Investigation of Coriolis Mixing in Benzene

Thesis by

John Hulett Runnels

In Partial Fulfillment of the Requirements for the Degree of

Master of Science

California Institute of Technology

Pasadena, California

1983

To the Memory of My Mother

Acknowledgments

I would like to thank my parents for their guidance and support over the years; my research advisor, Professor R. A. Marcus, for his understanding, insight, and generosity with his time; fellow group members Paul Siders and Bob Cave for many fruitful discussions; and the Fannie and John Hertz Foundation for their generous support of my graduate studies.

Abstract

An explanation for some recent observations in the electronic absorption spectrum of benzene by Schlag and coworkers[1] is proposed. Several vibrational lines of the S_0 to S_1 transition have been studied by these authors with the Doppler-free, two-photon technique developed earlier[2]. The resolution of this technique is so high that individual $\Delta J=0$, $\Delta K=0$ rotational lines in the Q-branch of a given vibrational transition may be seen in the electronic absorption spectrum. A major progression in the two-photon spectrum is the $14_0^1 1_0^n$ progression[3]. It was found that the $14_0^1 1_0^0$ and $14_0^1 1_0^1$ transitions had well-resolved rotational structure, but the $14_0^1 1_0^2$ transition had reduced, not well resolved rotational structure--except for the prominent K=0 lines for small to medium values of J. This suggested to us Coriolis mixing. The model presented here utilizes a suggestion of Riedle *et al*[1].The Coriolis coupling to neighboring vibrational states is followed by a rapid radiationless depletion of these states, consistent with the decreased fluorescence yield observed by Wunsch *et al*[4]. Estimates are made of the density of states of the various symmetries; these estimates are then used to estimate the extent of the relevant Coriolis mixing. The model results in a large decrease in intensity of non-zero K lines relative to the K=0 lines for the $14_0^1 1_0^2$ transition, but not

for the $14_0^1 1_0^0$ and $14_0^1 1_0^1$ transitions, in agreement with the experimental observations, making a few assumptions discussed below, but without the use of adjustable parameters. Predictions are then made for the rotational structure of other strong transitions in the two-photon spectrum of benzene.

Table of Contents

Investigation of Coriolis Mixing in Benzene

Introduction

The field of two-photon molecular spectroscopy has been a fruitful one in recent years[4]. Many states forbidden to one-photon processes may be observed with two photons. In particular, most ground-state wavefunctions are totally symmetric. For molecules with a center of symmetry, this means a g state. Only transitions from g to u states are allowed with a single photon, but many g to g transitions may be observed with two photons. The symmetry of a given vibrational state can often be inferred from polarization-dependent two-photon spectra, even in a liquid or gas, provided that the time of interaction with the photons is short compared with the mean rotation time[4]. Another advantage of two-photon spectroscopy is that Doppler-free (or nearly Doppler-free) spectra can be taken of a sample in the gas phase at relatively high temperatures by putting two laser beams of equal (or nearly equal) frequencies at 180^{o} to one another, thus making the net momentum transfer zero (or nearly zero) and eliminating the (first-order) Doppler effect. This permits higher resolution spectra than could otherwise be observed.

Recently Riedle *et al* measured the first Doppler-free two-photon spectrum of a polyatomic molecule, that of benzene[2]. The resolution $\omega/\Delta\omega$ achieved, 1.5×10^7, was high enough that individual rotational lines in the Q-branches of the vibrational transitions could be distinguished. The position of these lines depends not on the rotational constants of either the ground state or the excited state, but on the differences of the rotational constants between the two states, and the lines are thus closely spaced. (The difference in frequencies for the Q-branch S_0 to S_1 transitions of the J=0, K=0 and J=10, K=0 states is less than 1 cm^{-1}.)

After this initial work was published, Schlag and coworkers studied[1] more closely the structure of the Q-branches of the $14_0^1 1_0^n$ transitions for n = 0, 1, and 2. These are among the most prominent lines of the spectrum. The ν_1 mode is the symmetric C-C stretch, with a_{1g} symmetry, and the ν_{14} mode is the antisymmetric C-C stretch, with b_{2u} symmetry. The symmetry of the S_1 state is B_{2u}, so each of the $14_0^1 1_0^n$ vibronic transitions has symmetry A_{1g}, and is strongly allowed with two photons. The frequencies of the peaks of these transitions relative to the electronic origin were reported as 1564, 2488, and 3414 cm^{-1}, respectively[3]. (The positions of the rotationless vibrational origins are slightly different; e.g., the fundamental is 1570 cm^{-1}.) The Q-branches of the

$14_0^1 1_0^0$ and $14_0^1 1_0^1$ transitions showed well-resolved rotational structure, but the rotational structure of the Q-branch of the $14_0^1 1_0^2$ transition was reduced and not well resolved, except for the sharp K=0 line for each small to medium value of J. (For large J (around 20), even the K=0 lines disappeared, and a new, unidentified spectrum was seen instead.)

The persistence of the K=0 lines when the others are reduced is suggestive of Coriolis coupling. Following a suggestion of Riedle *et al*[1], we calculated the harmonic density of states of the upper surface of benzene as a function of the states' symmetries, and found that it is reasonable to anticipate Coriolis coupling at the higher energy, but not the lower energies. With the *ad hoc* assumption that at least one of these Coriolis-coupled states is strongly coupled to a non-radiative manifold, one obtains a strong reduction in the intensity of the nonzero K lines. For example, if there is equal mixing of the initial state with one other state, the fluorescence from the initial level is now spread over two to four states (see below), which in turn are distributed over a 0.15 cm^{-1} width (see also below). This effect is sufficient to reduce considerably the fluorescence intensity from those of lines of original width of 0.01 cm^{-1} to those of lines distributed over a region of width 0.15 cm^{-1} or greater, depending on the value of K. The broadened nonzero K lines

now largely form a "background" on which the K=0 lines stand out as silhouettes. Any substantial radiationless transition of the new states reduces this background by a factor of ten or greater (see below). At higher energies, lifetime broadening from non-radiative decay can reach the order of 0.1 cm^{-1}[4], so the effect could occur with a lower density of states than would otherwise be required.

Methods

The perturbing Coriolis Hamiltonian for a symmetric top molecule is

$$H' = -P_z p_z / I_z \quad ,$$

where P_z is the component of the total angular momentum about the z-axis, p_z is the component of the vibrational angular momentum about the z-axis, and I_z is the moment of inertia about the z-axis. (The z-axis is the sixfold symmetry axis of the benzene molecule.) Coriolis coupling between degenerate states gives rise to a first-order splitting of the energy[6], $\pm 2\xi AK$, where ξ represents the Coriolis constant, and $A = \hbar^2 / 2I_z$. We estimated the strength of the interaction between two nearly degenerate states by assuming an "effective Coriolis constant" of 0.8 (in line with the larger ones calculated by Robey and Schlag[7]), K=1 (since the intensity is decreased even for small K), and A=0.09 cm^{-1}[2]. This gives a Coriolis interaction energy of about 0.15 cm^{-1}. We therefore assume Coriolis coupling, followed by coupling to a non-radiative manifold, occurs when the density of states of the appropriate symmetry reaches the order of six per wavenumber. In this case, the intensity of the non-zero K lines in the calculated spectrum was reduced by a factor of ten, since a reduction of the fluorescence excitation spectrum by at least such a factor was observed experimentally[1]. The rotational

constants used to calculate the spectrum were taken from Riedle *et al*[2]. The original, unperturbed spectrum of the Q-branch is shown in figure 1.

