2</sub>O/HF pair of isomers and also for two covalent organic molecules with conformational isomers.

## EXPERIMENTAL

The rotational transitions were observed using the Balle-Flygare Mark II spectrometer which has been described elsewhere.<sup>12</sup> The conditions under which the dimer

was found are as follows. The carrier gas was neon "first run" (Airco), a 70/30 mix of Ne and He which we refer to as Ne. The concentrations of HCN (Fumico) and of CO<sub>2</sub> (Linde) at the nozzle were 0.3% and 3%, respectively. The backing pressure was 1.5 atm and the nozzle diameter was 1.0 mm. A set of <sup>14</sup>N hfs was found centered at about 4231.5 MHz while searching for the HCN-(CO<sub>2</sub>)<sub>2</sub> trimer. It was soon realized that the signals optimized at a lower concentration of CO<sub>2</sub>, ~2%, than would a transition of the trimer, and the species was identified as outlined in the next section.

The S/N ratio for a single free induction decay (FID) of the  $J = 1 \rightarrow 2$  transition of linear CO<sub>2</sub>-HC<sup>15</sup>N (no hfs) in Ne is ~15.1. Under a variety of conditions in Ar carrier, no FID was observable for the same transition, even after averaging for 24 000 FIDs. A search for the  $J = 2 \rightarrow 3$  transition was also unsuccessful. Use of pure He gave signals approximately as strong as in Ne. By comparison, the T-shaped HCN-CO<sub>2</sub> had a S/N ratio of 200:1 per FID in Ne, but also about 175:1 per FID in Ar.

In connection with our observations of the dependence of isomer signal strength upon carrier gas we estimated the relative intensities of pairs of transitions, one from each isomer. This was done by counting the number of digitized, microwave FID's needed from each transition to cause the signal averager to overflow. Precautions were taken to make the results as comparable for the isomers as possible. Transitions close in frequency and similar in  $J$  and  $K$  were chosen. The master oscillator was displaced from the transitions by the same amount. The same microwave pulse amplitude and width were used and cavity mode effects were avoided. Transitions without hfs were selected.

The isotopic derivatives were prepared by reacting orthophosphoric acid with KC<sup>15</sup>N and K<sup>13</sup>CN (Cambridge Isotopes), and deuterated orthophosphoric acid with KCN for the DCN. The labeled <sup>13</sup>CO<sub>2</sub> and <sup>18</sup>OC<sup>16</sup>O were purchased from Cambridge Isotopes.

## RESULTS AND ANALYSIS

### Identification, hfs, and rotational constants

The hfs associated with the transition at 4231.5 MHz was indicative of a single HCN with isotropic vibrational averaging about the molecular axis. Also, the splittings clearly showed that it was a  $J = 1 \rightarrow 2$ ,  $K = 0$ , rotational transition. Then a set of hfs was found at approximately  $3/2 \times 4231.5$  MHz, confirming a linear or symmetric top species with  $B \approx 1057.9$  MHz. Initially, because of its  $C_3$  symmetry with  $I = 0$  nuclei, the possibility of HCN-(CO<sub>2</sub>)<sub>3</sub> could not be excluded, though this would require an extremely short C to N distance of 2.72 Å compared with the 3.00 Å in the T-shaped trimer. However, D and <sup>15</sup>N isotopic substitution soon demonstrated that the complex is a linear hydrogen-bonded dimer of CO<sub>2</sub> and HCN. This was further confirmed later when transitions for the two <sup>13</sup>C and two <sup>18</sup>OC<sup>16</sup>O containing species were observed. An example of the hfs is shown in Fig. 1, which gives the  $J = 3 \rightarrow 4$  transition observed for the usual isotopic species.

