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Excited ν_3 vibrational state of the Ar–HCN and Kr–HCN dimers

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Rotational spectra have been observed for an excited vibrational state of the Ar/Kr–HCN dimers in a Balle–Flygare Fourier transform microwave spectrometer with a high temperature nozzle that can be heated to $\sim$1300 K. The B, D_J, and H_J rotational constants found for the excited parent Ar–HCN isotopic species are 1602.475(3) MHz, 164.2(6) kHz, and 309(5) Hz, and for Kr–HCN they are 1176.4493(3) MHz, 41.7(1) kHz, and 56(1) Hz. The ^{14}N quadrupole interaction $\chi_a(J=1)$ observed in the excited state is -2.824 (-3.239) MHz for Ar(Kr)–HCN, slightly smaller than the -2.844 (-3.268) MHz in the ground state. A substitution analysis based on the C and N isotopic species reveals that the C–N distance r_s (CN) increases by $\sim$0.013 (0.020 Å) on excitation of Ar(Kr)–HCN. A similar analysis for free DC^{15}N gives an increase in r_s(CN) upon ν_3 excitation of 0.0022 Å. Assignment of the excited state in the dimer as the ν_3C–N stretch of the HCN is proposed and discussed. © *1995 American Institute of Physics.*

INTRODUCTION

The rotational spectrum of the Ar–HCN dimer was first reported by Leopold *et al.*[1] ten years ago. Since then, experimental[2–7] and theoretical[8–10] investigations of this interesting system have continued, encouraged no doubt by the unusually strong angular-radial coupling in the intermolecular potential energy surface (PES). A brief but graphic review of this provacative ''rod and ball'' system has been presented recently[11] by the Klemperer ''group.''

In principle, excited rovibrational states of floppy species are a rich source of information about the PES.[12] However, observation of their rotational spectra is made difficult by the low population of excited vibrational states in pulsed nozzles. Even so several vibrational studies have been reported for the Ar–HCN dimer. Fraser and Pine[4] found the C–H stretch (ν_1 of HCN) and a combination band later assigned[6] as $\nu_1+\Pi_1$, where Π_1 is a van der Waals bend. Clary *et al.*[8] have calculated for this dimer the excited van der Waals modes, using a theoretical PES. They predict three sets of states, Σ and Π bends, and ''$j=2$'' internal rotation of the HCN, at frequencies of 5, 7, and 11 cm^{-1}, respectively. An exhaustive study of the lowest excited bending states, Σ_1 and Π_1, has been made recently with a sophisticated electric resonance optothermal spectrometer.[6]

In the present case,[13] we have observed progressions of $K=0$ transitions for Ar(Kr)–HCN fitted by B and D_J values slightly smaller (6 MHz and 7 kHz, respectively) than those found earlier for their ground state. The small decrease between ground and excited states for B contrasts with the large *increases* in B values of 350 and 420 MHz for Σ_1 and Π_1 of Ar–HCN. The latter indicate a contraction of $\sim$0.5 Å in the Ar to c.m. (HCN) distance upon bending excitation of the dimer. The small decrease in B for the new species is consistent with excitation of one of the much stiffer HCN modes. Details are presented below along with the observa-

tion and analysis of the ^{14}N quadrupole interaction in the excited state.

EXPERIMENT

The rotational spectra of Ar(Kr)–HCN in the excited state were observed with a Balle–Flygare Fourier transform microwave spectrometer,[14] using a high temperature nozzle. The nozzle is of the same basic design as that used for the pyrolytic formation of dimethylsilaethylene,[15] but with a cylindrical brass shield to strengthen the assembly and reduce heat losses. With the nozzle in place, the gas mixture could be heated to 1300 K before expansion. Heating of the gas was necessary to populate adequately the vibrational levels of interest in the expanded jet.

The Ar was obtained from Liquid Air and the Kr from MG Industries. The ^{13}C and ^{15}N labeled HCN were synthesized from enriched KCN (Isotec) by standard methods. The excited state of Ar–HCN was formed by expanding $\sim$0.15% HCN in Ar with a backing pressure of 2 atm at about 1100 K. (For room temperature experiments with Ar carrier gas the backing pressure is normally $\sim$0.75 atm.) The Kr–HCN was formed in a similar way by using 5% Kr in Ar as the carrier.

