

Molecular beam infrared spectroscopy of the HCCCN–HCCH and HCN–HCCCCH van der Waals complexes

X. Yang,^{a)} R. Z. Pearson, K. K. Lehmann, and G. Scoles
Department of Chemistry, Princeton University, Princeton, New Jersey 08544

(Received 15 May 1995; accepted 19 September 1996)

High resolution IR spectra of the linear HCCCN–HCCH and HCN–HCCCCH hydrogen bonded complexes have been obtained using optothermal detection molecular beam techniques. Two vibrational bands have been observed for each complex, which correspond to the terminal “free” C–H stretch vibrations (ν_2) of the cyano units and the hydrogen bonded vibrations (ν_3) of the acetylenic CH stretches. For both complexes, accurate molecular constants have been obtained. Furthermore, predissociation lifetimes for the $\nu_3=1$ states of the both complexes have been determined. The results are compared with those of the linear HCN–HCCH complex obtained by Block *et al.* [Chem. Phys. **139**, 15 (1989)]. © 1996 American Institute of Physics. [S0021-9606(96)01448-1]

I. INTRODUCTION

The study of weakly bound complexes provides an important window to the world of intermolecular forces, and high resolution IR spectroscopy has certainly been one of the most fruitful techniques in this area. During the last decade or so, a large body of experimental data has been obtained using IR spectroscopy,^{1–3} providing insight into intermolecular forces and the predissociation dynamics of these complexes. Two general aspects of the predissociation process are firmly established. The first is that predissociation occurs preferentially to those final states which involve transferring the least energy into the translational motion of the complex's fragments. This stems from the need to maximize overlap between the wave function of the molecule bound in the complex with the continuum wave functions in the dissociative products. The second is the correlation proposed by Miller² between the predissociation lifetime and the square of the vibrational frequency shift (see LeRoy⁴ for a theoretical justification). Even though these criteria generally hold, not every case follows these rules since every species is unique in its own way. Indeed, “resonant” predissociation pathways have been demonstrated to be an important factor in the predissociation process, and they are the rule, rather than the exception in determining predissociation rates, especially for small complexes.³ As the size of the molecules increases, more and more vibrational and rotational channels become open and it is possible that a more statistical treatment will emerge for the rationalization of predissociation lifetimes and the prediction of fragment energy distribution. This would be welcome since it is precisely for the larger complexes that a detailed state-by-state theoretical treatment becomes impractical if not impossible with present methods. One way to shed new light on this subject is by changing the size of one or both monomers with minimal change in the

force that binds them together and then observe the resulting change in the structure and the predissociation dynamics of the modified complex.

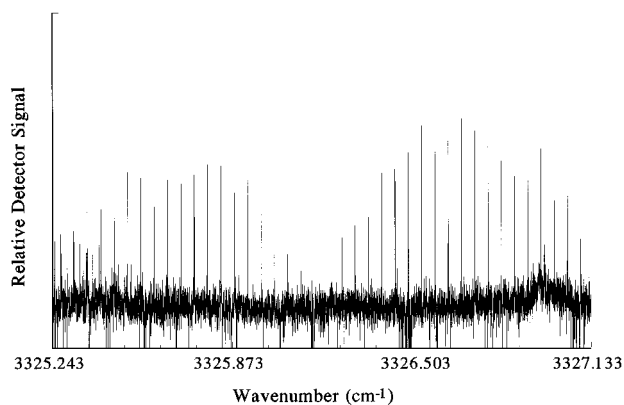
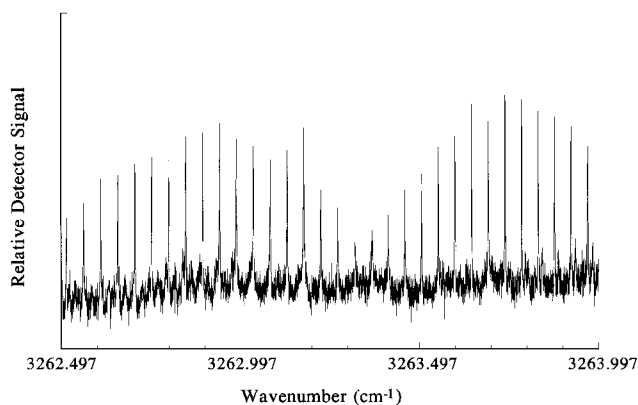
In the present work, we exploit the above strategy as we replace twice one of the two moieties in the HCN–HCCH complex with a chemically similar molecule, without changing substantially the strength or angular dependence of the intermolecular hydrogen bond. The HCN–HCCH complex was studied by Block *et al.*⁵ Two structural isomers were observed, both of which are hydrogen bonded. One is linear with a CH of HCCH bonded to the N of HCN while the other is T-shaped with the CH of HCN bonded to the π electrons of HCCH. In order to study complexes similar to HCN–HCCH, we replaced first the HCN moiety by cyanoacetylene, HC₃N, to form the HC₃N–HCCH complex; then, the HCCH moiety was replaced by diacetylene, C₄H₂, to form the HCN–C₄H₂ complex. The IR spectra of HC₃N and C₄H₂ have been previously studied in detail^{6,7} and their structures and vibrational frequencies are known with high accuracy, allowing us to determine precise spectral shifts produced by complexation. The spectra obtained for each of the new complexes indicate a linear configuration which we compare to the linear isomer of HCN–HCCH.

This paper is organized as follows: First we give a brief description of the experimental apparatus and technique. Second, the spectra obtained for both the HC₃N–HCCH and HCN–C₄H₂ complexes will be presented and analyzed. These results will then be compared to those obtained by Miller *et al.* for the HCN–HCCH complex. Finally, the main conclusions will be summarized.

II. EXPERIMENT

Both HC₃N and C₄H₂ were prepared in our laboratory. The HC₃N sample was synthesized by heating HC₃ONH₂ and P₂O₅ together with clean white sand as a heat conductor.⁸ No obvious impurities were found in the final product when analyzed by means of FTIR spectroscopy. C₄H₂ was prepared by the dehydrochlorination of 1,4-dichloro-2-butyne with aqueous potassium hydroxide.⁸ The

^{a)}Present address: Institute of Atomic and Molecular Sciences Academia Sinica, P.O. Box 23-166, Taipei, Taiwan 10764.