The Hamiltonian  $H = H_R + H_Q$  was used to fit the dimer spectra.  $H_R$  is the linear molecule, semirigid rotor

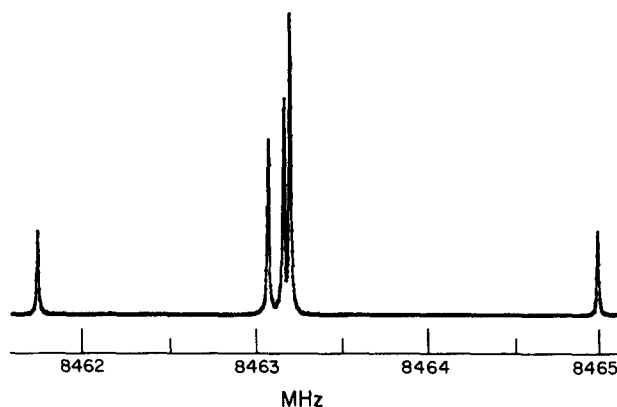


FIG. 1. The <sup>14</sup>N hfs observed for the  $J = 3 \rightarrow 4$  transition of the linear CO<sub>2</sub>-HCN dimer. The plot is a composite of three segments each with less than two minutes of signal averaging, with neon "first run" as carrier gas.

Hamiltonian given by

$$E_J = B_Q J(J+1) - D_J J^2(J+1)^2, \quad (1)$$

to which the line centers were fitted. The line centers were determined by fitting the hfs to the nuclear quadrupole Hamiltonian,<sup>13</sup>

$$E_Q = -\chi_{aa} Y(J, I, F). \quad (2)$$

A two-spin quadrupole Hamiltonian was used to analyze the CO<sub>2</sub>-DCN hfs. The details of the hfs are available elsewhere.<sup>14</sup> In fitting the hfs the residues averaged less than a kHz. The line centers obtained are listed in Table I. The standard deviation in their frequencies averages about 1 kHz. The spectroscopic constants ( $B_0$ ,  $D_J$ , and  $\chi_{aa}$ ) for the seven isotopic species investigated are presented in Table II. For the <sup>13</sup>CO<sub>2</sub>-HCN and <sup>16</sup>OC<sup>18</sup>O-HCN species, only a single line center was determined.  $B_0$ 's were obtained for them by estimating their  $D_J$  from the results for CO<sub>2</sub>-HCN and CO<sub>2</sub>-HC<sup>15</sup>N.

### Structural determination

The  $B_0$ 's for the mono-isotopically substituted dimers enable us to determine a full  $r_s$  substitution structure for the dimer by using the Kraitchman equation for a linear molecule<sup>13</sup>

$$I'_b = I_b + \mu_s a_i^2, \quad (3)$$

where the prime indicates the substituted species,  $I_b$  is the moment of inertia given by  $I_b \times B_0 = 505\,379.07 \text{ u } \text{Å}^2 \text{ MHz}$ ,  $\mu_s$  is the reduced mass of the substitution, and  $a_i$  is the distance along the  $a$ -axis of the substituted atom  $i$  from the center of mass (c.m.) of the parent molecule. The  $a_i$  positions are averaged over the zero-point vibrations, which are assumed to be unchanged by the substitution. In the dimer, the vibrations are largely the torsional oscillations of the relatively rigid monomers about their own c.m., and the positions are the projections on the  $a$ -axis of each monomer at its average angular displacement, as seen in Fig. 2. This is the basis of a fruitful method for determining a monomer's torsional amplitude ( $\theta$ ) in a linear dimer, for which<sup>15,16</sup>

$$r_s^d = r_s^m \langle \cos \theta \rangle. \quad (4)$$

Here,  $r_s^m$  is the substitution bond distance observed in the

TABLE I. Line centers in MHz determined for several isotopic species of the linear OCO-HCN dimer.<sup>a</sup>

| Transition | OCO-HCN   | <sup>18</sup> OCO-HCN | O <sup>13</sup> CO-HCN | OC <sup>18</sup> O-HCN | OCO-DCN   | OCO-H <sup>13</sup> CN | OCO-HC <sup>15</sup> N |
|------------|-----------|-----------------------|------------------------|------------------------|-----------|------------------------|------------------------|
| 1 → 2      | 4231.7145 | 4075.6251             | 4199.9334              | 4219.5504              | 4211.8824 | 4174.2874              | 4115.3974              |
| 2 → 3      | 6347.4908 | 6113.3630             | ...                    | ...                    | 6317.7404 | 6261.3495              | 6173.0188              |
| 3 → 4      | 8463.1664 | ...                   | ...                    | ...                    | ...       | ...                    | ...                    |

<sup>a</sup>All transitions except for those of OCO-HC<sup>15</sup>N have hfs which was fitted as described in the text to determine the line centers given here.

free monomer and  $r_s^d$  is the projected value in the dimer.

