HEAT CAPACITY AND VAPOR PRESSURE OF CRYSTALLINE BIS(BENZENE)CHROMIUM. THIRD-LAW ENTROPY COMPARISON AND THERMODYNAMIC EVIDENCE CONCERNING THE STRUCTURE OF BIS(BENZENE)CHROMIUM*

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SUMMARY

Heat capacity measurements from 5 to 350°K and vapor pressure measurements on bis(benzene)chromium together with the published frequency assignments permit a correlation between the third-law and spectroscopic entropies. Neither thermal anomalies nor zero point entropy were found. The agreement is consistent with free rotation about the ring to metal bonds and D_{6h} symmetry for the molecule as proposed by Cotton. The thermodynamic functions for the crystal at 298.15°K are 53.52, 54.07, 26.77, and -27.30 cal·mole^{-1}·°K^{-1} for the heat capacity, entropy, enthalpy function, and Gibbs function, respectively. The vapor pressure over the range 310 to 365°K is represented by $\log_{10} p$ (mm) $= 27.42 - 5451/T - 5.535 \log_{10} T$, ($T$ in °K).

INTRODUCTION

The π-complexes of transition metals with aromatic molecules are sandwich compounds in which the aromatic ring may rotate about the ring-to-metal bond. We report here the results of a thermal investigation of bis(benzene)chromium undertaken to determine the magnitude of the energy barrier to this rotation of the rings, and also to ascertain the possible presence of thermodynamic evidence for a distorted ring structure in this compound. Theoretical arguments[1,2] suggest that the rings might be trigonally distorted (alternating short and long C–C bonds as in a Kekulé benzene structure) and Jellinek[3] has reported an X-ray diffractional analysis consistent with this distortion and D_{3d} symmetry for the molecule. Later workers (Cotton, Dollase and Wood)[4] in an independent X-ray investigation reported a molecular symmetry of D_{6h} with hexagonally symmetric benzene rings. The existence of ring distortion would be of thermodynamic interest, for it would imply (a) that the distorted molecules might fit into the crystal lattice in two distinct orientations related

one to the other by 60° rotation about the threefold axis of the molecule, and (b) that the resulting crystal phase might be ordered or disordered with respect to these orientations. Such a disordered phase would have $R \cdot \ln 2$ more entropy than the ordered one. Jellinek suggested[5] that the discrepancy in the X-ray results would be explained if he had, by chance, investigated an ordered crystal, while Cotton et al. had a disordered crystal and had therefore reported a structure based on the average of the two orientations.

We measured the heat capacity from 5 to 350°K and the vapor pressure from 323 to 363°K of bis(benzene)chromium to look for direct indications of an order–disorder transition. These data also were used to compute the gas phase entropy which was then compared with that calculated by statistico-mechanical methods to check the possibility of a residual zero point entropy of $R \cdot \ln 2$. This would be expected if the supposedly disordered crystal phase had persisted below the temperature range of the heat capacity measurements. The entropy comparison also provides information on the energy barrier to ring rotation.

EXPERIMENTAL

Preparation and characterization of the sample

The bis(benzene)chromium sample was prepared at Lund with the method advocated by Fischer[6], and was purified, as he recommended, by washing with ether followed by sublimation under high vacuum at 160°. The sample then consisted of well-formed, blunt-acicular, lustrous-black crystals, of length 0.5 to 3 mm.

The chromium content of this material was determined (after decomposition with hydrogen peroxide and nitric acid and oxidation with persulfuric acid) by titration against Fe^{II}. Two series of triplicated analyses were performed, and gave mean chromium contents of 24.81% and 24.94% (theoretical value 24.98%). Pyrolysis of a portion of the sample at 450° showed that it was possible to decompose bis-(benzene)chromium to about 25% chromium, 73% benzene, 2% carbon, and 0.2% hydrogen. Slight traces of other organic decomposition products were found by GLC. The melting point of the sample was found to be 285.6°; this agrees well with the literature value[6] of 284.5°. The sample was sealed in glass under vacuum for transportation to Ann Arbor and was handled only in a nitrogen-filled dry box.