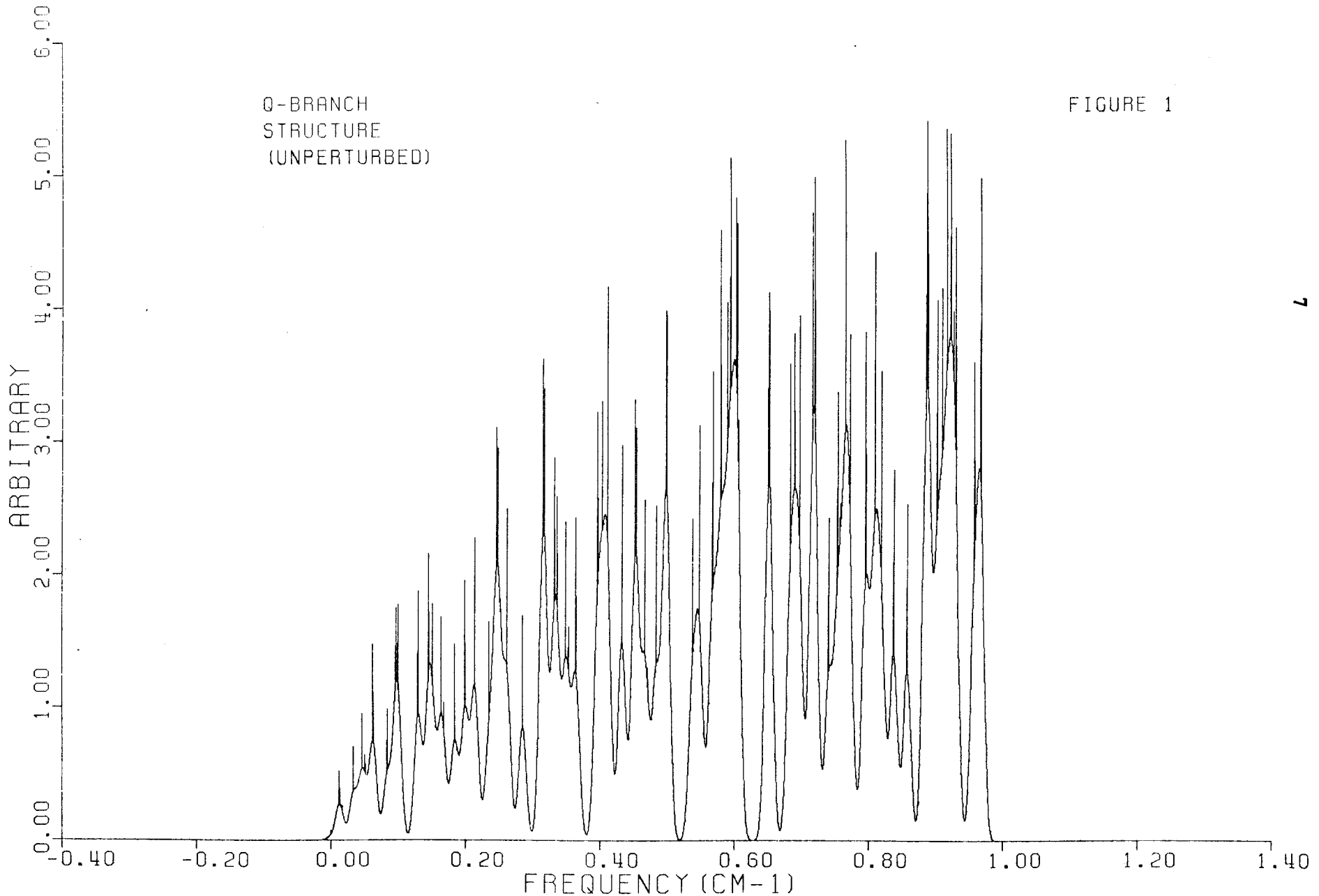

Q-BRANCH
STRUCTURE
(UNPERTURBED)
ARBITRARY
0.00
1.00
2.00
3.00
4.00
5.00
6.00
-0.40
-0.20
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
FREQUENCY (CM-1)

FIGURE 1

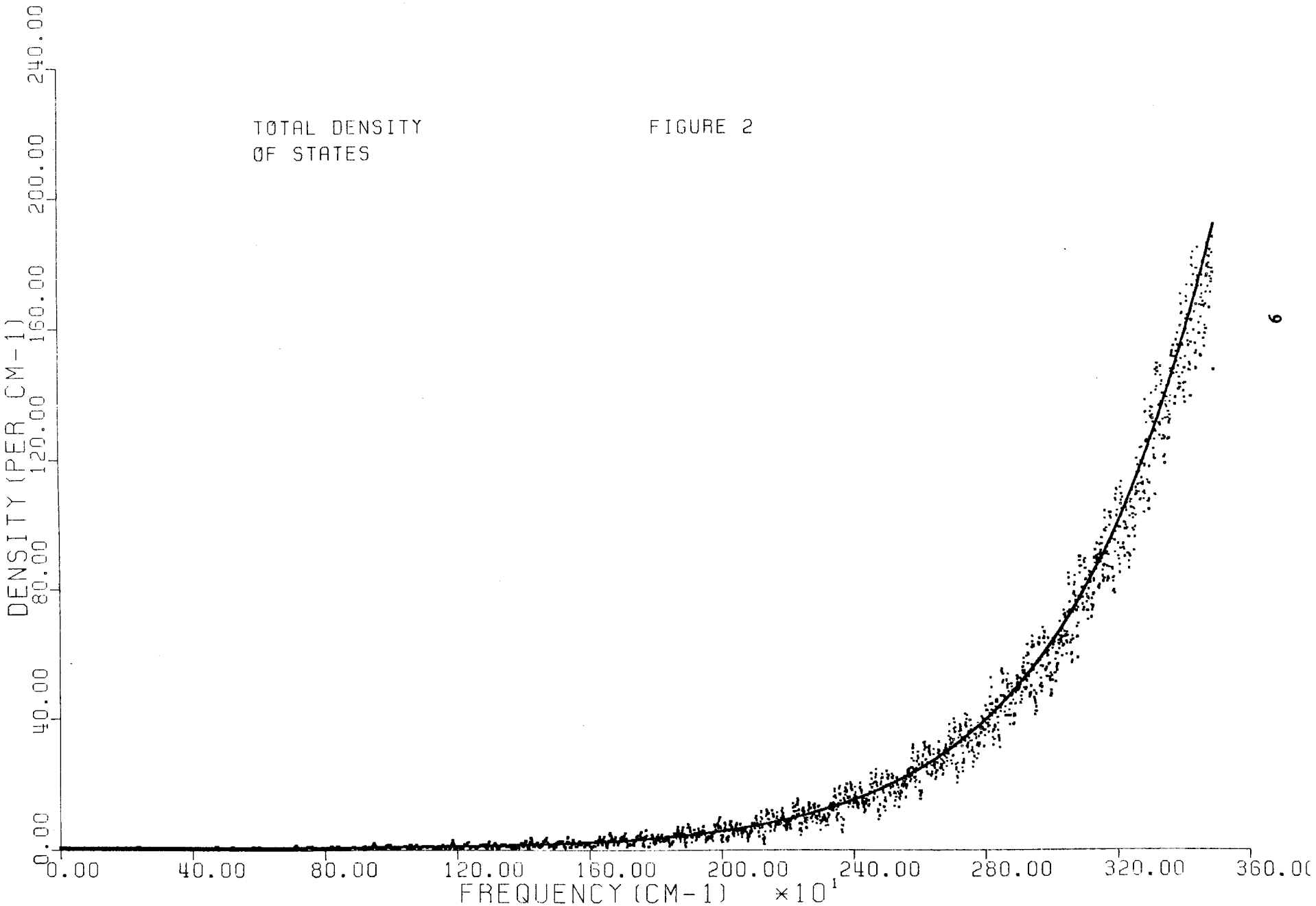
Results and Discussion

(a) Results of Riedle *et al*

Two (harmonic) vibrations will undergo Coriolis coupling if the direct product of the symmetries contains the symmetry of the rotation involved[6]. In the case of benzene, which has point group D_{6h}, the relevant rotation is that about the figure axis, R_z, which has symmetry a_{2g}. The $14^1 1^n$ states have symmetry b_{2u}, and will therefore couple with states of symmetry b_{1u} since the direct product of these symmetries is $b_{1u} \times b_{2u} = a_{2g}$[8]. The strength of this coupling depends on both the difference in energy of the two states, which we consider here, and on the Coriolis matrix element, which we have assumed to be that resulting from an "effective Coriolis constant" of 0.8 (see above). The total density of vibrational states as a function of energy is shown in figure 2. The scattered points are the result of direct counting, while the solid line is obtained from the Whitten-Rabinovitch approximation[9]. The agreement between the two is remarkably close. (The frequencies for this calculation were taken from Ref. 7.) The total number of states of energy up to 3500 cm^{-1} was found to be about 80,000; this calculation took about 3 CPU seconds on a VAX 11/780.