RESULTS AND ANALYSIS

Search and assignment

The hyperfine structure (hfs) of the $J=0\rightarrow1$ transition for the excited Ar–HCN state was observed during an unsuccessful search for the Ar–HNC dimer with a heated nozzle. The ^{14}N origin of the hfs was immediately obvious and it was noted that the splittings were nearly the same as for ground state Ar–HCN. These lines disappeared as the temperature was lowered below $\sim$800 K. The higher J transitions were observed and it was found that the rotational constants B, D_J, and H_J are very nearly the same as for the Ar–HCN ground state.

The ν_1 and ν_5 states of the dimer have been reported.[4,6] Observation of the $J=0\rightarrow1$ transition for the new state rules out its being the degenerate ν_2 bending state. This leaves only the C–N stretch (ν_3) and the van der Waals stretch ν_4 as

TABLE I. Rotational and centrifugal distortion constants determined for the Ar(Kr)–HCN ground and $\nu_3=1$ vibrational states.

Isotopic species[a]	B (MHz)	D_J (kHz)	H_J (Hz)	ΔB[b] (MHz)
Ar–HCN[c]	1609.832(6)	172.3(6)	320(18)	7.357
	1602.475(3)	164.2(3)	309(5)	
Ar–H^{13}CN[c]	1583.714(8)	152.2(2)	244(26)	6.743
	1576.971	144.7		
Ar–HC^{15}N[c]	1556.996(6)	158.0(6)	311(14)	6.803
	1550.193	148.9		
^{84}Kr–HCN[d]	1181.5519(4)	47.9(2)	72(7)	5.103
	1176.4493(3)	41.7(1)	56(1)	
^{84}Kr–H^{13}CN	1156.9093	40.7	44	4.486
	1152.4235	35.9		
^{82}Kr–HC^{15}N[d]	1144.0161(4)	40.7(2)	56(8)	4.647
	1139.369	35.5		
^{84}Kr–HC^{15}N[d]	1137.1419(7)	39.9(1)	53(1)	4.606
	1132.536	34.9		
^{86}Kr–HC^{15}N[d]	1130.5851(4)	39.3(1)	53(1)	4.569
	1126.016	34.4		

[a]For each isotopic species the lower set of constants is for ν_3. The values of B and D_J for ν_3 of the ^{13}C and ^{15}N isotopomers were obtained by observing two transitions and fitting them exactly.
[b]$\Delta B = B$ (ground state)$-B(\nu_3)$.
[c]The ground state constants are from Ref. 2.
[d]The ground state constants are from Ref. 16.

TABLE II. Line centers and ^{14}N quadrupole hyperfine constants (MHz) in the ground and excited (ν_3) states of Ar(Kr)–HCN for the parent isotopic species.

$J \to J'$		Ground state		Excited state (ν_3)	
		Frequency	χ_a	Frequency	χ_a
			Ar–HCN[a]		
0	1	3 218.9853	−2.8443(6)	3 204.303	−2.824(3)
1	2	6 433.8853	−2.8565(9)	6 404.711	−2.835(5)
2	3	9 640.8722	−2.8741(12)	9 597.567	−2.873(8)
3	4	12 836.5972	−2.8987(31)	12 779.699	−2.907(5)
4	5	16 018.3628	−2.9241(55)	15 948.495	⋯
			Kr–HCN[b]		
0	1	2 362.9175	−3.2685(3)	2 352.7323	−3.235
1	2	4 724.7198	−3.2733(6)	4 704.4740	−3.223(5)
2	3	7 084.3436	−3.2796(25)	7 054.2790	−3.226(18)
3	4	9 440.8210	−3.2880(31)	9 401.2740	−3.297(24)
4	5	11 793.3158	−3.2981(32)	11 744.7180	−3.314(33)

[a]The ground state data are from Ref. 2.
[b]The ground state data are from Ref. 16 for ^{84}Kr.

possible candidates for the transitions found. The effect of temperature on the spectra, we believe, favors ν_3 over ν_4 and henceforth we so designate it.