Calorimetric procedure

The calorimetric sample (mass 20.5773 g *in vacuo*) was loaded mechanically into the goldplated copper calorimeter (laboratory designation W-39) with an internal volume of 22.7 cm^3 and a mass of 13.11 g including the closure. A helium pressure of 44 mm at 300°K was introduced into the calorimeter to facilitate thermal equilibration, and the calorimeter was then sealed with an annealed gold gasket and screw cap. Heat capacity measurements were made in the Mark II adiabatic cryostat[7]. Temperatures were measured with a 25-ohm, capsule-type, platinum-resistance thermometer (laboratory designation A-5) situated within the axial well of the calorimeter. These temperatures are believed to be in accord with the thermodynamic temperature scale within 0.03° from 10 to 90°K, and within 0.04° from 90 to 350°K. The heat capacity of the empty calorimeter was determined in a separate experimental series, small corrections being applied for differences between the loaded and empty

calorimeter in the quantities of helium and thermal-conduction (Apiezon T) grease. Measurements of mass, voltage, current, time and temperature were referred to calibrations or standardizations performed by the National Bureau of Standards.

Vapor pressure determinations

The vapor pressure of bis(benzene)chromium was determined on a portion of the calorimetric sample by the Knudsen effusion technique. The apparatus was similar to that of Edwards and Kington[8]. The effusion cell was of copper 1.25 cm in diameter and fitted with a screw cap. The effusion hole with a radius of 0.417 mm was drilled in 0.0173 mm thick copper foil soldered to this cap. The diameter of the hole was measured with a metallurgical measuring microscope, the area of the hole being (0.547 ± 0.001) mm². A water thermostat, controlled by a Leeds and Northrup three action proportional controller and a nickel resistance thermometer, was used to obtain temperature control better than ± 0.003° over the period of the runs. Temperatures were measured with a Dymec digital quartz thermometer, which had been calibrated against a 25-ohm, platinum-resistance thermometer.

The basic expression for relating the rate of material loss from the effusion cell with the equilibrium vapor pressure was derived by Langmuir (given, for example, by Thomson[9]). This expression holds only in the limits of an effusion hole of zero length, and a mean free path of the molecule much greater than the diameter of the effusion hole. In order to correct for the finite length of the hole, a correction factor given by Knudsen[10] is applied, and a further factor (due to Hiby and Pahl[11]) adjusts the vapor pressures at high pressures where the mean free path is no longer large compared with the diameter d of the effusion hole. In this research, the mean free path varied from approximately d to $100\ d$. This question is treated more thoroughly by Edwards and Kington[8] and by Carman[12].

The pressure is then calculated according to the relationship:

$$p = \frac{g}{t \cdot A} \cdot \left(\frac{2\pi R \cdot T}{M}\right)^{\frac{1}{2}} \cdot \left(\frac{8r+3l}{8r}\right) \cdot \left(\frac{1}{1+0.48r/2\lambda}\right)$$

λ = Mean free path $[\lambda = k \cdot T/(\sqrt{2}\pi\sigma^2 \cdot p)]$ (cm), p = pressure (dyne·cm^{-2}), g = weight loss in run (g), t = duration of run (sec), A = area of effusion hole (cm²), R = gas constant (erg·°K^{-1}·mole^{-1}), T = temperature of run (°K), M = molecular weight (g·mole^{-1}), r = radius of effusion hole (cm), l = length of effusion hole (cm), k = Boltzmann constant (erg·°K^{-1}), σ = collision diameter of molecule (cm) = 6.99×10^{-8} (cm) (twice the geometric mean of the principal radii).

RESULTS

The experimental heat capacity points are presented in chronological order in Table 1 and graphically in Fig. 1. The temperature increments employed in their determination may usually be inferred from the difference between adjacent mean temperatures. The values have been adjusted for curvature occasioned by the finite temperature differences employed and are based upon the defined thermochemical calorie equal to 4.1840 J, an ice point of 273.15°K, and a gram formula mass for bis(benzene)chromium of 208.225. The heat capacities have a standard deviation of about 0.5% from 10 to 15°K which rapidly decreases to 0.1% at higher temperatures.