FIG. 1. The ν_2 band of the HC_3N – HCCH complex.FIG. 2. The ν_3 band of the HC_3N – HCCH complex.

diacetylene evolved was then dried over calcium chloride and collected in a liquid nitrogen trap. Again no substantial impurity was found in the sample.

High resolution IR spectra were obtained for the title complexes by the optothermal technique as described in Ref. 10. The apparatus has been described in detail previously.¹¹ The HC_3N – C_2H_2 complex was produced in a supersonic beam by expanding a mixture with volume concentrations of 0.5% HC_3N and 2% C_2H_2 by volume in He through a 50 μm pinhole at a stagnation pressure of about 4 atm (400 kPa). The HCN – C_4H_2 complex was prepared in a similar way by expanding a mixture of 0.5% HCN and 1% C_4H_2 in He. After the expansion, the molecular beam is collimated by a skimmer and detected by a bolometer (IR Laboratories) operating at 1.5 K. The spectral lines of the dimers were observed as a decrease in the energy hitting the bolometer, indicating that the complexes dissociate upon vibrational excitation. Radiation was generated by a computer controlled color center laser. The output power of the laser in the 3 μm region was normally about 20 mW. The IR laser radiation crossed the molecular beam multiple times through a multipass cell made of two parallel gold-coated mirrors. The spectral resolution of the apparatus was about 10 MHz full-width at half-maximum. This arose from the Doppler shifts caused by changes in the laser-beam crossing angle due to slight misalignment of the multipass cell mirrors. The absolute laser frequency was calibrated by means of acetylene absorption lines in a gas cell at room temperature. The calibration uncertainties are of the order of 0.001 cm^{-1} (which is mainly caused by the uncertainties in determining the center of the absorption lines). The laser frequency was monitored by two scanning étalons (one with a 7.5 GHz and the other with a 150 MHz free spectral range). The latter was used to provide relative frequency spacing. The laser was mechanically chopped at about 280 Hz. Typical scan speeds were in the range of 1–2 cm^{-1} per h.

III. RESULTS AND ANALYSIS

A. HC_3N – HCCH

Two vibrational bands were observed in the molecular beam produced by expanding the mixture of HC_3N and

HCCH in He. One is centered at 3326.142 cm^{-1} (Fig. 1), and the other at 3263.313 cm^{-1} (Fig. 2). Fits of the rovibrational transitions to Eq. (1) gave almost identical ground state rotational constants (B''), implying that they derive from the same isomer. Neither of these spectra contains a Q branch nor resolved K structure, indicating Σ – Σ transitions of a linear molecule. An extra small peak was observed in the gap between $P(1)$ and $R(0)$ of the second band. This peak is assigned to hot band. No perturbations are evident in either band. The band observed at 3326.142 cm^{-1} is only slightly (-1.23 cm^{-1}) shifted from the C–H fundamental of the HC_3N monomer and has instrumentally limited line shapes. Therefore, it is assigned to the “free” C–H stretching of the HC_3N unit in a linear HC_3N – HCCH complex. The band at 3263.313 cm^{-1} is much more red (towards lower wave number) shifted and displays lifetime broadened lines. It is assigned to the hydrogen bonded C–H stretch vibration of the HCCH unit. The fact that the frequency shift and the predissociation lifetime of this band are similar to the corresponding band of the linear HCN – HCCH complex supports this assignment. No T-shaped HC_3N – HCCH complex has been observed. However, owing to the much larger partition function expected for such an asymmetric top, our sensitivity for detection of this conformer would be much lower. According to the normal mode labeling convention, we can assign the first band (centered at 3326.142 cm^{-1}) to the ν_2 fundamental band, the second band (centered at 3263.313 cm^{-1}) to the ν_3

TABLE I. Molecular constants obtained for the HC_3N – HCCH complex.^a

	Free C–H stretch band ν_2	H-bond C–H stretch band ν_3
ν_0	3 326.142 39(4)	3 263.312 88(13)
B''	0.023 408 4(27)	0.023 389 0(92)
$\Delta B = B' - B''$	$-5.53(22) \times 10^{-6}$	$-2.53(13) \times 10^{-6}$
$D'' = D'$	$5.02(50) \times 10^{-8}$	$-1.16(2.38) \times 10^{-8}$
stand. dev.	1.7×10^{-4}	5.0×10^{-4}
Fit to ground state combination differences		
B''	0.023 408 8(27)	0.023 387 5(135)
D''	$5.16(57) \times 10^{-8}$	$-2.4(4.6) \times 10^{-8}$

^aAll units are in cm^{-1} .

TABLE II. Observed wave numbers and fitting residuals for the ν_2 band transitions of the HC₃N–HCCH complex (all units in cm⁻¹).

Assignment	Obs	Obs–Calc×10 ⁴
P(19)	3 325.252 85	4.90
P(18)	3 325.298 80	-3.70
P(17)	3 325.345 75	-2.40
P(16)	3 325.392 62	-2.40
P(15)	3 325.439 64	-0.17
P(14)	3 325.486 47	-0.33
P(13)	3 325.533 46	1.07
P(12)	3 325.580 32	1.11
P(11)	3 325.627 24	1.73
P(10)	3 325.673 95	0.22
P(9)	3 325.720 84	0.50
P(8)	3 325.767 77	1.18
P(7)	3 325.814 61	0.97
P(6)	3 325.861 47	1.00
P(5)	3 325.908 41	1.86
P(4)	3 325.955 01	-0.63
P(3)	3 326.001 61	-3.06
P(2)	3 326.048 55	-2.01
P(1)	3 326.095 18	-3.97
R(1)	3 326.236 00	0.07
R(2)	3 326.282 85	0.77
R(3)	3 326.329 63	0.92
R(4)	3 326.376 38	0.93
R(5)	3 326.423 10	0.81
R(6)	3 326.469 77	0.37
R(7)	3 326.516 42	-0.07
R(8)	3 326.563 18	0.79
R(9)	3 326.609 75	-0.02
R(10)	3 326.656 43	0.49
R(11)	3 326.703 02	0.35
R(12)	3 326.749 52	-0.43
R(13)	3 326.796 05	-0.66
R(14)	3 326.842 62	-0.19
R(15)	3 326.889 17	0.36
R(16)	3 326.935 49	-1.09
R(17)	3 326.982 00	-0.31
R(18)	3 327.028 43	-0.01
R(19)	3 327.074 80	0.03
R(20)	3 327.121 19	0.62

band. The ν_1 vibration should be the free C–H stretch of the HCCH unit, which was not observed in this experiment.