The atomic positions, bond distances, and torsional amplitudes determined this way for OCO-HCN are given in Table III. The positions of the inner oxygen and of the hydrogen are poorly determined, the oxygen because of its closeness to the dimer's c.m. and the H because of deuterium's large effect upon vibrations in the HCN monomer. The bond distances found for the outer O-C and for C-N should be reliable. In Eq. (4), with the corresponding bond distances of the free monomers (Table IV),<sup>17,18</sup> they give torsional amplitudes in the dimer of 7.58° for CO<sub>2</sub> ( $\alpha$ ) and 12.40° for HCN ( $\gamma$ ). For CO<sub>2</sub>, the <sup>18</sup>O/<sup>16</sup>O substitution has a discernible effect upon  $\alpha$ . One may correct for it with the relation<sup>19</sup>

$$\alpha(\text{CO}_2 = \alpha(^{18}\text{OCO}) [I(^{18}\text{OCO})/I(\text{CO}_2)]^{1/4} \quad (5)$$

which increases  $\alpha$  from 7.58° to 7.66°.

If dimer formation did not change the <sup>14</sup>N quadrupole interaction constant from its value  $\chi_0^m$  in the free monomer,  $\gamma$  could be found from the  $\chi_a$  observed in the dimer by using the projection operator<sup>13</sup>

$$\chi_a^d = (\chi_0^m/2) \langle 3 \cos^2 \gamma - 1 \rangle. \quad (6)$$

In this manner, the values for  $\chi_a^d$  and  $\chi_0^m$  in Tables II and IV give  $\gamma = 14.81^\circ$ , significantly larger than the 12.40° from the substitution method. The difference is attributable to charge redistribution effects of dimer formation which make  $\chi_a^d$  differ from  $\chi_0^m$  for HCN in strong hydrogen bonds.<sup>15</sup> With  $\gamma = 12.40^\circ$  and the experimental value of  $-4.2466$  MHz for  $\chi_a^d$ , Eq. (6) gives  $\chi_0^m$  to be  $-4.5621$  MHz compared with the value of  $-4.7079$  MHz for  $\chi_0^m$ . The value of  $\chi_a^d$  in the T-

TABLE II. Rotational and hyperfine interaction constants found for several isotopic species of linear OCO-HCN dimer.<sup>a</sup>

| Species <sup>b</sup>   | $B_0$ (MHz)  | $D_J$ (kHz)       | $\chi_N$ (MHz)           |
|------------------------|--------------|-------------------|--------------------------|
| OCO-HCN                | 1057.9397(2) | 1.372(8)          | -4.2466(5)               |
| <sup>18</sup> OCO-HCN  | 1018.9165    | 1.27              | -4.2442(23)              |
| O <sup>13</sup> CO-HCN | 1049.9940    | 1.35 <sup>c</sup> | -4.2461(32)              |
| OC <sup>18</sup> O-HCN | 1054.898     | 1.36 <sup>c</sup> | -4.2505(28)              |
| OCO-DCN                | 1052.9817    | 1.38              | -4.2826(27) <sup>d</sup> |
| OCO-H <sup>13</sup> CN | 1043.5827    | 1.36              | -4.2494(24)              |
| OCO-HC <sup>15</sup> N | 1028.8596    | 1.289             | ...                      |

<sup>a</sup>Numbers in parentheses are one standard deviation of the fit. Only in the case of the parent species were enough (3) line centers found to determine a standard deviation for  $B_0$  and  $D_J$ .

<sup>b</sup>Only the substituted isotope is identified.

<sup>c</sup>Only a single line center was determined;  $D_J$  was scaled from the results for CO<sub>2</sub>-HCN and CO<sub>2</sub>-HC<sup>15</sup>N.

<sup>d</sup>An approximate value of 204 kHz was found for  $\chi_D$  from the fit.

shaped dimer<sup>10</sup> is considerably smaller ( $-4.075$  MHz) than in the linear form indicating a  $\gamma$  larger by about 2.6°.