The transitions of the ν_3 state were observed for the H^{13}CN and HC^{15}N isotopomers of Ar–HCN to compare the C–N distance in the ground and excited states. The corresponding transitions for the Kr–HCN isotopomers of the state were readily found for confirmation and comparison. Table I lists the rotational constants for the ν_3 state along with the ground state values for all of the Ar(Kr)–HCN isotopomers studied. Earlier work on the Kr–HCN ground state[16] did not include Kr–H^{13}CN, so it was included in this study. The decrease in B between the ground and excited states is about 7 MHz for Ar–HCN and 5 MHz for Kr–HCN. The D_J and H_J centrifugal distortion constants also exhibit a moderate decrease in going from the ground to excited state.

A search for the DCN and Ne–HCN analogs was not successful. In the case of Rg–DCN this may be due to faster predissociation because the C–N and D–C stretch modes couple more readily than the C–N and H–C. Even at 1300 K, the ν_1 state of Ar–HCN could not be observed in our spectrometer. Fraser and Pine[4] reported a lifetime of <1 ms for the ν_1 state. Our observation of the ν_3 state suggests that its lifetime should be >2 ms. Such mode specific dissociation rates have been seen in several dimers[17,18] including (HF)$_2$ and HCN–HF.

$\chi(^{14}$N$)$ and its dependence on J and ν_3 excitation

The ^{14}N hfs for the dimers is little affected by excitation of ν_3. The results of fitting the hfs for individual transitions to the unperturbed line center and the projection of $\chi(^{14}$N$)$ on the a axis are found in Table II. Values of $\chi_a(^{14}$N$)$ are given for the ground[2,16] and ν_3 excited states of the two parent

species. At $J>2$ some of the weaker components of the hfs could not be observed for the excited state. This can be seen in the larger rms deviations of the fits.

It is known that in the ground state χ_a increases somewhat with J for both[2,16] Ar–HCN and Kr–HCN as well as for Ne–HCN.[19] This is evident in Table II, which also shows that in the ν_3 state the values of χ_a at $J=0$ are slightly smaller, 20 (38) kHz, than in the ground state. However, the J dependence is slightly greater for ν_3 so that by $J=4$ the χ_a's are about the same in the ground and ν_3 states. It is well established[11,19] that the J dependence is evidence of coupling by the PES between radial and angular centrifugal distortion of the dimer. These results show that the coupling is not greatly affected by the vibrational excitation.

Inertial analysis and structure

We follow earlier work[2] on the ground state of Ar–HCN in estimating R and θ, where R is the center of mass (c.m.) to c.m. distance between Ar(Kr) and HCN and θ is the on average angle between the HCN axis and the a axis of the dimer. The angle θ is estimated from $\chi_a(^{14}$N$)$ with the relation

$$\chi_a = (\chi_0/2)\langle 3\cos^2\theta - 1\rangle. \tag{1}$$

Here χ_0 is the quadrupole coupling constant of free HCN in the ν_3 state, determined by DeLeon and Muenter[20] to be −4.6081(2) MHz. With this value in Eq. (1), the experimental χ_a for the parent Ar–HCN (ν_3, $J=1$) gives an angle of 30.53° compared to 30.91° for the ground state. For the parent Kr–HCN these values are 26.47° and 26.84°. Clearly, the C–N excitation leads to a modest decrease in the bending amplitude, which implies a slight increase in R via the PES.[2]

With values for θ in hand, we can estimate R with

$$I_b = \mu_c R^2 + \tfrac{1}{2}\langle 1 + \cos^2\theta\rangle I_{HCN}. \tag{2}$$

Here, I_{HCN} is the moment of inertial for HCN(ν_3). For Ar–HCN(ν_3) the R is determined to be 4.353 Å compared to 4.344 for the ground state while for ^{84}Kr–HCN (ν_3) the cor-

responding values are 4.530 and 4.520 Å. In both instances the c.m. to c.m. distance increases by ~0.01 Å due to the excitation.