TOTAL DENSITY
OF STATES

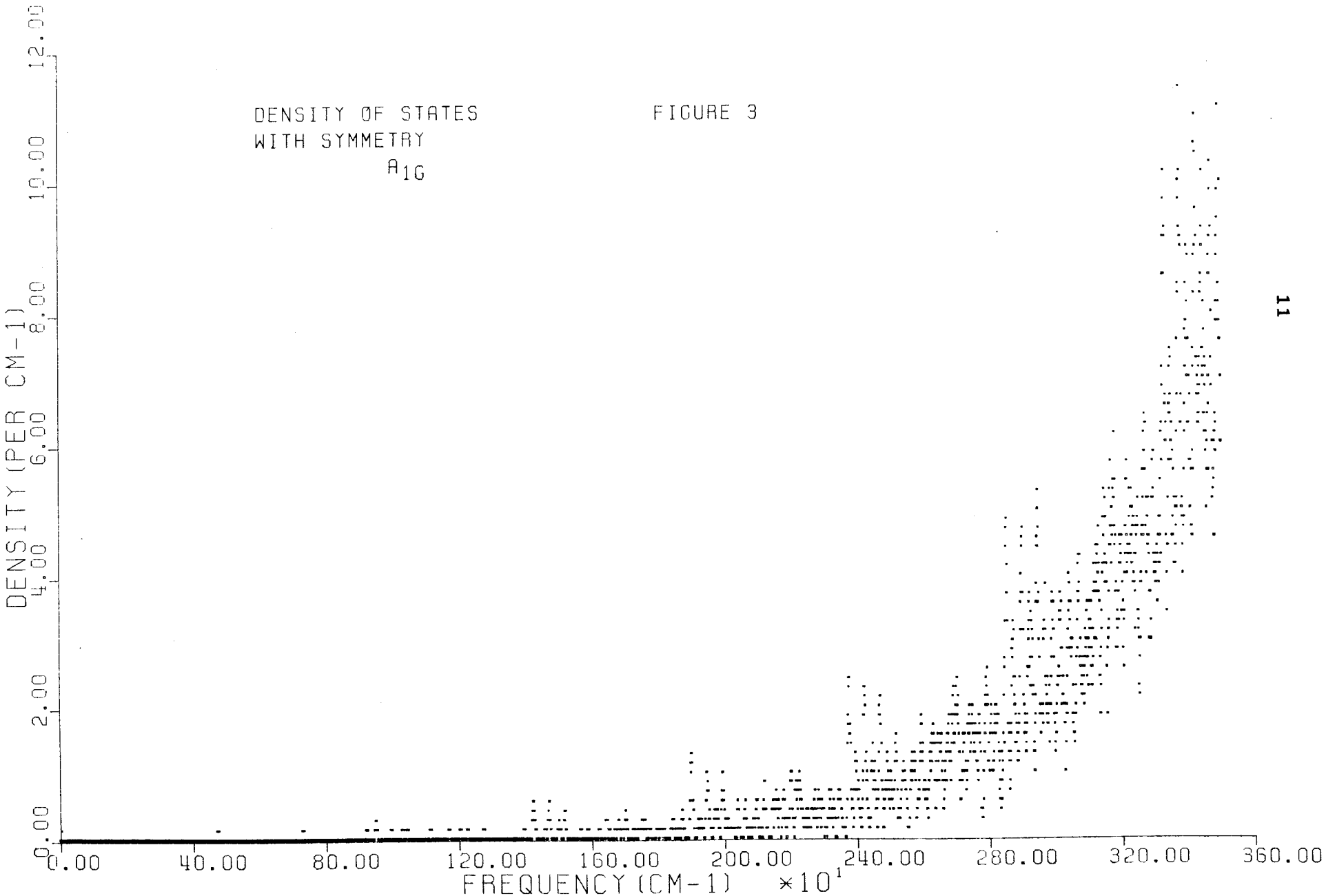
FIGURE 2



The next step was to calculate the density of states of a given symmetry as a function of energy. This was done by detailed counting on a digital computer, taking into account the symmetries of combination and overtone states[10,11]. The results for each of the twelve symmetries of a D_{6h} molecule are shown in figures 3 through 14. Particular attention should be directed to figure 9, which shows the density of states for symmetry b_{1u}. The densities are about 7, 1, and <1/2 states per cm^{-1} for energies of 3414, 2488, and 1564 cm^{-1}, respectively, corresponding to the $14^1 1^n$ states for n = 2, 1, and 0, respectively. The first density is high enough to satisfy the criterion described above, around 6 states per cm^{-1}, especially when it is considered that anharmonic considerations will increase the density of states somewhat. The second and third densities are too low for there to be a high probability of coupling to the non-radiative manifold. With the *ad hoc* assumption that at least one state coupled to the $14^1 1^2$ state is strongly coupled to the non-radiative manifold, and that this coupling thereby reduces the intensity of nonzero K lines by a factor of ten, we get the perturbed spectrum shown in figure 15. The nonzero K lines would actually be spread out even further because of Coriolis splitting, and perhaps the $\pm$K degeneracy would be split by higher-order Coriolis interactions as well. In the absence of detailed calculations of these two splittings, we have omitted their