The rotational assignment of both bands was straightforward. Transition wave numbers were fit to a standard linear molecular model,

$$\nu_m = \nu_0 + (2B'' + \Delta B)m + (\Delta B'' - \Delta D)m^2 - 2(2D'' + \Delta D)m^3 - \Delta Dm^4, \quad (1)$$

where $m = -J$ for the *P* branch, and $m = J + 1$ for the *R* branch. The molecular constants obtained for these two bands are listed in Table I. We constrained the upper and lower state distortion constants to be equal ($\Delta D = 0$) since this difference was not statistically significant when they were allowed to vary independently. The constants B'' and D'' were found to be highly correlated with a correlation coefficient of ~ 0.9 , while other correlations were small (< 0.6). All errors listed in the table are 1σ statistical errors predicted from the fits, assuming uncorrelated random errors.

TABLE III. Observed wave numbers and fitting residuals for the ν_3 band transitions of the HC₃N–HCCH complex (all units in cm⁻¹).

Assignment	Obs	Obs–Calc×10 ⁴
P(21)	3 262.319 16	-3.15
P(20)	3 262.367 32	-0.05
P(19)	3 262.415 35	2.31
P(18)	3 262.462 90	0.43
P(17)	3 262.510 98	4.41
P(16)	3 262.558 30	1.34
P(15)	3 262.605 81	7.29
P(14)	3 262.652 95	-3.04
P(13)	3 262.700 44	-2.76
P(12)	3 262.747 69	-4.34
P(11)	3 262.795 12	-3.58
P(10)	3 262.842 61	-1.68
P(9)	3 262.889 77	-2.55
P(8)	3 262.939 67	24.5
P(7)	3 262.983 92	-4.39
P(6)	3 263.031 30	-1.47
P(5)	3 263.078 08	-4.03
P(4)	3 263.125 35	-1.16
P(3)	3 263.172 19	-2.08
P(2)	3 263.219 21	-0.68
P(1)	3 263.266 09	-0.17
R(0)	3 263.359 89	2.77
R(1)	3 263.406 09	-2.00
R(2)	3 263.452 83	-8.66
R(3)	3 263.499 37	-1.24
R(4)	3 263.546 03	0.09
R(5)	3 263.592 34	-1.59
R(6)	3 263.639 12	1.91
R(7)	3 263.685 54	2.31
R(8)	3 263.731 73	0.89
R(9)	3 263.778 00	0.75
R(10)	3 263.824 18	0.19
R(11)	3 263.870 31	-0.39
R(12)	3 263.916 49	0.00
R(13)	3 263.962 44	-1.44

The estimated uncertainty for the band centers is of the order of 0.001 cm^{-1} , due to the limitations of our calibration procedure. All observed wave numbers and the fitting residuals for both the ν_2 band and the ν_3 band are listed in Tables II and III, respectively. In Fig. 2 one can see that the *P*(3) transition of the ν_3 band is substantially higher than its neighboring transitions. This is likely due to an overlapping *Q* branch of a hot band.

The centrifugal distortion constants determined for the two bands are in poor agreement, though the error for the hydrogen bonded fundamental has a large error bar. Fits to the ground state combination difference also yielded inconsistent ground state distortion constants. We believe these constants arise from systematic errors in the calibration of our spectra and thus do not have any physical significance. Based upon the hydrogen bonding force constant of 0.046 mdyne/\AA (4.6 N/m) reported by Block *et al.*⁵ for HCN–HCCH, we can predict that the distortion constant of the ground state of HC₃N–HCCH should be $2 \times 10^{-8} \text{ cm}^{-1}$.

The observed transitions of the hydrogen bonded ν_3 band show evidence of line broadening which is believed due to predissociation of the complex. From a Voigt profile fit to

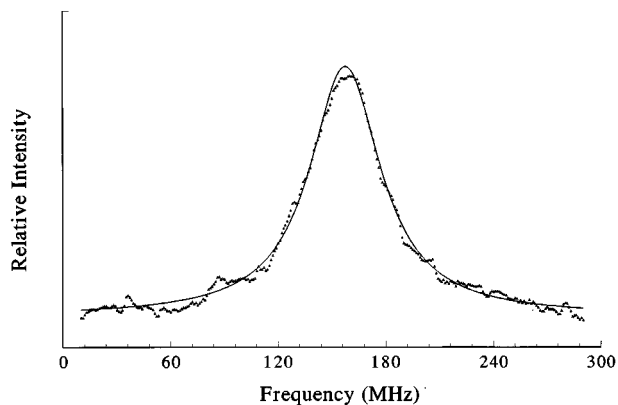


FIG. 3. The observed and the fitted (Voigt) line shapes of the $R(9)$ transition of the ν_3 band of $\text{HC}_3\text{N-HCCH}$. A Gaussian component of 10 MHz was used in the Voigt profile fitting. The predissociation linewidth was determined to be 49.6(5) MHz.

the $R(12)$ line shape (Fig. 3), using a Gaussian component of 10 MHz (see below), the Lorentzian full width is determined to be 49.6(5) MHz, corresponding to a predissociation lifetime of 3.21(3) ns for the $\nu_3=1$ state. No rotational dependence of the predissociation lifetime was found. For the free C–H stretch band ν_2 , the linewidths are instrument-limited to about 10 MHz, indicating the Lorentzian linewidth of a few MHz or less, as pointed out by placing the lower limit for the predissociation lifetime to about 100 ns. Since the phase of the observed signal for this band is opposite to that of the monomer HC_3N transitions, one can conclude that the upper state of the ν_2 band of the complex predissociates before reaching the detector, about 100 μs . Therefore the predissociation lifetime of the $\nu_2=1$ state is in between 100 ns and 100 μs .

B. HCN– C_4H_2

Two vibrational bands have been observed in the expansion of the mixture of HCN and C_4H_2 in He. The first band is centered at 3309.76 cm^{-1} (Fig. 4). The extra lines observed in the spectrum derive from the $(\text{HCN})_2 \nu_1$ band,¹⁰ and were used in the calibration of the spectrum. The second band is

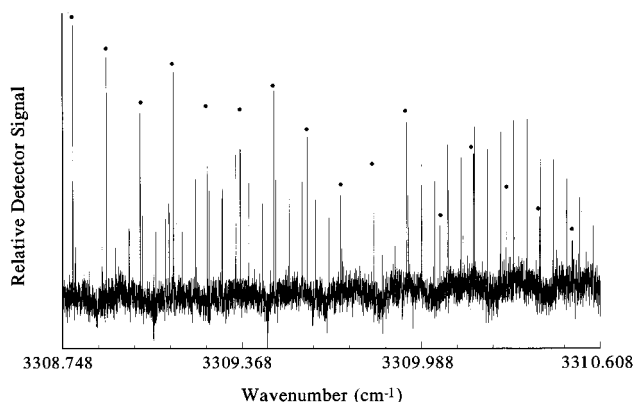


FIG. 4. The ν_2 band of the HCN– C_4H_2 complex. Peaks marked with \cdot are $(\text{HCN})_2 \nu_1$ band transitions which were used to calibrate this spectrum.