TABLE 1

EXPERIMENTAL HEAT CAPACITY OF BIS(BENZENE)CHROMIUM[a]

| $\overline{T}$	C_p	$\overline{T}$	C_p	$\overline{T}$	C_p
Series I		243.30	42.83	22.54	4.96
		252.45	44.60	25.30	5.94
93.38	17.70	261.88	46.47	28.59	6.99
98.44	18.36	271.04	48.25	32.06	8.00
108.46	19.70	279.94	49.99	35.53	8.91
120.15	21.36	288.61	51.63	38.92	9.69
126.47	22.30	297.05	53.28	42.66	10.47
134.42	23.51	305.30	54.90	47.01	11.30
143.94	25.00	313.61	56.50	51.86	12.11
154.00	26.63	322.01	58.02	56.88	12.88
163.55	28.21	330.21	59.66	61.49	13.58
172.70	29.77	338.24	61.22	66.46	14.25
		346.32	62.80		
Series II				*Series VI*	
163.95	28.26	*Series IV*		67.78	14.42
173.46	29.89	6.26	0.16	74.88	15.30
182.54	31.48	6.81	0.21	81.45	16.19
191.27	33.09	7.68	0.32	87.59	17.04
199.69	34.61	8.64	0.46	93.42	17.74
207.83	36.10	9.70	0.69	95.02	17.92
215.72	37.60	10.76	0.92	ΔH Run A	
223.38	39.06	11.82	1.16	ΔH Run B	
230.83	40.47			285.97	51.16
238.08	41.87	*Series V*		294.10	52.77
245.15	43.21	11.68	1.14	302.00	54.26
		12.82	1.47	310.29	55.80
Series III		14.03	1.85	318.62	57.44
205.95	35.74	15.35	2.30	326.78	58.93
215.81	37.59	16.78	2.84	334.77	60.85
225.28	39.42	18.40	3.43	342.61	62.26
234.43	41.19	20.28	4.12	348.04	62.88

[a] Units: cal, mole, °K.
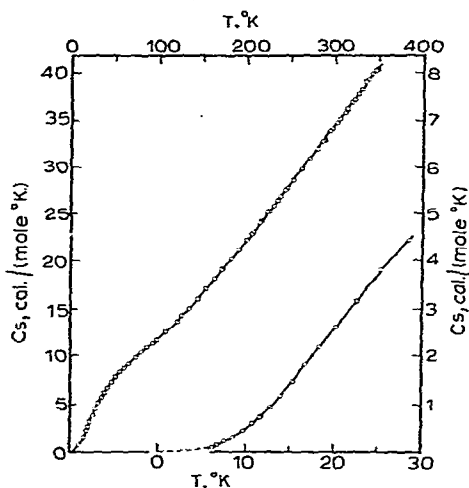
Fig. 1. The heat capacity of bis(benzene)chromium.

TABLE 2

THERMODYNAMIC FUNCTIONS OF BIS(BENZENE)CHROMIUM[a]

T	C_p	S°	$H^\circ-H_0^\circ$	$(H^\circ-H_0^\circ)/T$	$-(G^\circ-H_0^\circ)/T$
5	0.087	0.029	0.109	0.022	0.007
10	0.732	0.234	1.768	0.177	0.057
15	2.180	0.783	8.783	0.586	0.198
20	4.025	1.659	24.230	1.212	0.448
25	5.834	2.755	48.958	1.958	0.797
30	7.419	3.963	82.194	2.740	1.223
35	8.772	5.211	122.76	3.508	1.704
40	9.928	6.460	169.59	4.240	2.220
45	10.928	7.688	221.8	4.929	2.760
50	11.81	8.886	278.7	5.573	3.313
60	13.35	11.179	404.6	6.744	4.435
70	14.71	13.340	545.0	7.786	5.554
80	16.00	15.390	698.7	8.733	6.656
90	17.28	17.349	865.1	9.612	7.786
100	18.58	19.236	1044.4	10.444	8.792
110	19.93	21.07	1236.9	11.244	9.826
120	21.34	22.86	1443.2	12.03	10.84
130	22.83	24.63	1664	12.80	11.83
140	24.37	26.38	1900	13.57	12.81
150	25.97	28.11	2152	14.34	13.77
160	27.62	29.84	2419	15.12	14.72
170	29.31	31.57	2704	15.91	15.66
180	31.04	33.29	3006	16.70	16.59
190	32.82	35.02	3325	17.50	17.52
200	34.65	36.75	3662	18.31	18.44
210	36.52	38.48	4018	19.13	19.35
220	38.41	40.22	4393	19.97	20.26
230	40.31	41.97	4786	20.81	21.16
240	42.23	43.73	5199	21.66	22.07
250	44.15	45.49	5631	22.52	22.97
260	46.09	47.26	6082	23.39	23.87
270	48.03	49.04	6553	24.27	24.77
273.15	48.65	49.60	6705	24.55	25.05
280	49.99	50.82	7043	25.15	25.67
290	51.94	52.61	7552	26.04	26.57
298.15	53.52	54.07	7982	26.77	27.30
300	53.88	54.40	8082	26.94	27.46
310	55.78	56.20	8630	27.84	28.36
320	57.67	58.00	9197	28.74	29.26
330	59.59	59.80	9783	29.65	30.16
340	61.57	61.61	10389	30.56	31.06
350	63.46	63.43	11015	31.47	31.96