DENSITY OF STATES
WITH SYMMETRY
A_{1G}

FIGURE 3



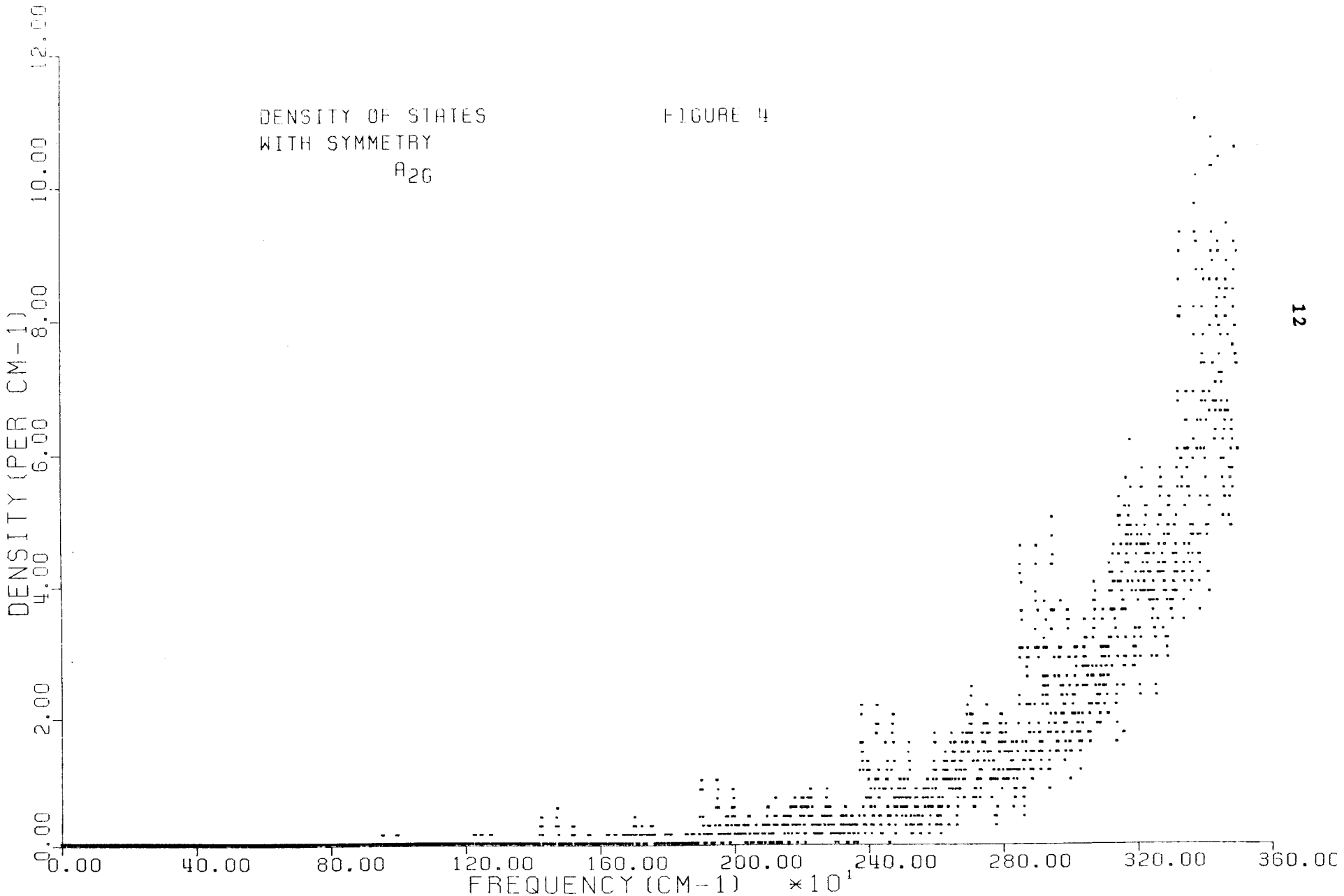
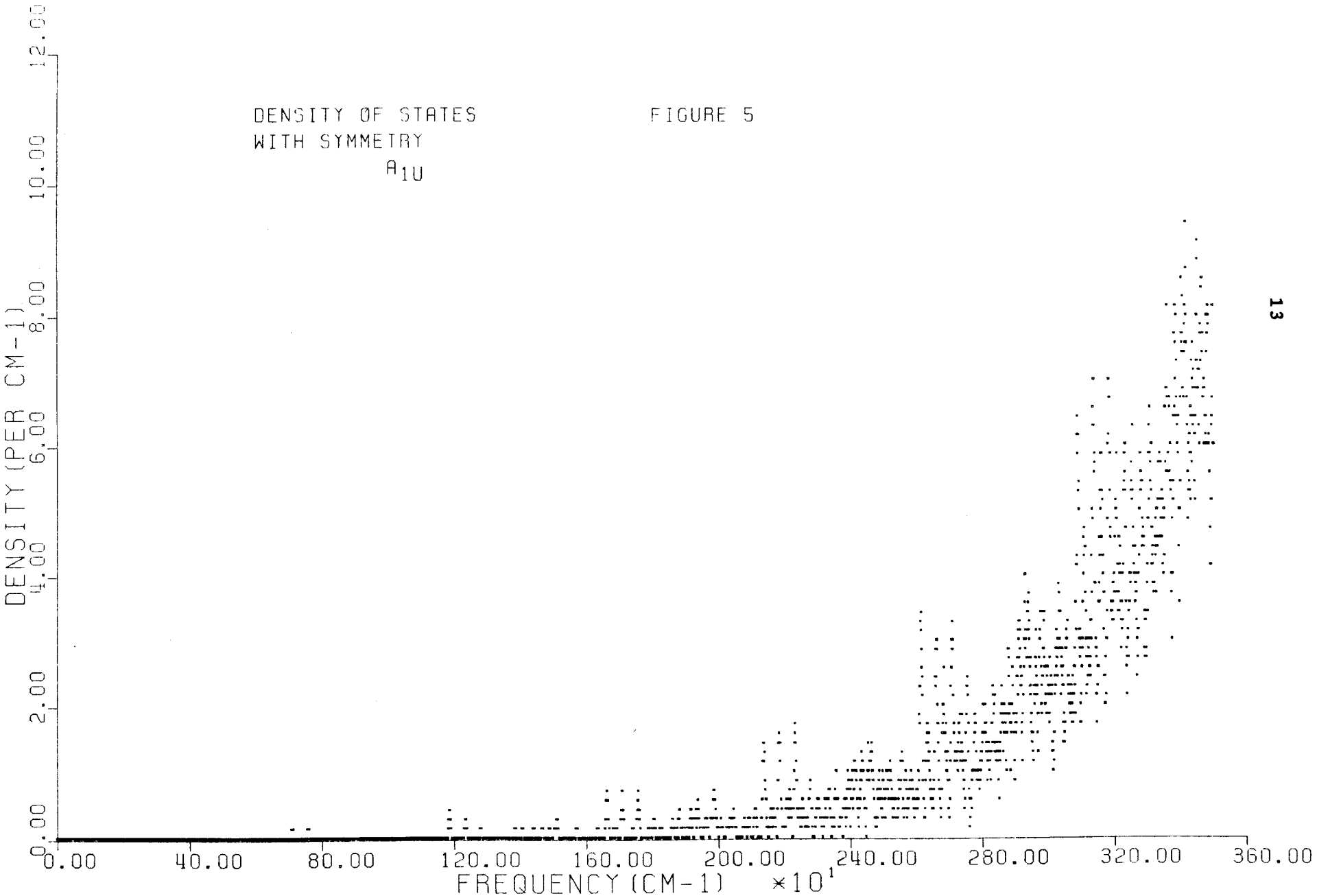

DENSITY OF STATES
WITH SYMMETRY
A_{2G}
DENSITY (PER CM-1)
0.00
2.00
4.00
6.00
8.00
10.00
12.00
0.00
40.00
80.00
120.00
160.00
200.00
240.00
280.00
320.00
360.00
FREQUENCY (CM-1) $\times 10^1$