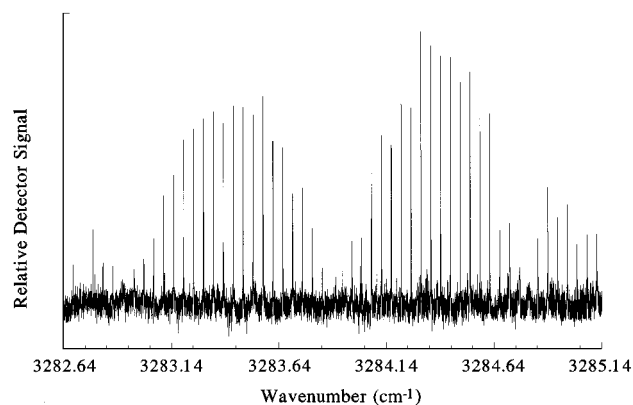


FIG. 5. The ν_3 band of the HCN– C_4H_2 complex, exhibits strong local resonance around the $J'=20$ level.

centered at 3283.888 cm^{-1} (Fig. 5). The B'' constants obtained from fits to the two bands are the same within fitting uncertainty, indicating that these two bands belong to the same complex. No Q branch nor K structure is observed in either band, implying $\Sigma-\Sigma$ transitions of a linear molecule. Comparing these results with those of the linear complexes of HCN–HCCH and $\text{HC}_3\text{N-HCCH}$, the first band is assigned to the “free” C–H stretch (ν_2) of the HCN unit, the second to the hydrogen bonded C–H stretch (ν_3) of the C_4H_2 unit of the HCN– complex. The ν_1 vibration is the “free” C–H stretch of the C_4H_2 unit, which is not observed in this C_4H_2 experiment. These assignments are also consistent with the predissociation linewidths observed for both bands. Like the previous case, the distortion constants returned from the fits are believed to be a reflection of errors in the frequency calibration of the spectrum. Based upon the HCN–HCCH force constant, we predict a value of $1.9 \times 10^{-8} \text{ cm}^{-1}$ for D'' .

Bands were fit by the formula given in Eq. (1). No perturbation has been observed in the ν_2 band. The molecular constants obtained are listed in Table IV. The observed wavenumbers and the fitting residuals are listed in Table V. For the ν_3 band, a local resonance near the $J'=20$ level has been observed. Both $P(21)$ and $R(19)$ are nearly missing from the spectrum (see Fig. 5), indicating the “dark” state has a much faster predissociation rate than the bright state. The intensities of the lines near the resonance are significantly perturbed. When fit to Eq. (1), the residual (fit 1 in Table VI)

TABLE IV. Molecular constants obtained for the HCN– C_4H_2 complex.^a

	Free C–H stretch band ν_2	H-bonded C–H stretch band ν_3
ν_0	3 309.759 755(17)	3 283.888 19(5)
B''	0.022 949 3(11)	0.022 956 1(24)
$\Delta B = B' - B''$	$-1.082(10) \times 10^{-5}$	$-1.23(8) \times 10^{-5}$
$D' = D''$	$-1.20(21) \times 10^{-8}$	
stand. dev.	0.65×10^{-4}	1.7×10^{-4}
Fit to ground state combination differences		
B''	0.022 948 4(12)	0.022 957 9(25)
D''	$-1.45(26) \times 10^{-8}$	$-0.64(48) \times 10^{-8}$

^aAll units are in cm^{-1} .

TABLE V. Observed wave numbers and fitting residuals for the ν_2 band transitions of the HCN–C₄H₂ complex (all units in cm⁻¹).

Assignment	Obs	Obs–Calc×10 ⁴
P(21)	3 308.790 96	–0.70
P(20)	3 308.837 31	–0.28
P(19)	3 308.883 68	–0.32
P(18)	3 308.929 87	1.16
P(17)	3 308.976 26	0.36
P(16)	3 309.022 63	–0.49
P(15)	3 309.068 75	0.89
P(14)	3 309.114 95	1.22
P(13)	3 309.161 19	0.88
P(12)	3 309.207 49	–0.31
P(11)	3 309.253 66	–0.45
P(10)	3 309.299 82	–0.74
P(9)	3 309.345 96	–1.07
P(8)	3 309.392 04	–1.05
P(7)	3 309.438 09	–0.96
P(6)	3 309.484 03	–1.56
P(5)	3 309.530 01	0.30
P(4)	3 309.576 04	–0.12
P(3)	3 309.622 01	–0.17
P(2)	3 309.667 89	0.46
P(1)	3 309.713 77	0.87
R(1)	3 309.851 49	–0.02
R(2)	3 309.897 31	0.13
R(3)	3 309.943 07	0.67
R(4)	3 309.988 84	0.90
R(5)	3 310.034 70	0.03
R(6)	3 310.080 44	0.16
R(7)	3 310.126 24	–0.50
R(8)	3 310.171 91	–0.06
R(9)	3 310.217 57	0.30
R(10)	3 310.263 27	0.06
R(11)	3 310.308 95	–0.16
R(12)	3 310.354 63	–0.57
R(13)	3 310.400 29	–0.95
R(14)	3 310.445 85	–0.50
R(15)	3 310.491 41	–0.23
R(16)	3 310.536 91	0.47
R(17)	3 310.582 43	0.80

reaches a maximum near the perturbation as shown in Fig. 6. The molecular constants listed in Table IV for this band are obtained from a fit (fit 2 in Table VI) that excluded transitions near the perturbation. Since no splittings near the perturbation have been observed, molecular constants for the perturbing level cannot be determined. However, a two level model has been used to simulate the perturbed spectrum in order to get some information on the perturbation. The molecular constants of the $\nu_3=1$ state (Table IV) and the estimated constants for the dark states were used in the simulation. The simple two level model used here can be described by a 2×2 matrix,

$$\begin{pmatrix} E_1 & W \\ W & E_2 \end{pmatrix},$$

where E_i is equal to $\nu_0+B_iJ(J+1)$, and W is the interaction matrix element. Linewidths for spectral transitions were calculated by a weighted average of the widths for the bright and dark states. A linewidth of 27.7 MHz was used for the

TABLE VI. Observed wave numbers and fitting residuals for the ν_3 band transitions of the HCN–C₄H₂ complex (all units in cm⁻¹).