The substitution positions enable one to find  $R$ , the c.m. to c.m. separation of the two monomers. Figure 2 shows that  $R$  is the distance between the two carbons plus the projection on the  $a$  axis of the C to c.m. distance in the HCN. This gives  $R = 5.0349$  Å. Alternatively,  $R$  may be determined from  $B_0$  with the following expression for the moment of inertia of a linear dimer in which the monomers oscillate isotropically about their centers of mass,

$$I_b = \mu_c R^2 + \frac{1}{2} \langle \cos^2 \alpha + 1 \rangle I(\text{CO}_2) + \frac{1}{2} \langle \cos^2 \gamma + 1 \rangle I(\text{HCN}), \quad (7)$$

where  $\mu_c$  is the reduced mass of the complex treated as pseudodiatomic and the angles  $\alpha$  and  $\gamma$  are treated as uncoupled.<sup>10</sup> The value for  $R$  is sensitive to the torsional amplitudes because of the relatively large moments of inertia for the monomers, especially CO<sub>2</sub>. With the substitution angles, and the  $B_0$  for CO<sub>2</sub>-HCN,  $R$  is found to be 5.032 Å. Comparable values averaging 5.029 Å are found for the other isotopic species when allowance is made for the effect on  $R$  of the isotopic shifts in c.m. So the values from Eq. (7) are in reasonable agreement with the substitution value of 5.035 Å.

### Interaction potential

The centrifugal distortion constant  $D_J$  may be used to evaluate the stretching force constant between the two monomers in the linear dimer. We make the usual approximations,<sup>20</sup> assuming that the two monomers are rigid and that the bending modes of the dimer are not coupled to the stretch. This gives a force constant  $k_s = 3.38$  N/M for the linear CO<sub>2</sub>-HCN dimer. For the isomeric, T-shaped asymmetric rotor the centrifugal distortion constant,  $\Delta_J$  is also relatable to  $k_s$  with the recent approximation given elsewhere.<sup>20</sup> It leads to  $k_s = 4.2$  N/M, a somewhat smaller value than reported originally.<sup>10</sup>

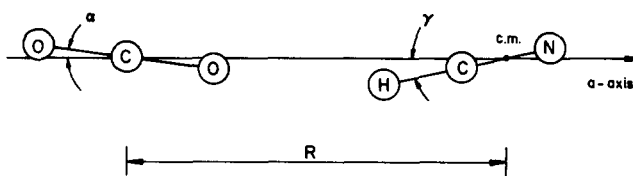


FIG. 2. Geometrical structure of the linear CO<sub>2</sub>-HCN dimer. Dimensions are to scale.

TABLE III. Substitution positions, bond distances, and average torsional amplitudes of the monomers in linear OCO-HCN.<sup>a</sup>

| Atom | Position (Å) | Bond                | Distance(Å)              |
|------|--------------|---------------------|--------------------------|
| O    | - 3.0634     | O-C <sup>b</sup>    | 1.1519                   |
| C    | - 1.9115     | C-N                 | 1.1284                   |
| O    | - 0.8405     | R                   | 5.0349                   |
| H    | 1.5056       | monomer             | angle (deg)              |
| C    | 2.5773       | CO <sub>2</sub> (α) | 7.58 (7.66) <sup>c</sup> |
| N    | 3.7057       | HCN(γ)              | 12.40                    |

<sup>a</sup>Based on  $B_0$  values in Table II with the normal isotopic species as the parent.

<sup>b</sup>This is the outer O-C distance; the inner oxygen is too close to the dimer's c.m. for accurate determination.

<sup>c</sup>The value in parentheses is corrected for the effects of <sup>18</sup>O substitution.

Interpretation of a bending force constant for the HCN is complicated by the occurrence of two doubly degenerate bends in a linear dimer with two molecular monomers. However, we may determine an average or effective force constant for the HCN by using the equation customarily applied to dimers with only one oscillating monomer,<sup>19</sup>

$$k_b = \hbar^2 / I_b \langle \gamma^2 \rangle^2. \quad (8)$$

The bending amplitude is given by  $\langle \gamma^2 \rangle$ , and  $I_b$  is the moment of inertia of the (harmonic) bender. Because of the fourth power dependence  $k_b$  is very sensitive to  $\gamma$ . With the substitution value of 12.40° for  $\gamma$ , we find  $k_b = 0.0268$  mdyn Å.