FIGURE 4

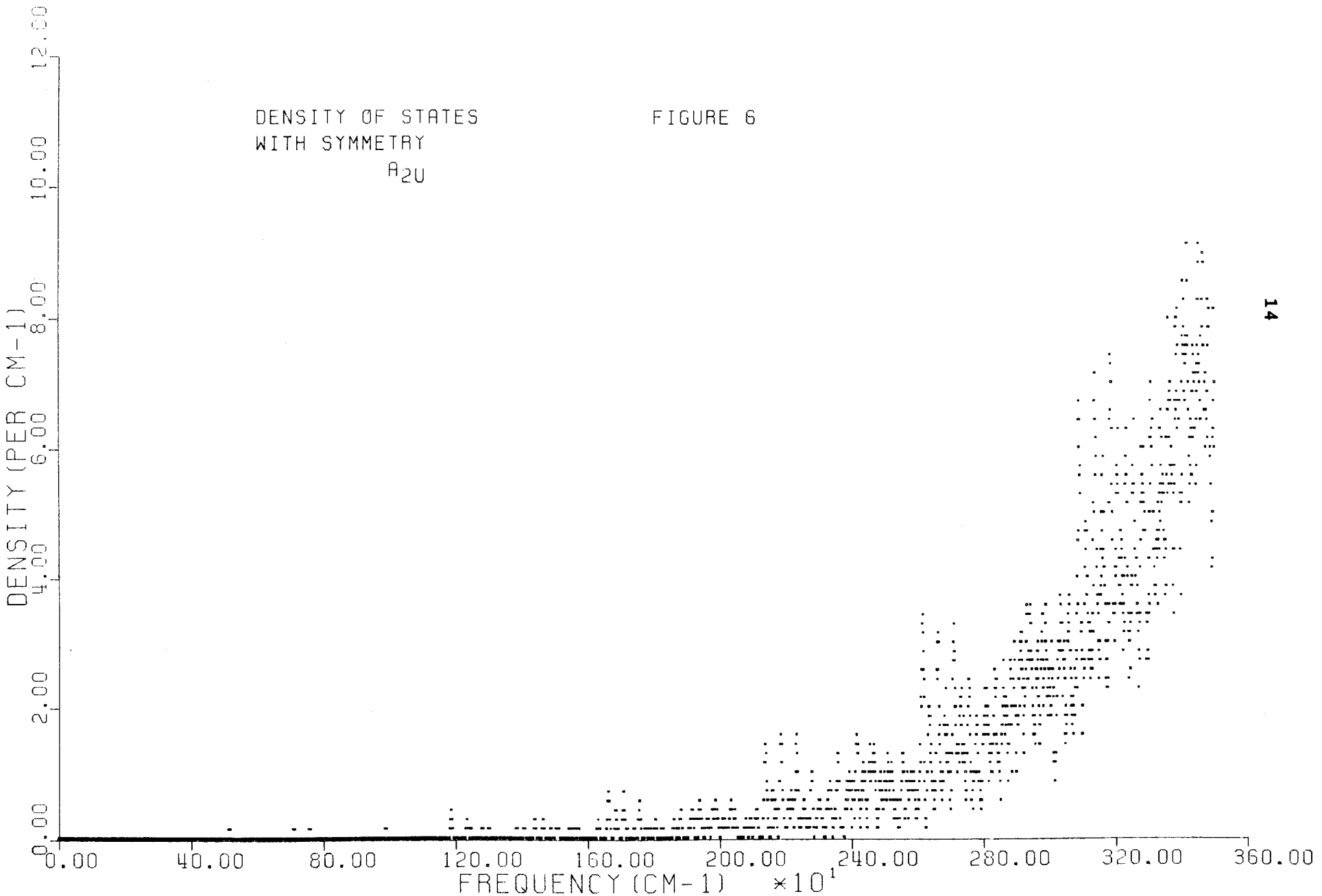
DENSITY OF STATES
WITH SYMMETRY
A_{1U}

FIGURE 5



DENSITY OF STATES
WITH SYMMETRY
A_{2U}

FIGURE 6



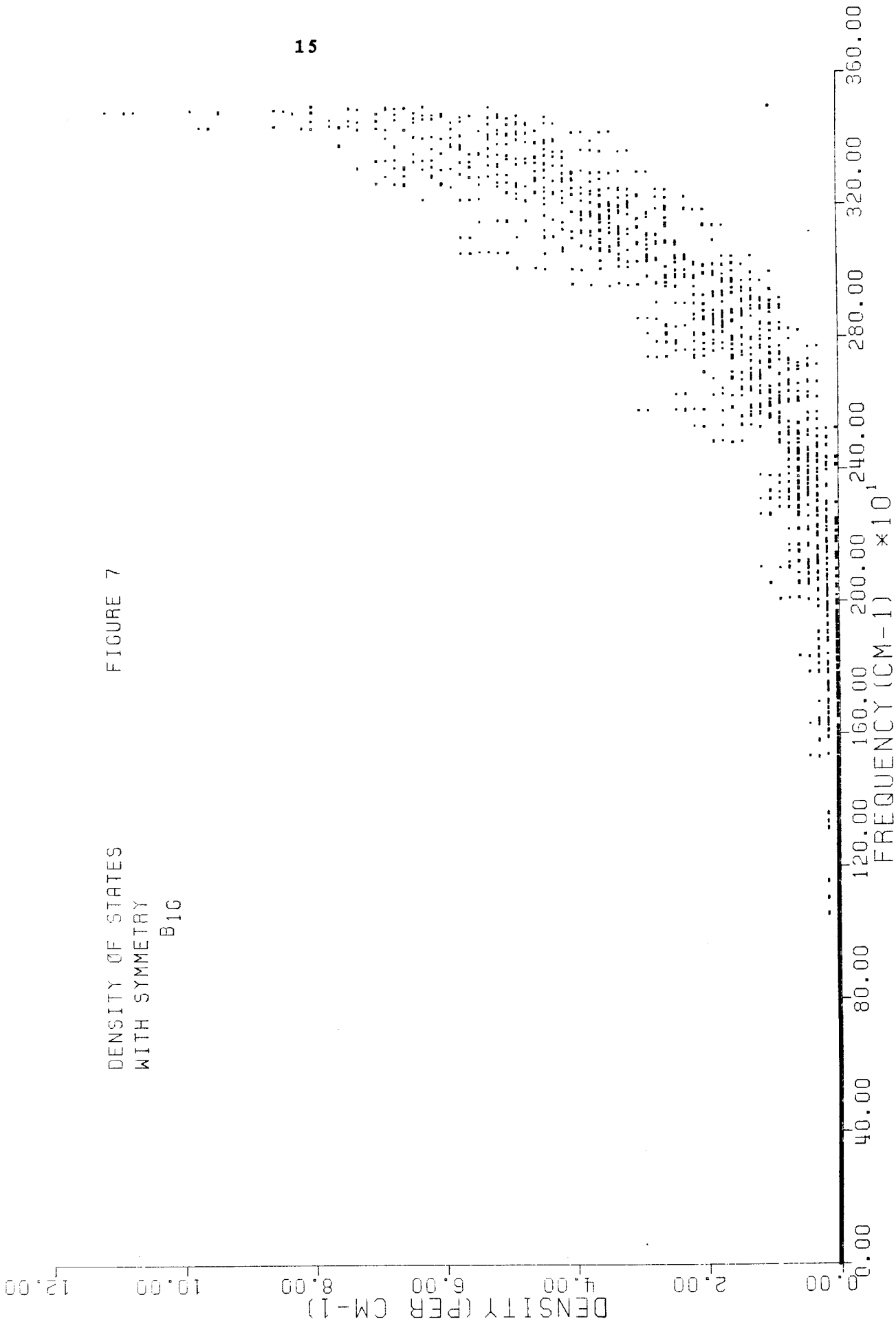
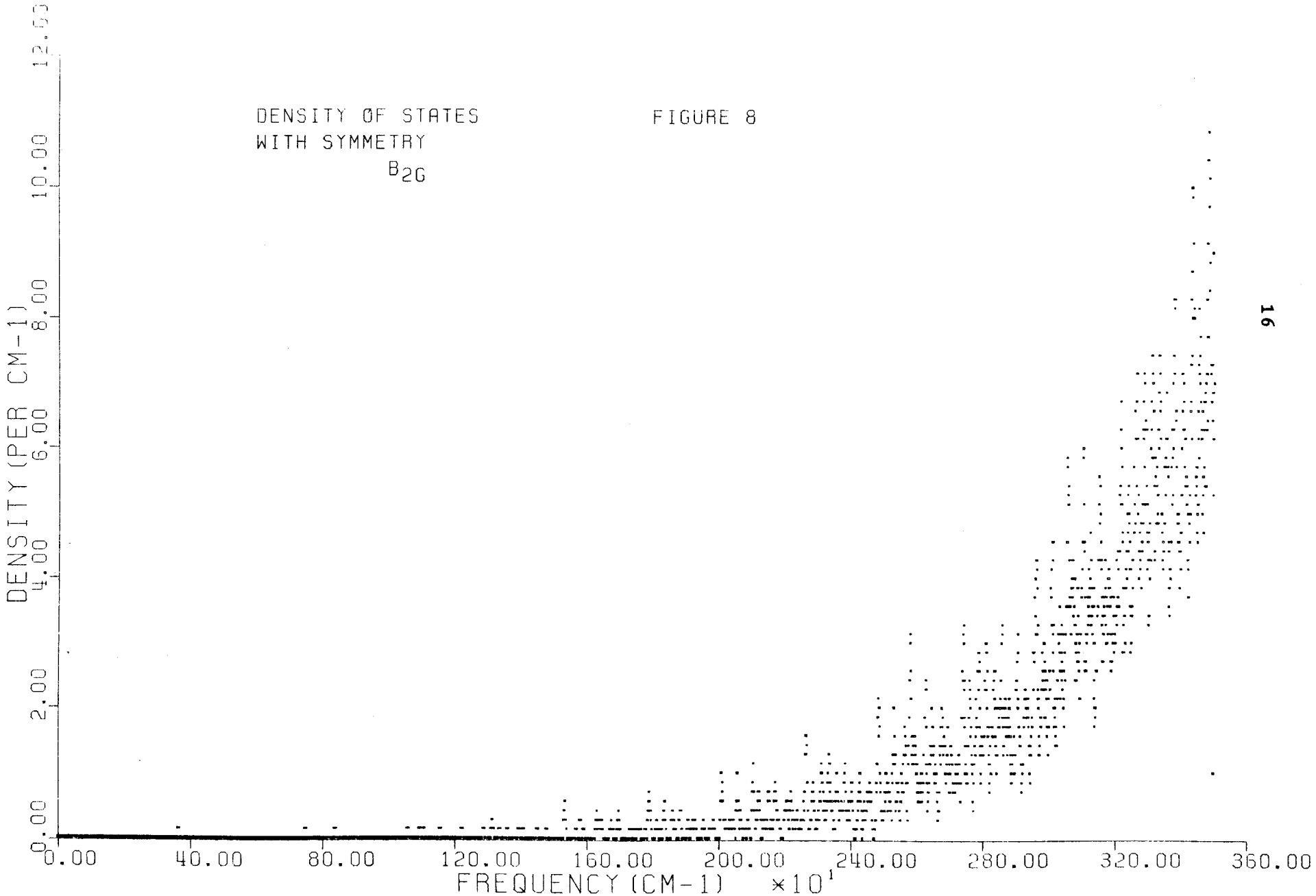