Assignment	Obs	Obs–Calc×10 ⁴ (fit 1)	Obs–Calc×10 ⁴ (fit 2)
P(26)	3 282.683 25	–8.18	
P(25)	3 282.729 93	–8.76	
P(24)	3 282.776 47	–10.4	
P(23)	3 282.822 70	–14.8	
P(22)	3 282.868 71	–21.1	
P(20)	3 282.967 37	33.6	
P(19)	3 283.012 74	21.9	
P(18)	3 283.058 58	15.2	
P(17)	3 283.104 52	9.77	
P(16)	3 283.150 79	8.01	
P(15)	3 283.196 88	4.77	
P(14)	3 283.243 15	3.65	
P(13)	3 283.289 38	2.46	
P(12)	3 283.335 60	1.49	–0.29
P(11)	3 283.381 77	0.35	–0.41
P(10)	3 283.427 95	–0.37	–0.18
P(9)	3 283.474 17	–0.37	0.67
P(8)	3 283.520 24	–1.5	0.30
P(7)	3 283.566 29	–2.59	0.03
P(6)	3 283.612 42	–2.52	0.07
P(5)	3 283.658 11	–6.52	–2.78
P(4)	3 283.704 47	–3.50	0.72
P(3)	3 283.750 46	–3.86	0.76
P(2)	3 283.796 20	–6.39	–1.45
P(1)	3 283.842 54	–2.59	2.58
R(0)	3 283.934 43	–1.94	3.48
R(1)	3 283.979 88	–6.07	–0.65
R(2)	3 284.025 96	–3.59	–1.76
R(3)	3 284.071 23	–8.87	–3.68
R(4)	3 284.117 26	–6.24	–1.28
R(5)	3 284.163 02	–5.98	–1.33
R(6)	3 284.208 84	–4.80	–0.54
R(7)	3 284.254 56	–4.29	–0.50
R(8)	3 284.300 30	–3.26	–0.02
R(9)	3 284.346 05	–1.80	0.81
R(10)	3 284.391 75	–0.53	0.14
R(11)	3 284.437 55	2.08	
R(12)	3 284.483 19	3.40	
R(13)	3 284.528 82	4.95	
R(14)	3 284.574 44	6.72	
R(15)	3 284.620 19	10.1	
R(16)	3 284.665 86	13.0	
R(17)	3 284.711 99	20.9	
R(18)	3 284.758 14	29.3	
R(20)	3 284.843 36	–23.8	
R(21)	3 284.889 69	–12.7	
R(22)	3 284.935 11	–10.3	
R(23)	3 284.980 71	–5.85	
R(24)	3 285.026 12	–2.94	
R(25)	3 285.071 31	–1.90	
R(26)	3 285.116 72	1.66	
R(27)	3 285.162 10	5.24	

bright state transitions (obtained from the linewidth measurements far from the crossing), while the linewidth of the dark state transition was assumed to be 500 MHz (estimated roughly from the intensity changes due to perturbation in the spectrum), which corresponds to a predissociation lifetime of 315 ps. Figure 7 shows the comparison of the simulated R branch and the observed R branch of the ν_3 band. The rota-

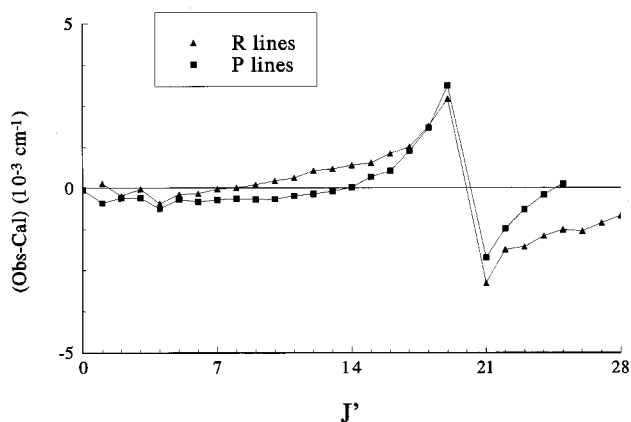


FIG. 6. The plot of fitting residual vs J' . The perturbation site ($J'=20$) shows the largest deviation from the linear molecule model.

tional temperature of the HCN–C₄H₂ complex in the molecular beam was assumed to be 6 K in the simulation. The molecular constants used for the dark state in the simulation are

$$\nu_0 = 3283.813 \text{ cm}^{-1}, \quad (2)$$

$$B = 0.023133 \text{ cm}^{-1}, \quad (3)$$

$$W = 0.0049 \text{ cm}^{-1}, \quad (4)$$

where ν_0 is the band center, B the rotational constants, W the interaction matrix element. These numbers were chosen so

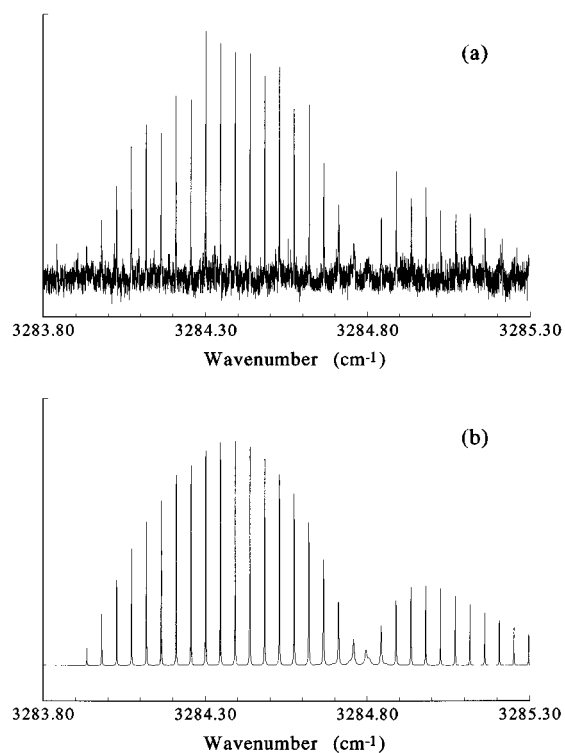


FIG. 7. (a) The observed R branch of the ν_3 band of the HCN–C₄H₂ complex. (b) The simulated R branch of the ν_3 band of the HCN–C₄H₂ complex. The parameters used in the simulation can be found in the text.