The well depth  $\epsilon$  may be calculated for the dimer from the pseudodiatomic stretching force constant by assuming a 6-12 potential.<sup>21</sup> This simple model predicts that the linear dimer is lower in energy (590 cm<sup>-1</sup>) than the T-shaped form (370 cm<sup>-1</sup>). However, this prediction is likely to be approximate because of the different shapes of the dimers. The values of  $k_s$ ,  $k_b$ , and  $\epsilon$  estimated for the linear CO<sub>2</sub>-HCN dimer are compared in Table V with those for the T-shaped form and for several other HCN containing linear dimers, including SCO-HCN.<sup>22</sup> The dimers are listed in order of increasing well depth. The values for  $k_s$  and  $k_b$  increase in about the same order.

### Dependence of isomer formation on carrier gas

Our inability to observe the linear OCO-HCN dimer with Ar as the carrier gas after finding strong signals from it

TABLE IV. Properties of the free monomers.

| HCN <sup>a</sup>          |              | CO <sub>2</sub> <sup>b</sup> |           |
|---------------------------|--------------|------------------------------|-----------|
| Property                  | Value        | Property                     | Value     |
| $B_0$ (MHz)               | 44 315.975 7 | $B_0$ (MHz)                  | 11 698.2  |
| $r_s$ H-C (Å)             | 1.063 17     | $r_0$ C=O (Å)                | 1.162 08  |
| $r_s$ C-N (Å)             | 1.155 12     | $I_0$ (u Å <sup>2</sup> )    | 43.200 70 |
| $\chi_0$ (MHz)            | - 4.707 9(1) |                              |           |
| $I_0$ (u Å <sup>2</sup> ) | 11.404 00    |                              |           |

<sup>a</sup>References 17 and 26.

<sup>b</sup>Reference 18. The moment of inertia for <sup>18</sup>OCO was calculated by assuming the same  $r_0$  as is given for CO<sub>2</sub>.

TABLE V. Comparison of stretching and bending force constants and well depths for several related dimers containing HCN.<sup>a</sup>

| Dimer                            | $k_s$ (N/M) | $k_b$ (mdyn Å) <sup>b</sup> | $\epsilon$ (cm <sup>-1</sup> ) |
|----------------------------------|-------------|-----------------------------|--------------------------------|
| HCN-CO <sub>2</sub> <sup>c</sup> | 3.2         | ...                         | 370                            |
| OC-HCN <sup>d</sup>              | 3.30        | 0.0157                      | 530 <sup>e</sup>               |
| CO <sub>2</sub> -HCN             | 3.38        | 0.0268                      | 590                            |
| SCO-HCN <sup>f</sup>             | 3.18        | ...                         | 680 <sup>e</sup>               |
| HCN-HCN <sup>g</sup>             | 8.14        | 0.0966                      | 1110                           |

<sup>a</sup>The dimers are linear except for the T-shaped HCN-CO<sub>2</sub>.

<sup>b</sup>Values are given only where the bending amplitude has been determined by the substitution method, Eq. (4)

<sup>c</sup>Calculated using the data from Ref. 10.

<sup>d</sup>Reference 16.

<sup>e</sup>The value of  $\epsilon$  for this dimer was calculated by us from the reported centrifugal distortion.

<sup>f</sup>Reference 22.

<sup>g</sup>Reference 15.

in Ne first run is an interesting effect. Rotational relaxation generally is fast compared with equilibration of other internal modes.<sup>23</sup> Therefore the rotational intensities for the two isomers should be a valid measure of their relative concentrations. Accordingly, the linear dimer is present after the supersonic expansion of seeded neon but not with seeded argon, while the T-shaped form is present with both.