DENSITY OF STATES
WITH SYMMETRY
B1G
DENSITY (PER CM-1)
0.00
2.00
4.00
6.00
8.00
10.00
12.00
0.00
40.00
80.00
120.00
160.00
200.00
240.00
280.00
320.00
360.00
FREQUENCY (CM-1) *10¹

FIGURE 7


DENSITY OF STATES
WITH SYMMETRY
B_{2G}
FIGURE 8
DENSITY (PER CM-1)
0.00
2.00
4.00
6.00
8.00
10.00
12.00
0.00
40.00
80.00
120.00
160.00
200.00
240.00
280.00
320.00
360.00
FREQUENCY (CM-1) $\times 10^1$

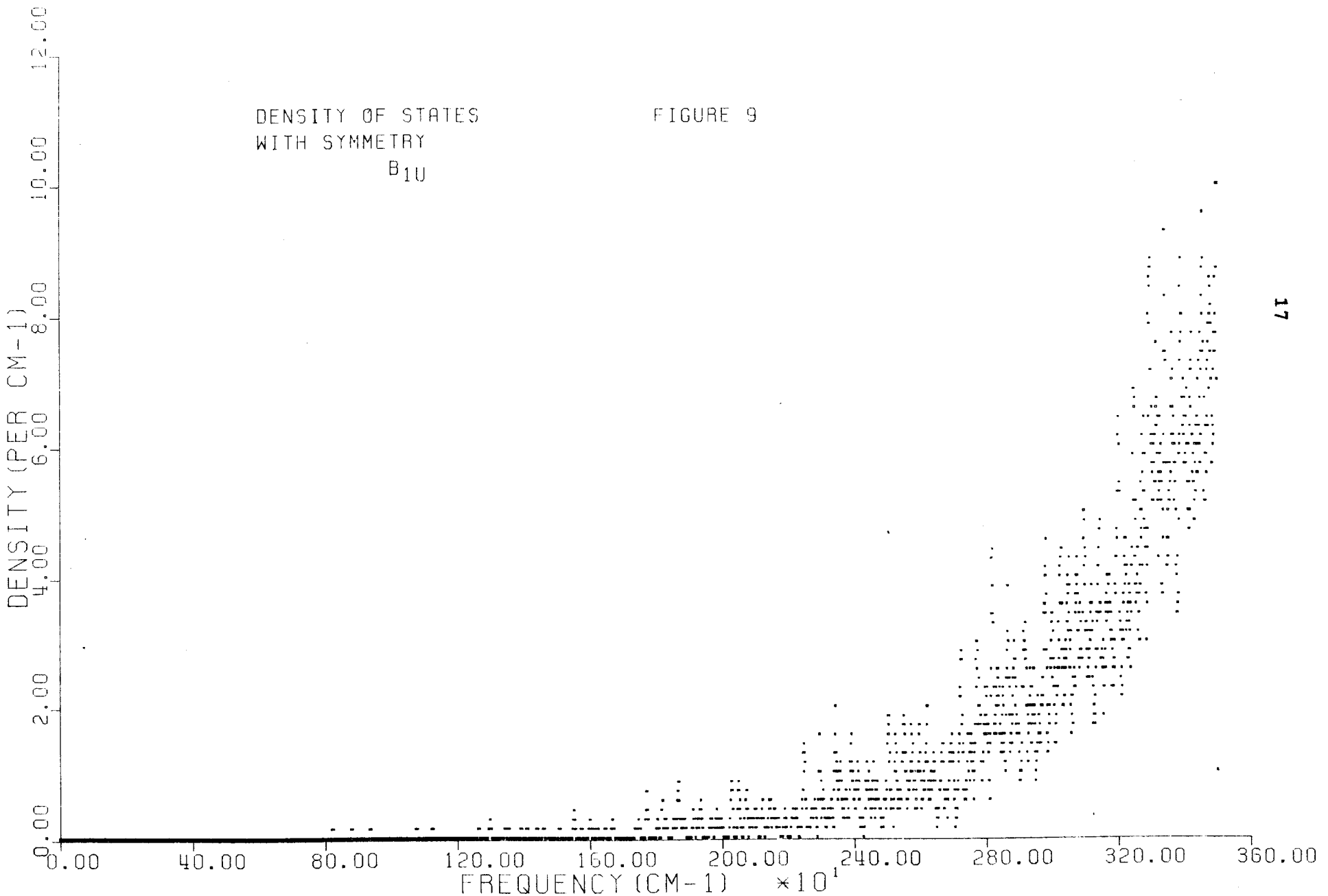

DENSITY OF STATES
WITH SYMMETRY
B_{1U}
DENSITY (PER CM-1)
0.00
2.00
4.00
6.00
8.00
10.00
12.00
0.00
40.00
80.00
120.00
160.00
200.00
240.00
280.00
320.00
360.00
FREQUENCY (CM-1) $\times 10^1$