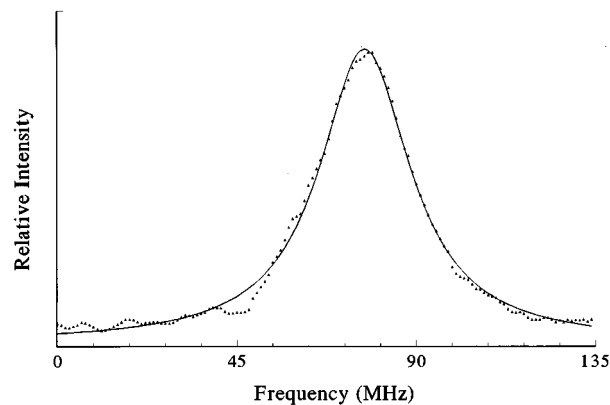


FIG. 8. The observed and the fitted (Voigt) line shapes of the $R(12)$ transition of the ν_3 band of HCN–C₄H₂. A Gaussian component of 10 MHz was used in the Voigt profile fitting. The predissociation linewidth was determined to be 27.7(4) MHz.

that the calculated perturbation site and the transition intensities are close to the experimental observation. Since the perturbation is very local, the intensity analysis of the perturbed lines and the simulation is insensitive to the type of the interaction (Coriolis interaction or Fermi resonance). The assignment of the “dark” state is not practical since most of the vibrational frequencies of the complex are not known. The rotational constant of the “dark” state, however, is larger than that of the $\nu_3=1$ state, suggesting a state with bending excitation. We wish to stress that the above dark state constants are not unique, due to the lack of observed transitions to levels with primarily dark state character.

Linewidths of the observed transitions were also obtained, yielding information on predissociation of the observed vibrational levels. Similar to the complex of HC₃N–HCCH, the ν_2 band for the HCN–C₄H₂ complex is instrument limited, implying its predissociation linewidth is less than about 1 MHz, corresponding to a predissociation lifetime longer than 100 ns. The phase of the signal implies that the excited complex dissociates before reaching the bolometer detector, i.e., 100 μ s. The linewidths of the ν_3 band of the HCN–C₄H₂ complex, however, are not instrument-limited. The predissociation linewidths can be determined by fitting the observed line shapes to a Voigt profile. By fitting the $R(12)$ transition to a Voigt profile with a Gaussian component of 10 MHz (typical instrument-limited width), the predissociation linewidth for this transition is determined to be 27.7(4) MHz (see Fig. 8), corresponding to a predissociation lifetime of 5.75(8) ns.

C. Comparison with HCN–C₂H₂

The rotational constants and vibrational frequency shifts yield information about the strength of intermolecular interactions. First we will consider the rotational constants, and then we will consider the vibrational data. From the observed rotational constants of the complexes and the rotational constants of the monomers, one can deduce the center of mass distance, R_{com} , between the units if one assumes a rigid

structure. This gives $R_{\text{com}}=5.876 \text{ \AA}$ for the $\text{HC}_3\text{N-HCCH}$ complex and $R_{\text{com}}=5.941 \text{ \AA}$ for the $\text{HCN-C}_4\text{H}_2$ complex. We do not report an error estimate since this will be dominated by the assumption of a rigid structure. Using standard bond lengths,¹³ we can estimate the N–H hydrogen bond length from these R_{com} values as 2.33 and 2.34 \AA for $\text{HC}_3\text{N-HCCH}$ and $\text{HCN-C}_4\text{H}_2$, respectively. This can be compared to the value 2.345 \AA calculated by Block *et al.* for the linear HCN-HCCH complex.⁵ The agreement is better than expected, given the approximations involved, but shows that the hydrogen bonds are of very similar character for all three systems. From the ground state centrifugal distortion constants, one can also in principle estimate the force constant for the hydrogen bond, but as discussed earlier these are too small in the present case to be determined given the frequency calibration of our spectrometer.

It is interesting to note that ΔB is negative for the excitation of the hydrogen bonded CH, opposite to the positive value typically observed for hydrogen bonding stretches such as in the case of the HCN dimer,¹² but the same sign as for linear HCN-HCCH .⁵ The positive value for ΔB is usually interpreted as due to a shortening of the hydrogen bonding distance, which is increased in strength by the red shift. A physical model for the decrease in the rotational constant in the excited state, despite the stronger hydrogen bond is that with a stronger bond, one will have a reduced bending amplitude that can lead to an increase in the center of mass separation of the two monomers.¹⁴

Let us now compare the van der Waals interactions in these three analogous complexes as they are reflected by the predissociation lifetimes and the red shifts of the hydrogen bonded C–H stretching fundamentals. The analysis of the vibrational frequency shifts for the complexes is complicated by the symmetry lowering of the acetylene and diacetylene units in the three systems. The complexation with the cyano-bearing moiety shifts the frequency of the C–H stretching bands (reflecting the deepening of the intermolecular well with intramolecular excitation). Simply measuring the shift in the absorption from the asymmetric C–H stretch of the isolated molecule ignores the fact that excitation is no longer purely an asymmetric stretch. We have estimated the local C–H stretch red shift by solving the energy level matrix for free C_2H_2 ,

$$\begin{pmatrix} \nu_{\text{CH}} & W \\ W & \nu_{\text{CH}} \end{pmatrix} \quad (5)$$

to obtain the known eigenvalues $\nu_1(3372.85 \text{ cm}^{-1})$ [Ref. 15(a)] and the “deperturbed” value for $\nu_3(3288.58 \text{ cm}^{-1})$.^{15(b)} The ν_3 fundamental of the acetylene monomer is in a strong anharmonic resonance with the level $\nu_2 + \nu_4 + \nu_5$. However, we expect the complex induced shift of the $\nu_2 + \nu_4 + \nu_5$ to be much less than for the ν_3 mode and the resonance to be much less important. If we assume no shift for the $\nu_2 + \nu_4 + \nu_5$ level and the same anharmonic interaction matrix element in the complex as for the monomer, ν_3 is predicted to be red shifted by $\sim 0.6 \text{ cm}^{-1}$, which is small enough that it can be neglected compared to other sources of error in our approximations. This procedure yields a “pure”

TABLE VII. Comparison of the vibrational frequency shifts and predissociation linewidths of the ν_2 and the ν_3 bands of the HCN-HCCH , $\text{HC}_3\text{N-HCCH}$, $\text{HCN-C}_4\text{H}_2$ complexes.