In an effort to shed some light on this phenomenon we checked the formation of the two N<sub>2</sub>O/HF dimers in the 2 carrier gases. Both the linear and the bent forms<sup>8,9</sup> gave stronger signals by a factor of two in the Ne carrier compared to Ar. But we found no major differences between the isomers. The bent form is more stable by up to 300 cm<sup>-1</sup> per the evidence developed and reviewed by Lovejoy and Nesbitt in their recent infrared studies of the N<sub>2</sub>O/HF system.<sup>24</sup> However, they find the same relative intensity ratio for the isomers under several initial and final conditions in slit supersonic expansions. This is attributed to "freezing out" of the linear/bent proportions at a particular point during the expansion, by the barrier to interconversion of the isomers.

This leads to a possible interpretation of the CO<sub>2</sub>/HCN results. These two isomers could have an "intermediate" barrier between them, with argon much more efficient than neon at isomer interconversion. In the jet expansion with argon, the linear form is relaxed to the more stable T-shaped isomer, which is the only one observed. With neon, the probably non-equilibrium proportions of the isomers get frozen in during the formation process in the early stages of the expansion, and both are observed in the expanded jet. The model requires the linear form to be higher in energy than the T-shaped form which differs with our *approximate* determination of their well depths (Table V) from the centrifugal distortion. The plausibility of this interpretation is supported by studies of conformational relaxation in jet expansions of stable molecules,<sup>25</sup> two examples of which we give here, ethyl formate and chlorocyclohexane.

Ethyl formate (EF) has two conformers, *trans* (*t*) and *gauche* (*g*). The barrier to conversion is low (340 cm<sup>-1</sup>) and the energy difference between the two forms is 40 cm<sup>-1</sup> with the *trans* being more stable.<sup>26</sup> In several attempts using

Ar as the carrier gas, we could not observe the  $\alpha$ -dipole  $J = 0 \rightarrow 1$  transition of ( $g$ ) EF at 7052.42 MHz. However, with He as the carrier gas, it is roughly equivalent in strength to the  $\alpha$ -dipole  $0 \rightarrow 1$  transition of ( $t$ ) EF at 5483.87 MHz. On the other hand, the transition for ( $t$ ) EF has approximately equal signal strengths in either He or Ar. Chlorocyclohexane (CCH) has two conformers, equatorial ( $e$ ) and axial ( $a$ ), which have a large barrier of 4000 cm<sup>-1</sup> to interconversion.<sup>27</sup> However, the energy difference between the two conformers is only 170 cm<sup>-1</sup> with ( $e$ ) being the more stable. For CCH, the intensities of the  $1_{10} \rightarrow 2_{11}$  transition at 5318.29 MHz for the ( $e$ ) conformer and at 6790.31 MHz for the ( $a$ ) conformer were not affected appreciably when the carrier gas was changed between Ar and He. In other experiments on conformers, He and Ne first run gave very similar results.<sup>25</sup>

Our results indicate that barrier height may be an important factor in determining which conformers and isomers are observed in supersonic expansion of Ar carrier gas. In CCH, which has a very high barrier of 4000 cm<sup>-1</sup>, both ( $e$ ) and ( $a$ ) conformers have comparable intensity in both Ar and He. With the low barrier of 340 cm<sup>-1</sup> in EF, only the ( $t$ ) conformer was found in Ar though both ( $t$ ) and ( $g$ ) were strong in He. In the CO<sub>2</sub>/HCN dimer, with an unknown barrier, only the T-shaped dimer was found in Ar although both T-shaped and linear forms are strong in Ne. These findings suggest that the preferential appearance in Ar of the T-shaped dimer is caused by collisional interconversions which are less important with neon as the carrier.<sup>23</sup> Also, one would predict that the barrier to interconversion is higher for the N<sub>2</sub>O/HF dimers than for CO<sub>2</sub>/HCN.

## DISCUSSION

The two isomers of the CO<sub>2</sub>/HCN dimer have structures consistent with the first nonzero electrical moments of the two monomers. An interesting question is which isomer is most stable. The well-depth estimate from centrifugal distortion favors the linear form, 570 vs 390 cm<sup>-1</sup>, but it is not reliable because of the difference in shape, a problem also in bent NNO-HF.<sup>24</sup> Moreover, the signal strengths in Ne, and also that in Ar, are larger for the T-shaped form, and the stretching force constant recalculated for the T form<sup>10</sup> is 4.2 N/M vs 3.4 for the linear form (Table V). A better determination of the relative stability of the two isomers is needed.