[a] Units: cal, mole, °K.

The heat capacities in Table 2 were obtained from a smooth polynomial expression fitted by computer through the experimental points using least squares criteria. The extrapolation below 5°K was made using the Debye limiting law, fit from a plot of

TABLE 3

VAPOR PRESSURE OF BIS(BENZENE)CHROMIUM

T(°K)	$p \times 10^3$ (mm)
323.227	0.456
323.392	0.478
323.954	0.485
328.300	0.781
335.680	1.639
338.877	2.119
339.168	2.25
343.969	3.46
348.320	5.17
353.840	8.09
358.230	11.68
360.670	14.18
363.275	17.22

C_p/T vs. T^2. The thermodynamic functions in this table were obtained by integration of this curve, and are considered to have a precision corresponding to a standard deviation of 0.1% above 100°K. The entropies and Gibbs energies have not been adjusted for nuclear spin or isotopic mixing contributions, and are therefore practical chemical thermodynamic quantities.

The vapor pressure results are presented in Table 3 and in Fig. 2. For comparison, the results of Cordes and Schreiner[13], and Fischer and Schreiner[14] are plotted also. Least squares analysis was used to fit the function to the data (p in mm, T in °K):

$$\log_{10} p = A + B/T + C \cdot \log_{10} T.$$

The first two coefficients are: $A = (27.42 \pm 0.05)$, $B = (-5451 \pm 17.7)$ °K. The value of C was constrained to that calculated from the difference in heat capacity between the
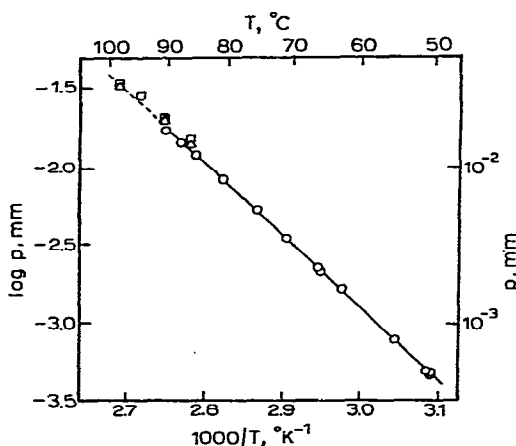

Fig. 2. The vapor pressure of bis(benzene)chromium as a function of temperature. The O represent the data of this research, □ those of Cordes and Schreiner[14], △ those of Fischer and Schreiner[15].

.crystal and gas phases (-5.535). The standard deviations of the coefficients were calculated by the procedure described by Baird[15].

The enthalpy of vaporization, ΔH_{vap}, and hence the entropy of vaporization, ΔS_{vap}, may then be expressed as a function of temperature:

$$\Delta H_{vap} = (24.94 \pm 0.08) - 0.011\ T \quad (kcal \cdot mole^{-1})$$
$$\Delta S_{vap} = (24940 \pm 80)/T - 11 \quad (cal \cdot mole^{-1} \cdot {}^{\circ}K^{-1})$$

The entropy of gaseous bis(benzene)chromium was calculated as a function of temperature, from the structural information of Haaland[16] (obtained by electron diffraction of the gas), and the frequency assignment of Fritz, Lüttke, Stammreich, and Forniers[17]. The internal rotation was assumed to be free, and the usual approximations of the rigid-rotor harmonic oscillator model were employed (overall symmetry number 12). The frequencies employed in the calculation are listed in Table 4

TABLE 4

FREQUENCY ASSIGNMENT FOR BIS(BENZENE)CHROMIUM[a]