Complex	Frequency shifts (cm^{-1})			Predissociation linewidth (MHz)
	ν_2	ν_3^{a}	ν_3^{b}	
HCN–HCCH	1.226	24.6	40.1	140
HC ₃ N–HCCH	1.232	25.3	41.0	50
HCH–HCCCCH	1.731	49.8	49.0	28

^aFrequency shift from the antisymmetric C–H stretching of HCCH, or C_4H_2 .

^bResonance corrected shift (see text). For the HCN-HCCH complex the band center given by Block *et al.* in Ref. 6 has been used.

C–H stretching frequency, $\nu_{\text{CH}}(3330.72 \text{ cm}^{-1})$ and an interaction matrix element, $W(42.13 \text{ cm}^{-1})$. The complex induced red shift can then be considered to affect the hydrogen bonded C–H stretch and not the free stretch, so that the new energy level matrix could be represented as

$$\begin{pmatrix} \nu_{\text{C-H}} - \delta & W \\ W & \nu_{\text{C-H}} \end{pmatrix}, \quad (6)$$

where δ is the hydrogen bond induced red shift in cm^{-1} . One of the eigenvalues of the matrix is known (i.e., the band center for the complex), so if we assume the interaction matrix element to remain unchanged, then the magnitude of the frequency shift, δ , can be calculated. Similar calculations can also be done for the $\text{HCN-C}_4\text{H}_2$ complex. Table VII gives the results of this analysis. It is seen that unlike the crude shifts (measured from the antisymmetric acetylenic CH mode of the monomers) our estimated red shift values are quite close. A similar analysis has been used by Fraser and co-workers in the study of the complexes of C_2H_2 and C_4H_2 with ammonia.¹⁶

The strong similarity of the red shifts for the three complexes appears to confirm the initial assertion that the electronic interaction is similar for the three complexes. However, the largest shift, for $\text{HCN-C}_4\text{H}_2$, is combined with the longest lifetime. This “discrepancy” is interesting in that it may elucidate the factors which may be responsible for the scatter in the correlation plot of Miller.²

Standard arguments regarding the qualitative dependence of the predissociation lifetimes for related complexes on the structures of the constituent monomers fail to properly account for the trend noted in our data, and in fact, many of these arguments predict an opposite trend. The monomer substitutions carried out in this study increase the number of vibrational modes for the van der Waals complexes from 16 modes for the linear HCN-HCCH complex to 22 modes for the two modified complexes. Thus although the ν_3 excitation occurs at very similar energies for the three complexes, we would expect the HC_3N and C_4H_2 complexes to have more rovibrational exit channels available for predissociation. A comparison of the number of predissociation channels alone fails to consider the fact that not all channels will be equally effective in promoting predissociation of the excited complexes, yet it suggests a pattern of stability contrary to the

experimental result which finds the substituted complexes more metastable than the original HCN–HCCN system. Clearly, there are other factors at work here.

In a previous comparison from this laboratory of the predissociation dynamics of $(\text{HCN})_2$ and $(\text{HC}_3\text{N})_2$, Yang *et al.*¹⁷ made use of the concept of vibrational predissociation as “a half-collision” process by referring to a vibrational energy transfer theory (SSH theory)¹⁸ originally developed by Schwartz, Slawsky, and Herzfeld for application to molecular collisions. This theory can also be applied to the present systems. In order to compare the three systems in this work, there are two major factors that have to be considered. First, we have to consider the coupling strengths for the three systems between the vibration and the predissociation coordinate. From the experimental data here it is well established that the coupling strengths, as measured by the red shifts, are similar, and the variation predicts the wrong variation of linewidth. Another important factor in the SSH theory is the reduced mass of the two colliding partners (in this case the reduced mass of the two fragments). In the case of vibration-to-translation energy transfer, it is well known that the vibrational de-excitation probability will decrease if the reduced mass of the two collisional partners increases according to the SSH theory. The presumption of this argument is that the three systems have similar interaction potentials, which is true in the present situation, at least near the equilibrium geometry. It also presumes that the fragments leave with the same translational energy, which is harder to justify given the importance of nearly resonant dissociation channels. Nevertheless, SSH theory predicts that the system with lower reduced mass should have a shorter predissociation lifetime. The reduced mass for the two fragments increases from 13.25 (HCN–HCCH) to 17.22 (HC_3N –HCCH) to 17.53 amu (HCN– C_4H_2) as we go down the series. This rationalizes the shorter lifetime of the HCN–HCCH complex, but does not explain the factor of 2 difference between HC_3N –HCCH and HCN– C_4H_2 .

The dissimilarity in size of the interacting monomers may be another contributing factor to the anomalous result. In the dissociation of a diatomic species yielding fragments of disparate masses, conservation of energy and momentum dictates that the light mass will carry away most of the energy released in the dissociative process. In the analogous dissociation of the large *I*–small *I* dimer, the small *I* fragment has to assume most of the rotational energy, assuming one can neglect both the relative orbital angular momenta of the two departing monomers and the initial rotational angular momentum of the complex. This restriction will leave fewer open dissociation channels for systems of disparate moments of inertia. Again, this argument rationalizes the shorter lifetime for the HCN–HCCH complex, but not the differences between the two heavier complexes.

Data for a doubly substituted HC_3N – C_4H_2 complex would help to assess the validity of these arguments, for we would expect a similar red shift to be accompanied by slower predissociation (i.e., longer lifetimes) as predicted by the reduced mass effect, or faster predissociation (i.e., shorter lifetimes) by the momentum imbalance effect. Despite extensive

searching, we only observed one very broad cluster peak when we attempted to observe this complex with the current apparatus. If this feature is in fact due to the linear HC_3N – C_4H_2 heterodimer, one would have to conclude that its lifetime is short and that the momentum imbalance factor dominates over the reduced mass effect. In the absence of further experimental data, model calculations of the predissociation dynamics could be carried out to confirm or contradict our tentative explanation. In fact, the systems discussed here appear to be a good case for theoretical treatment since uncertainties in the interactions should affect the relative values of the lifetimes less than their absolute values.