The strong dependence of dimer and conformer proportions upon the carrier gas points out the importance of collisional and structural complexities during an expansion. For example, in the case of dimers there might be preferential formation of a trimer by one of the isomers with one of the carrier gases, e.g. a strong Ar/CO<sub>2</sub>-HCN trimer but not one for Ar/HCN-CO<sub>2</sub>. Further study of the problem is indicated. The CO<sub>2</sub>/HCN and N<sub>2</sub>O/HF dimers are sufficiently simple that potential functions should be calculated for them and their interconversion. Also, it should be feasible to calculate the interactions of the two dimeric systems with Ar and Ne.

In considering the average torsional amplitude  $\gamma$  of the HCN in the linear CO<sub>2</sub>-HCN dimer, 12.40° was determined

via the substitution structure and 14.81° from  $\chi_a^d/\chi_0^m$  for the <sup>14</sup>N. The difference was ascribed to charge redistribution effects in the dimer which made  $\chi_0^d = -4.5621$  MHz rather than  $-4.7079$  MHz, the value in the free monomer  $\chi_0^m$ .<sup>28</sup> This gives  $\Delta\chi_0 = \chi_0^d - \chi_0^m$  in CO<sub>2</sub>-HCN to be 0.146 MHz, which is considerably larger than the 0.105 MHz found for the outer nitrogen in the HCN-HCN dimer.<sup>15</sup> Also, the substitution structure of the linear OC-HCN dimer is available<sup>16</sup> and a similar analysis for it leads to  $\Delta\chi_0 = 0.099$  MHz. These  $\Delta\chi$ 's are not correlated with the stretching force constants or well depths of the dimers (Table V), indicating the importance of other factors.

Both HCN and CO<sub>2</sub> have multiple weak-bonding sites. Because of this the number of possible isomeric clusters increases rapidly with cluster size. Discovery of the linear CO<sub>2</sub>-HCN dimer indicates that several CO<sub>2</sub>/HCN trimers should exist and be detectable. These include the T-shaped HCN-HCN-CO<sub>2</sub>, linear CO<sub>2</sub>-(HCN)<sub>2</sub> and NCH-CO<sub>2</sub>-HCN (nonpolar), and an L-shaped form with CO<sub>2</sub> at the bend. Of these, the T-shaped trimer has been found.<sup>27</sup> As to homotrimers, both linear<sup>3</sup> and cyclic<sup>4</sup> forms of (HCN)<sub>3</sub> have been reported along with a cyclic, pinwheel form of (CO<sub>2</sub>)<sub>3</sub>. The (CO<sub>2</sub>)<sub>2</sub>/HCN trimers are as yet not well defined. The (CO<sub>2</sub>)<sub>2</sub> dimer has a planar, "slipped parallel" structure.<sup>4</sup> One might expect an HCN to attach itself by either end to several points on the (CO<sub>2</sub>)<sub>2</sub>. Or a second CO<sub>2</sub> could be attached to one or the other of the two CO<sub>2</sub>/HCN dimers. Of these possibilities a T-shaped form with the HCN perpendicular to the (CO<sub>2</sub>)<sub>2</sub> dimer has been found.<sup>11</sup> The HCN is on the C<sub>2</sub> axis of the dimer, with the N end closest to the carbons. This diversity of something as simple as a trimer does indeed show "that the journey from the gas to condensed phases will be a very interesting and fruitful one."<sup>4</sup>

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<sup>1</sup>T. D. Klots, R. S. Ruoff, C. Chuang, T. Emilsson, and H. S. Gutowsky, *J. Chem. Phys.* **87**, 4383 (1987).

<sup>2</sup>D. W. Michael and J. M. Lisy, *J. Chem. Phys.* **85**, 2528 (1986).

<sup>3</sup>R. S. Ruoff, T. Emilsson, T. D. Klots, C. Chuang, and H. S. Gutowsky, *J. Chem. Phys.* **89**, 138 (1988).

<sup>4</sup>R. E. Miller, *Science* **240**, 447 (1988).

<sup>5</sup>J. M. Hutson, *J. Chem. Phys.* **81**, 2357 (1984).

<sup>6</sup>J. M. Hutson, *J. Chem. Soc. Faraday Trans.* **82**, 1163 (1986).