Substitution analysis

By using ^{13}C and ^{15}N substitution the positions along the a axis of C and N from the c.m. of the dimer can be determined. This then leads to the projected C–N distance r_s(CN) which is expected to increase upon ν_3 excitation. Such an analysis was made of the dimers, using the published rotational constants for the ground state[2,16] and those reported here for the ν_3 state. The analysis was based on the usual relation

$$\Delta I_b = \mu_s a_i^2, \tag{3}$$

where ΔI_b is the change in I_b on substitution and μ_s is the reduced mass for the substitution $m\Delta m/(m+\Delta m)$, and a_i is the distance along the a axis of the substituted atom from the center of mass.

The resulting values of r_s(CN) are 1.005 (1.085) Å for the ground state of Ar(Kr)–HCN and 1.018 (1.105) Å for the excited state. They correspond to increases in r_s(CN) upon excitation, Δr_s(CN), of 0.013 (0.0020) Å. By way of comparison it would be nice to have Δr_s(CN) for the free HCN monomer, Unfortunately the rotational constants for the (0,0,1) state of the ^{13}C and ^{15}N isotopomers are not available to the best of our knowledge. However, Preusser and Maki have recently reported[21] the necessary data for DCN isotopomers. Analysis of it gives a Δr_s(CN) of only 0.0022 Å in DCN. It is apparent that most of the large Δr_s(CN) found for the floppy dimer is not an increase in bond length but results from large isotopic changes in zero point motions.

There is another aspect of these results which is noteworthy. It is quite similar for the ground and ν_3 states, so we present the analysis for the ground state where the data are more reliable. The C–N distance in the free HCN monomer r_s^m(CN) is projected by $\langle\cos\theta\rangle$ into the smaller distance r_s^d(CN) along the a axis of the dimer, that is,[22]

$$r_s^d(\text{CN}) \simeq r_s^m(\text{CN})\langle\cos\theta\rangle. \tag{4}$$

If we use the θ's from χ_a via Eq. (1) and the 1.1551 Å value reported[23] for r_s^m(CN), Eq. (4) predicts r_s^d(CN) to be 0.991 (1.031) Å for Ar(Kr)–HCN. These are substantially smaller than the experimental results, 1.005 (1.085) Å, the difference being 0.014 (0.054) Å.

Two factors probably contribute to this differential discrepancy. Equation (1) assumes that dimer formation does not affect χ_0 of the monomer and Eq. (4) assumes that the θ in it is the same as that in Eq. (1). However, both are approximations depending on zero point averaging over the PES. The Ar(Kr)–HCN interaction energies, 85 and 108 cm^{-1}, and the shapes of their PES minima differ appreciably[19] and seem the most likely cause of the discrepancies.

Lifetime of the excited state

The signal strength observed for the excited state is lower than what would be expected if the vibrational tem-

perature of the HCN were 1100 K. This could be due to incomplete vibrational cooling during the jet expansion or the dissociation of the complex during its transit from the nozzle to the microwave field. In order to determine which is the case, the transit time can be increased by increasing the distance between the nozzle and the microwave field.

We performed such an experiment by measuring the ratio of the signal intensities for the same transition of the ground and excited states at two nozzle positions. An increase of about 0.5 ms in the transit time produced no measurable decrease in the excited state signal relative to the ground state. It appears therefore that the lifetime of the excited state is at least several milliseconds.

CONCLUSIONS

By incorporating a heated nozzle in the Balle–Flygare spectrometer, an excited state of the Ar(Kr)–HCN dimer has been observed. Several of its properties have been determined and compared with those of the ground state. The excitation produces appreciable structural changes which, however, are modest compared with excitation of van der Waals modes. This leads us to assign the excitation of the dimers to the C–N stretch (ν_3) of HCN.

Inertial analysis of the dimers along with the ^{14}N quadrupole coupling reveals that the Rg to HCN c.m. distance increases by 0.009 Å in ν_3 compared to the ground state. Also, a substitution analysis shows that r_s(CN) increases in the excited state by 0.013 Å (0.020 Å) for Ar(Kr)–HCN. A comparative analysis of inertial and quadrupole interaction effects discloses differences attributed to qualitative features of the potential energy surfaces for Ar–HCN and Kr–HCN. The experimental techniques employed should be generally applicable for observing excited vibrational states, provided their lifetime is favorable. Also, it should be feasible to obtain spectra for low volatility molecules and their complexes.

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