An interesting question concerns why we did not observe the “nonbonded” CH stretching mode of C_2H_2 or C_4H_2 in the complexes. While this mode will correlate with the IR inactive symmetric stretch in the free molecule, the asymmetry produced by the differential shift will lead to extensive localization of the vibrational excitation on the outer CH stretching coordinate. Using the model discussed above for C_2H_2 , the observed shift implies that ν_1 has about 1.6 times more “free CH” motion, than “bounded CH” motion. If the dipole derivatives of the two ends were the same, this would predict that ν_1 would have about 40% of the integrated intensity of ν_3 . Given that we would expect it to be narrower, we should have detected ν_1 if it was this strong. However, we expect the dipole derivative for the “bound” CH stretch to be enhanced, 2 to 3 times, by hydrogen bonding. In this case, the larger derivative can effectively counter the vibrational asymmetry, leading the ν_1 intensity to be zero for a dipole enhancement of 1.6, and to be 17 times weaker than ν_3 even for a dipole enhancement of 3. Thus, our failure to observe the “free CH” ν_1 band in HC_3N – HC_2H and Miller’s failure to observe the same band in HCN–HCCH can be rationalized. It is harder to understand why the ν_1 band is not observed for the HCN– HC_4H complex. Here the mixing of the “free” and “bound” CH stretch of C_4H_2 is only a few percent, and we would expect the ν_1 to have an intensity similar to the ν_3 , the unbound H–C stretch of HCN.

Finally it is noteworthy that both complexes studied in this experiment show no sign of the T-shaped structure despite that fact the T-shaped isomer is strongly favored in the molecular beam expansion of HCN–HCCH. One possible reason for the absence of T-shaped isomers in our experiment is the very asymmetric top character of these species which disperses their spectra and gives rise to an unfavorable partition function and consequently low signal to noise ratio. Further analysis of the potential energy surfaces for the C_4H_2 –HCCH and HCN– C_4H_2 interactions may reveal whether or not the kinetics of dimer formation should be considered in explaining the absence of T-shaped dimers, for one would expect here to be at least a local minimum for the potentials of the substituted complexes at the nonlinear configurations.

IV. CONCLUSIONS

Rotationally resolved infrared spectra of the linear HC_3N –HCCH and HCN– C_2H_4 complexes have been pro-

duced using the molecular beam optothermal method. The ν_2 and ν_3 bands of each complex were recorded and analyzed, providing an accurate set of molecular constants for each complex. The prediction linewidths were also explored for the $\nu_3=1$ state of $\text{HC}_3\text{N-HCCH}$ and $\text{HCN-C}_4\text{H}_2$ and were determined to be 50 and 28 MHz, respectively. The vibrational frequency shifts and predissociation lifetimes of the hydrogen bonded excitations of the complexes were compared with the corresponding quantities for HCN-HCCH . While the complexes exhibited similar shifts for ν_3 excitations, the associated lifetimes range from 1 to 5 ns. Tentatively, these findings were attributed to the increase in the reduced mass and the imbalance in the moments of inertia of the fragments of the linear complexes.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation through Grants Nos. CHE-9016491, CHE-9318725, and CHE-9322579. Dr. Jerry Fraser and Dr. William Klemperer are acknowledged for helpful discussions. It is a pleasure to thank also Dr. J. Muenter for two very careful readings of the manuscript.

¹D. J. Nesbitt, *Chem. Phys. Rev.* **88**, 843 (1988).

²(a) R. E. Miller, *J. Phys. Chem.* **90**, 3301 (1986); (b) *Advances in Molecu-*

lar Vibrations and Collision Dynamics, edited by J. M. Bowman and M. A. Ratner (JAI, London, 1991), Vol. 1A, p. 83.

³R. E. Miller, *Science* **240**, 447 (1988).

⁴R. J. LeRoy, M. R. Davis, and M. E. Lam, *J. Phys. Chem.* **95**, 2167 (1991).

⁵P. A. Block, K. W. Jucks, L. G. Pedersen, and R. E. Miller, *Chem. Phys.* **139**, 15 (1989).

⁶P. D. Mallinson and A. Fayt, *Mol. Phys.* **32**, 473 (1976).

⁷G. Guelachvili, A. M. Craig, and D. A. Ramsay, *J. Mol. Spectrosc.* **105**, 156 (1984); L. Pasternack and J. R. McDonald, *ibid.* **108**, 143 (1984); N. L. Owen, C. H. Smith, and G. A. Williams, *J. Mol. Struct.* **161**, 33 (1987).

⁸F. A. Miller and D. H. Lemmon, *Spectrochim. Acta* **23A**, 1415 (1967).

⁹J. B. Armitage, E. R. H. Jones, and W. C. Whiting, *J. Chem. Soc.* **1951**, 44.

¹⁰T. E. Gough, R. E. Miller, and G. Scoles, *J. Chem. Phys.* **69**, 1588 (1978); *Appl. Phys. Lett.* **30**, 338 (1977).

¹¹E. R. Th. Kerstel, K. K. Lehmann, T. F. Mentel, B. H. Pate, and G. Scoles, *J. Phys. Chem.* **95**, 8282 (1991).

¹²K. W. Jucks and R. E. Miller, *J. Chem. Phys.* **88**, 6059 (1988).

¹³The values used were $R(\equiv\text{C-H})=1.06 \text{ \AA}$, $R(\text{C-C})=1.46 \text{ \AA}$, $R(\text{C}\equiv\text{C})=1.21 \text{ \AA}$, $R(\text{C}\equiv\text{N})=1.16 \text{ \AA}$.

¹⁴The authors wish to acknowledge William Klemperer who proposed this model to one of the authors.

¹⁵(a) H. G. M. Edwards, *Spectrochim. Acta Part A* **46**, 97 (1990); (b) J. Vander Auwer, D. Hurtmans, M. Carleer, and M. Herman, *J. Mol. Spectrosc.* **157**, 337 (1993).

¹⁶J. Fraser (private communication).

¹⁷X. Yang, E. R. Th. Kerstel, and G. Scoles, *J. Chem. Phys.* **98**, 2727 (1993).

¹⁸R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, *J. Chem. Phys.* **20**, 1951 (1952); R. N. Schwartz and K. F. Herzfeld, *ibid.* **22**, 767 (1954).