<sup>7</sup>K. W. Jucks and R. E. Miller, *J. Chem. Phys.* **87**, 1450 (1987).

<sup>8</sup>C. M. Lovejoy and D. J. Nesbitt, *J. Chem. Phys.* **87**, 1450 (1987).

<sup>9</sup>C. H. Joyner, T. A. Dixon, F. A. Biocchi, and W. Klemperer, *J. Chem. Phys.* **74**, 6550 (1981).

<sup>10</sup>K. R. Leopold, G. T. Fraser, and W. Klemperer, *J. Chem. Phys.* **80**, 1039 (1984).

<sup>11</sup>R. S. Ruoff, P. J. Hajduk, J. Chen, T. D. Klots, T. Emilsson, and H. S. Gutowsky, *J. Chem. Phys.* (to be published).

- <sup>12</sup>E. J. Campbell, W. G. Read, and J. A. Shea, *Chem. Phys. Lett.* **94**, 69 (1983), and prior work cited therein. The spectrometer has been modified extensively; see e.g., H. S. Gutowsky, C. Chuang, T. D. Klots, T. Emilsson, R. S. Ruoff, and K. R. Krause, *J. Chem. Phys.* **88**, 2919 (1988).
- <sup>13</sup>W. Gordy and R. L. Cook, *Microwave Molecular Spectra* (Wiley, New York, 1984).
- <sup>14</sup>T. D. Klots, Ph.D. thesis, University of Illinois, 1988.
- <sup>15</sup>R. S. Ruoff, T. Emilsson, C. Chuang, T. D. Klots, and H. S. Gutowsky, *Chem. Phys. Lett.* **138**, 553 (1987).
- <sup>16</sup>E. J. Goodwin and A. C. Legon, *Chem. Phys.* **87**, 81 (1984).
- <sup>17</sup>E. F. Pearson, R. A. Creswell, M. Winnewisser, and G. Winnewisser, *Z. Naturforsch. Teil A31*, 1394 (1976).
- <sup>18</sup>G. T. Fraser, A. S. Pine, W. J. Lafferty, and R. E. Miller, *J. Chem. Phys.* **87**, 1502 (1987).
- <sup>19</sup>M. R. Keenan, L. W. Buxton, E. J. Campbell, A. C. Legon, and W. H. Flygare, *J. Chem. Phys.* **74**, 2133 (1981).
- <sup>20</sup>D. J. Millen, *Can. J. Chem.* **63**, 1477 (1985).
- <sup>21</sup>T. J. Balle, E. J. Campbell, M. R. Keenan, and W. H. Flygare, *J. Chem. Phys.* **71**, 2723 (1979); **72**, 922 (1980).
- <sup>22</sup>A. I. Jaman and A. C. Legon, *J. Mol. Struct.* **158**, 205 (1987).
- <sup>23</sup>P. Felder and H. H. Günthard, *Chem. Phys.* **71**, 9 (1982).
- <sup>24</sup>C. M. Lovejoy and D. J. Nesbitt, *J. Chem. Phys.* **90** (to be published). We thank the authors for sending us a preprint.
- <sup>25</sup>R. S. Ruoff, T. D. Klots, C. Chuang, P. J. Hajduk, T. I. Emilsson, and H. S. Gutowsky, *J. Chem. Phys.* (to be published).
- <sup>26</sup>J. M. Riveros and E. B. Wilson, Jr., *J. Chem. Phys.* **46**, 4605 (1967).
- <sup>27</sup>D. Damiani and H. Ferretti, *Chem. Phys. Lett.* **21**, 592 (1973); W. Caminati, F. Scappini, and D. Damiani, *J. Mol. Struct.* **108**, 387 (1984).
- <sup>28</sup>A. G. Maki, *J. Phys. Chem. Ref. Data* **3**, 221 (1974).
- <sup>29</sup>R. S. Ruoff, C. Chuang, T. Emilsson, T. D. Klots, and H. S. Gutowsky (to be published).
- <sup>30</sup>T. D. Klots, C. Chuang, R. S. Ruoff, T. Emilsson, and H. S. Gutowsky, *J. Chem. Phys.* **86**, 5315 (1987).