Benzene symmetry species[d]	Benzene frequency number	Benzene frequency (ref. 19)	BBC[b] symmetry species[d]	BBC frequency number	BBC frequency (ref. 17)	BBC$^+$I^{-c} frequency (ref. 17)	BBC frequency (ref. 18)	Frequency selected for BBC
A_{1g}	1	995.4	A_{1g}	1 s		973		972
			A_{2u}	1 as	971	972	970	971
	2	3073	A_{1g}	2 s		3095		3092
			A_{2u}	2 as	3037	3040		3037
A_{2g}	3	1350	A_{2g}	3 s				1350
			A_{1u}	3 as				1350
B_{2g}	4	707	B_{2g}	4 s				707
			B_{1u}	4 as				707
	5	990	B_{2g}	5 s				
			B_{1u}	5 as		(950)		950
E_g^+	6	608.0	E_g^+	6 s		616		616
			E_u^+	6 as		(630)		630
	7	3056	E_g^+	7 s		3074		3074
			E_u^+	7 as				3056
	8	1596	E_g^+	8 s		1620		1620
			E_u^+	8 as				1599
	9	1178	E_g^+	9 s		1148		1148
			E_u^+	9 as				1178
E_g^-	10	846	E_g^-	10 s		805		800
			E_u^-	10 as	833	857	1014	833
A_{2u}	11	674.0	A_{2u}	11 s	794	795		794
			A_{1g}	11 as		790	796	796
B_{1u}	12	1010	B_{1u}	12 s				1010
			B_{2g}	12 as				1010
	13	3057	B_{1u}	13 s				3057
			B_{2g}	13 as				3057

B_{2u}	14	1309	B_{2u}	14 s				1309
			B_{1g}	14 as				1309
	15	1146	B_{2u}	15 s				1146
			B_{1g}	15 as				1146
E_u^+	16	398.6	E_u^+	16 s		(543)		543
			E_g^+	16 as		420		420
	17	967	E_u^+	17 s				967
			E_g^+	17 as		940		940
E_u^-	18	1037	E_u^-	18 s	999	1000		999
			E_g^-	18 as		1004	1002	1002
	19	1482	E_u^-	19 s	1426	1430		1426
			E_g^-	19 as		1440	1430	1430
	20	3064	E_u^-	20 s	3037	3040		3037
			E_g^-	20 as		3095	3047	3047
			A_{1g}	21	270	279		270
			A_{1u}	22	(305)	(303)		(Torsion)
			A_{2u}	23	459	415	456	459
			E_g^-	24	332	333		332
			E_u^-	25	490	466	492	490
			E_u^-	26	(140)	144		140

[a] Units: cm^{-1}. [b] BBC: bis(benzene)chromium. [c] BBC^+I^-: bis(benzene)chromium iodide. [d] The frequencies of the E species are doubly degenerate.

TABLE 5

SPECTROSCOPIC ENTROPY OF BIS(BENZENE)CHROMIUM[a]

T	S_{trans}°	S_{rot}	S_{ir}	S_{vib}	S_{tot}°
298.15	41.91	25.25	5.61	20.10	92.87
320	42.26	25.47	5.68	22.75	96.16
350	42.70	25.73	5.76	26.48	100.67

[a] Units: cal, mole, $^{\circ}K$.

TABLE 6

ENTROPY COMPARISON FOR GASEOUS BIS(BENZENE)CHROMIUM[a]

T	$S^{\circ}(c)$[b]	ΔS_{vap}[c]	ΔS_{comp}[d]	$S^{\circ}(g)$ (3rd law)	$S^{\circ}(g)$[e] (spectro)	$S^{\circ}-S^{\circ}$
298.15	54.07				92.87	
310	56.20	69.46	−31.27	94.39	94.64	−0.25
320	58.00	66.95	−29.10	95.85	96.16	−0.31
330	59.80	64.58	−27.08	97.30	97.66	−0.36
340	61.61	62.36	−25.18	98.79	99.17	−0.38
350	63.43	60.27	−23.40	100.30	100.67	−0.37
	±0.06	±0.23	±0.14	±0.28	±0.3	±0.4[f]

[a] Units: cal, mole, $^{\circ}K$. [b] Standard entropy of the crystal. [c] ΔS_{vap} entropy of vaporization at T. [d] ΔS_{comp} entropy of compression of the gas from the saturation pressure to the standard pressure of one atm. [e] For the "free" rotator. [f] The precision indices are standard deviations.

and frequencies for those vibrations not assigned by Fritz *et al.* were estimated by comparison with data of Snyder[18] on bis(benzene)chromium and of Calloman, Dunn, and Mills[19] on benzene. Contributions to the spectroscopic entropy of bis(benzene)-chromium are listed for selected temperatures in Table 5, in which the total entropy is the sum of the entropies due to translation, rotation, internal rotation, and vibration $(S^\circ_{tot} = S^\circ_{trans} + S_{rot} + S_{ir} + S_{vib} = S'^\circ \text{ (g)})$.