FIGURE 9

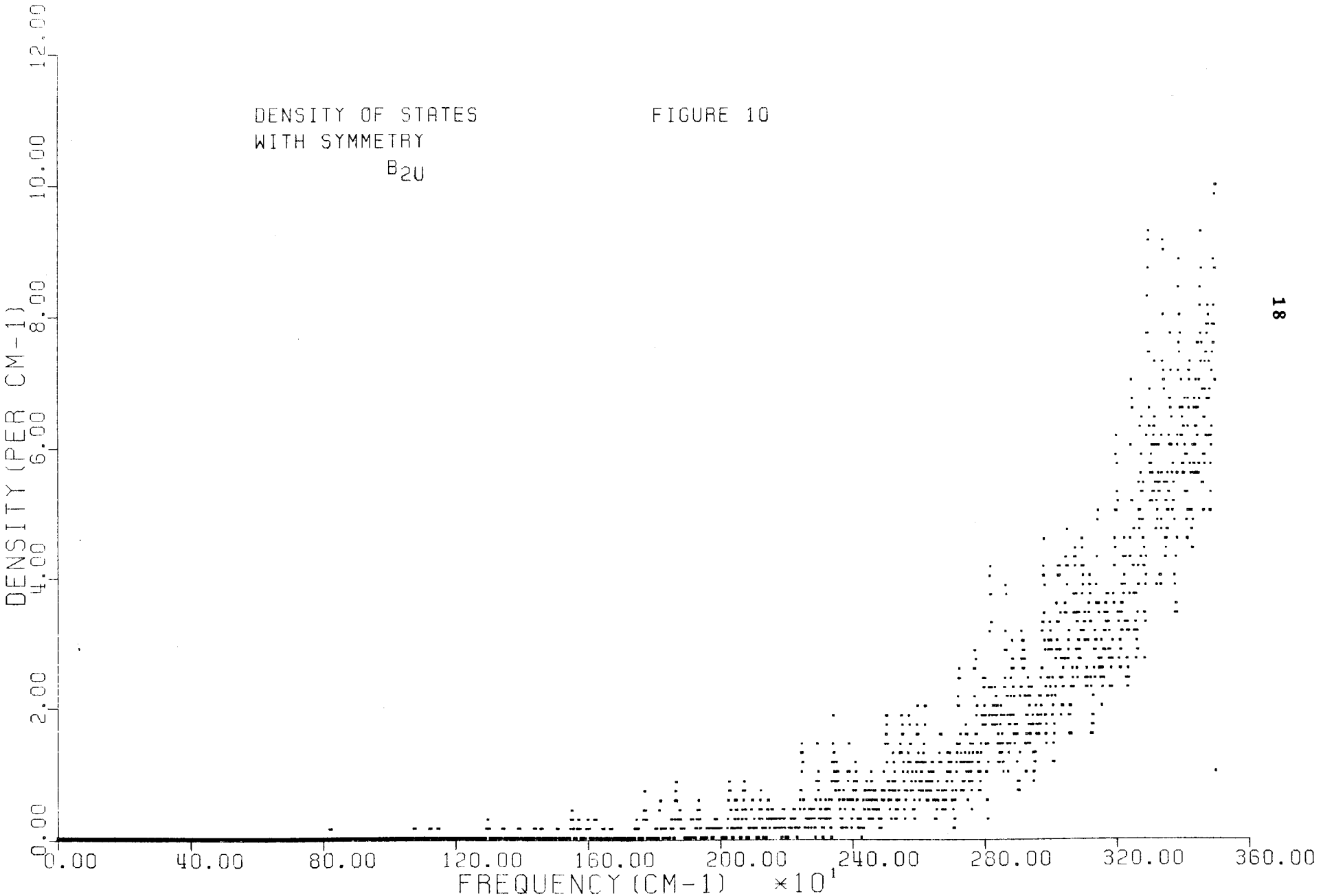
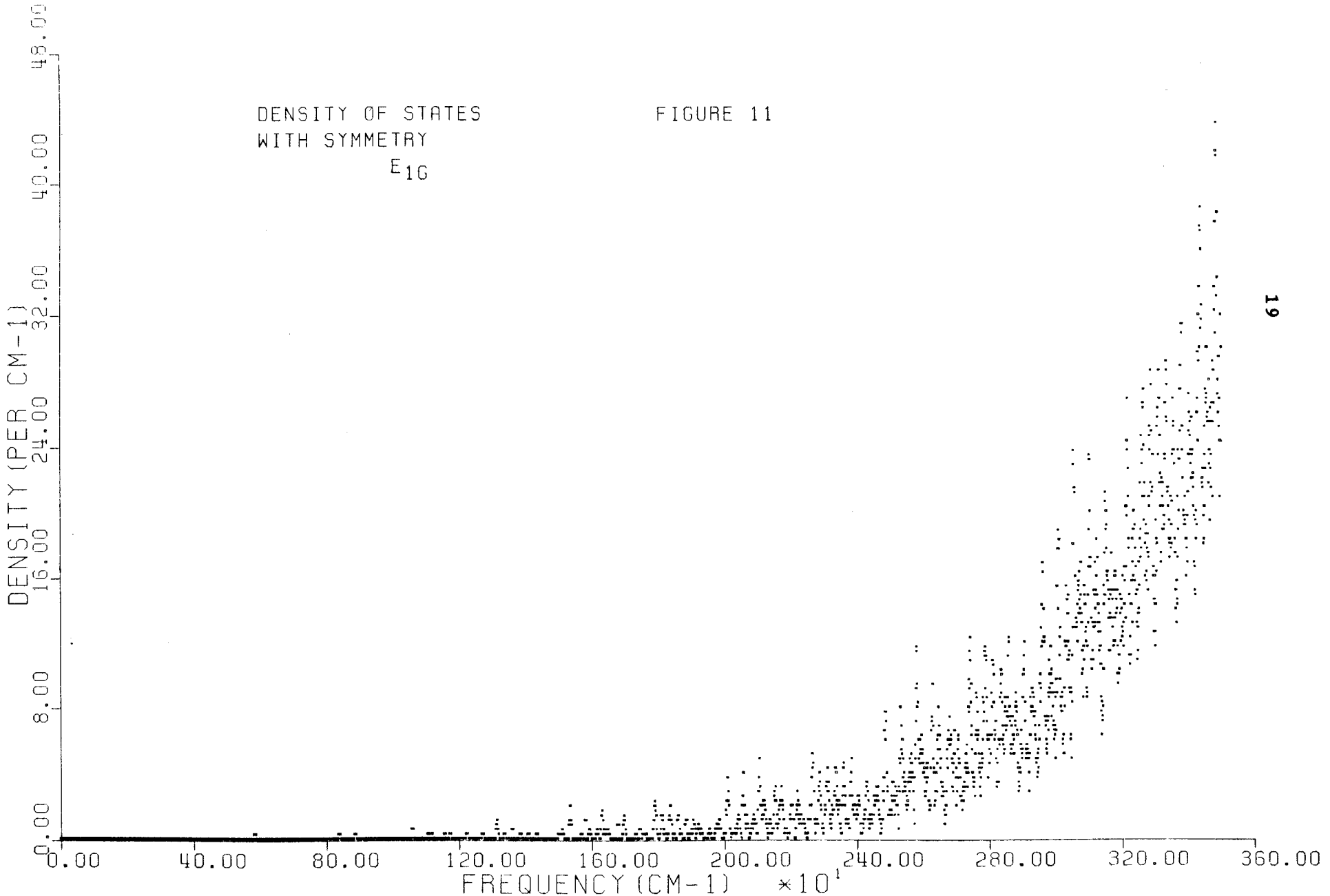
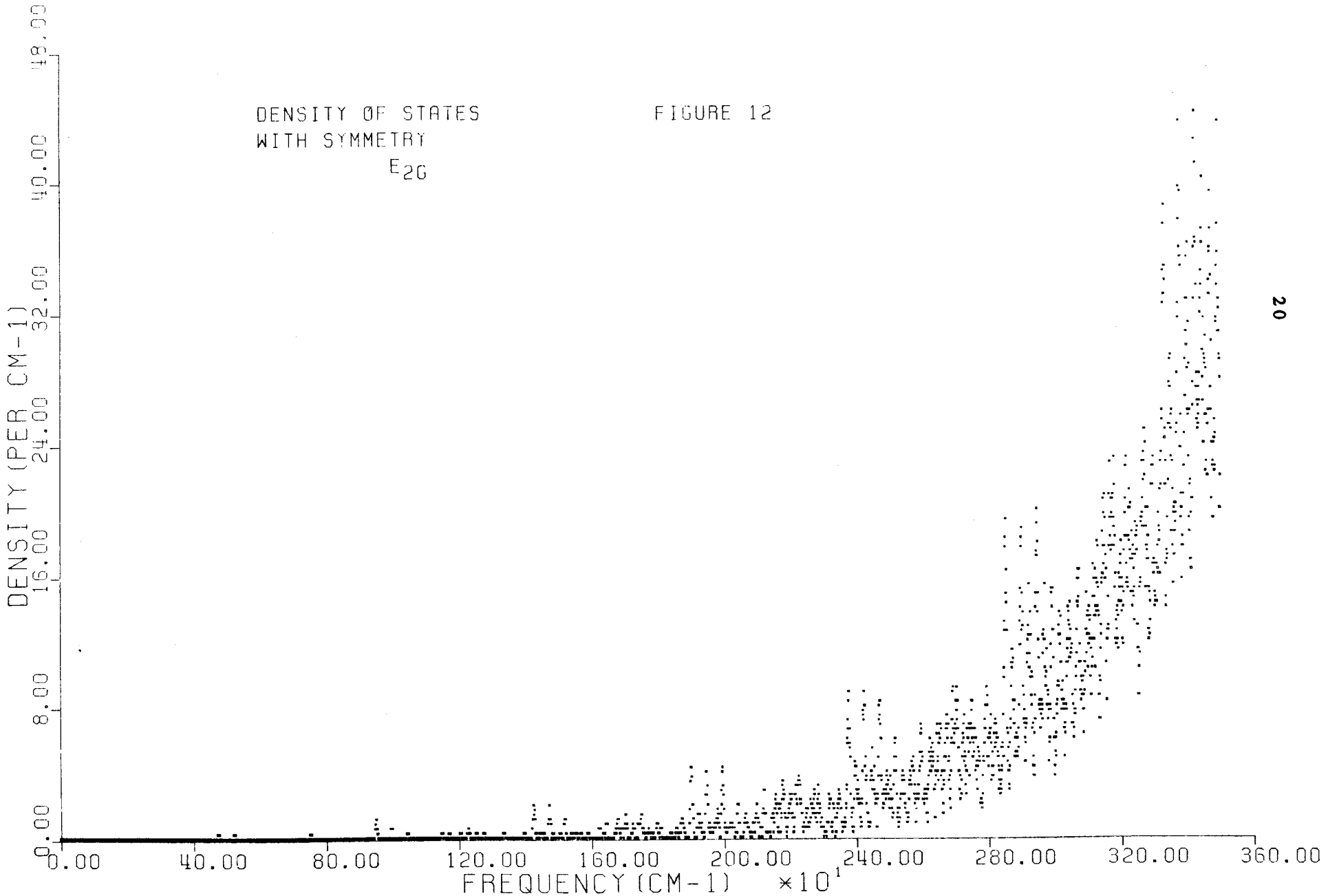