A comparison of the entropy calculated for the gas phase $[S'^\circ \text{(g)}]$ with that computed from the heat capacity and vapor pressure results by means of the third law $[S^\circ \text{(g)} = S^\circ \text{(c)} + \Delta S_{vap} + \Delta S_{comp}]$ is presented in Table 6.

DISCUSSION

The spectroscopic or statistical entropy calculated for bis(benzene)chromium with the assumption that the benzene rings are not distorted (*i.e.*, that the symmetry number is 12) listed in Table 6 agrees with the 3rd law value near 350°K to within the resultant standard deviation ($0.4 \text{ cal·mole}^{-1} \cdot °\text{K}^{-1}$) of the two entropy evaluations. As for ferrocene[23], the precision index is too large to exclude the possibility of a small barrier to internal rotation (*i.e.*, <1 kcal/mole). Inclusion of such a barrier would improve the fit of the spectroscopic and third-law entropies. However, if the molecule is distorted in the manner postulated by Jellinek[5] (molecular symmetry D_{3d}), the symmetry number is six, and the spectroscopic entropy should be $R \cdot \ln 2$ (or $R \cdot \ln 12 - R \cdot \ln 6$, ($= 1.38 \text{ cal·mole}^{-1} \cdot °\text{K}^{-1}$) greater than that of the undistorted molecule. The experimental third-law results are in agreement with the spectroscopic entropy for undistorted molecules; addition of $R \cdot \ln 2$ to the experimental entropy would be required to achieve agreement with the spectroscopic entropy for the gas of distorted molecules.

Jellinek[5] showed that if the molecule is distorted, then ordered and disordered crystal phases may exist, and he postulated (as noted above) that X-ray diffraction analysis had been done on both phases. We found no evidence of a phase transition in the heat capacity measurements, and conclude that the phase existing at 350°K is also stable at least as low as 5°K. If we assume that the molecule is distorted and that we made measurements on the disordered phase, then the absence of a transition shows that the disorder was "frozen" into our sample, and $R \cdot \ln 2$ zero point entropy should be added to the third-law entropy. In this case, the third-law and spectroscopic entropies (for the distorted molecule) would be in agreement. If, however, we assume that the molecule is distorted and that measurements were made on the ordered phase, we are at a loss to explain the discrepancy of $R \cdot \ln 2$ that would now exist between the spectroscopic and third-law values. Vibrational anharmonicities have not been considered in the spectroscopic entropy, but would not be expected to contribute more than 0.5 cal mole$^{-1} \cdot °\text{K}^{-1}$ at 350°K.

Two possibilities are, therefore, consistent with the observed quantities; either
(*a*) the molecule is undistorted, or
(*b*) the molecule is distorted to D_{3d} symmetry and the disordered phase persisted to at least 5°K.

We do not regard this latter possibility (*b*) as likely: the small difference between the molecular orientations postulated by Jellinek (60° rotation about the main symmetry axis) is such a small perturbation that it is unlikely to be "frozen in". The thermodyna-

mic evidence, then, favors a symmetric molecule in which the benzene rings are not distorted. This is in keeping with X-ray structures reported by Bailey and Dahl for (hexamethylbenzene)chromium tricarbonyl[20] and benzenechromium tricarbonyl[21]. In these molecules, the benzene rings possess full hexagonal symmetry, even though three-fold distortion might be encouraged by the trigonal chromium tricarbonyl moiety. A low temperature (100°K) X-ray study of the structure of bis(benzene)-chromium by Keulen and Jellinek[24] failed to disclose a three-fold distortion, and a recent neutron diffraction study also indicates that the molecule is not distorted[22]. It should further be noted that there is as yet no firm experimental basis for the value for the E_u^- mode, v 26, (Table 4). Determination of this mode in the gaseous phase is an obvious desideratum for the argument which depends critically on the less energetic modes.

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