DENSITY OF STATES
WITH SYMMETRY
B_{2U}
DENSITY (PER CM-1)
0.00
2.00
4.00
6.00
8.00
10.00
12.00
0.00
40.00
80.00
120.00
160.00
200.00
240.00
280.00
320.00
360.00
FREQUENCY (CM-1) $\times 10^1$

FIGURE 10

DENSITY OF STATES
WITH SYMMETRY
E_{1G}

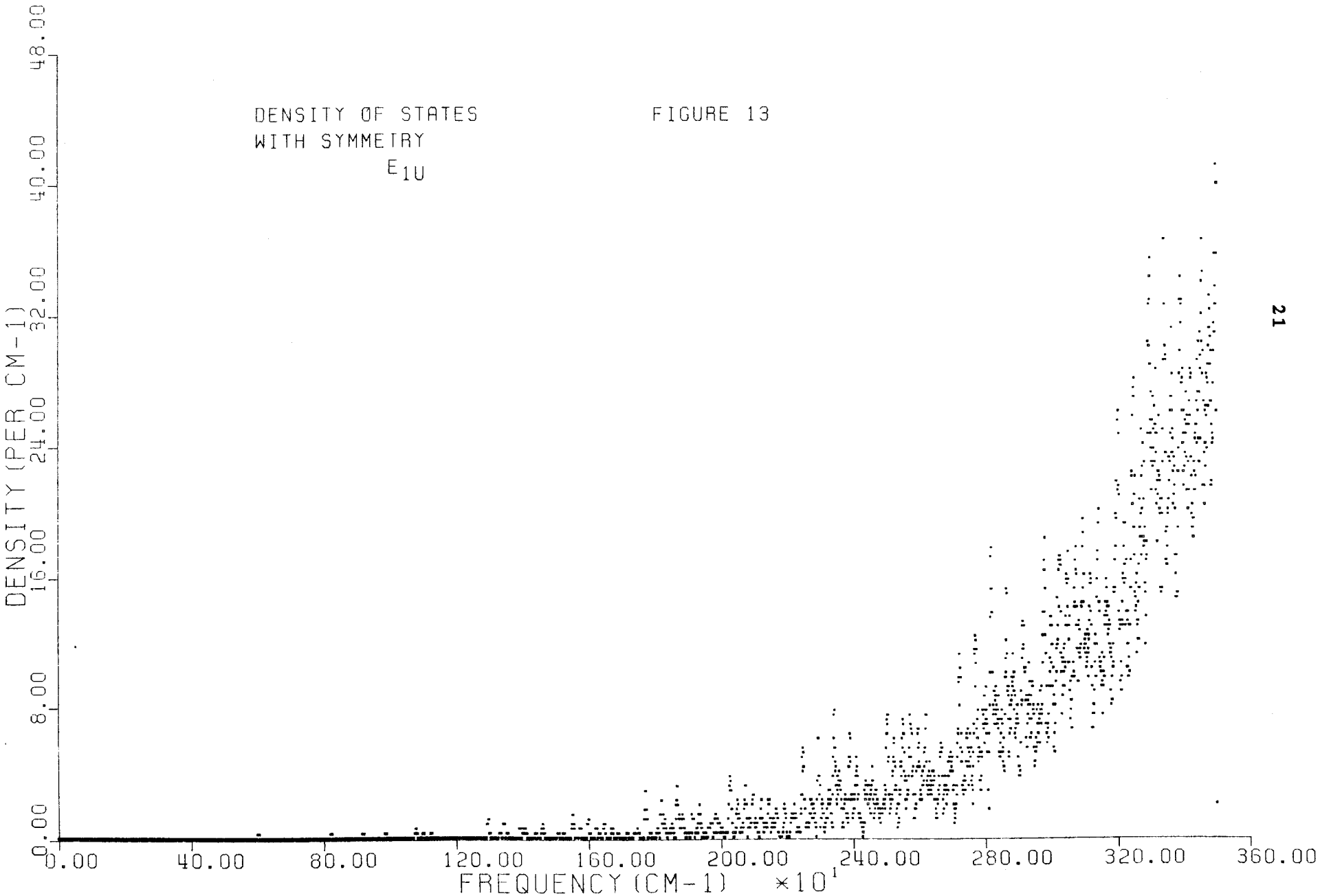
FIGURE 11

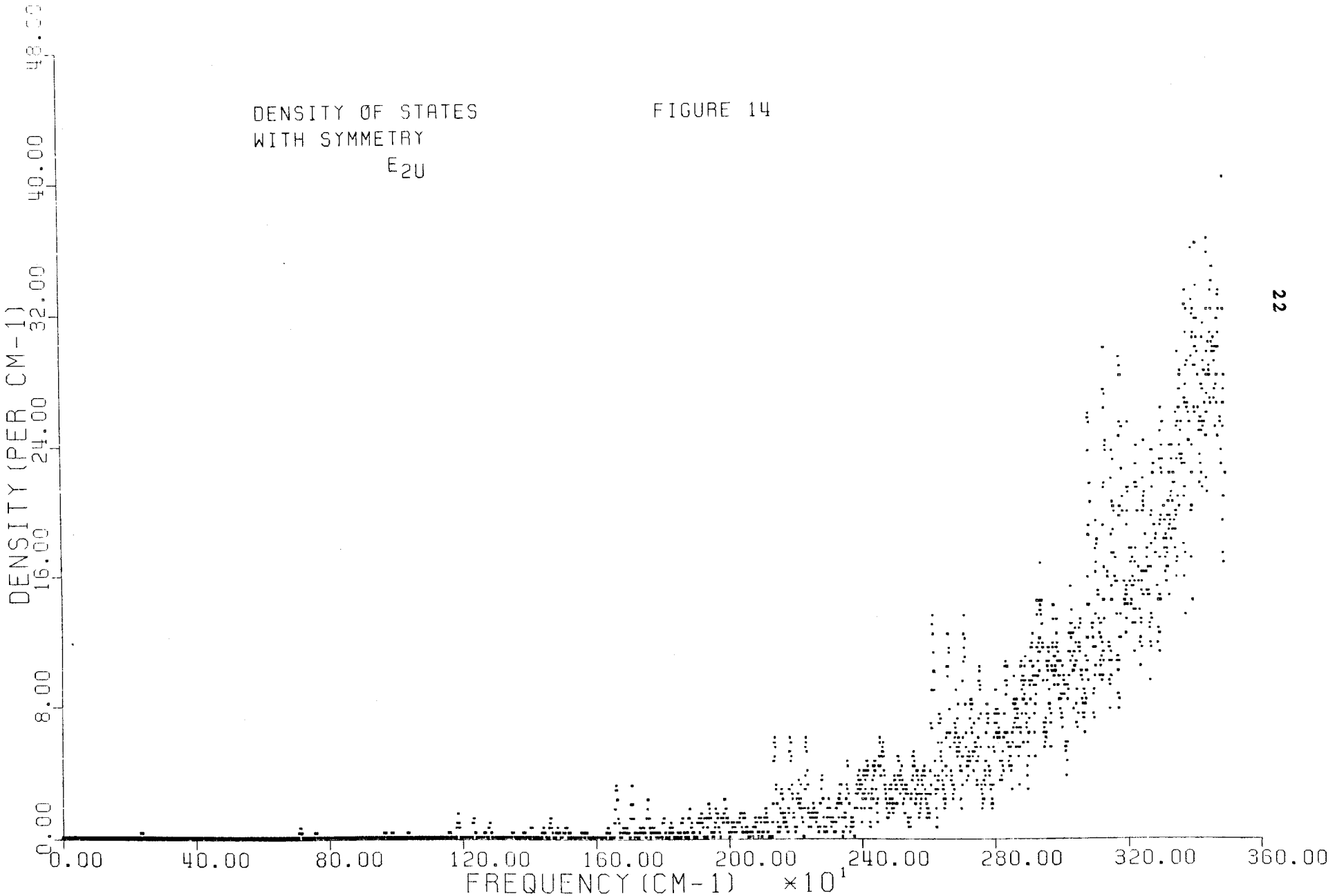



DENSITY OF STATES
WITH SYMMETRY
E_{2G}
FIGURE 12
DENSITY (PER CM-1)
0.00
8.00
16.00
24.00
32.00
40.00
48.00
0.00
40.00
80.00
120.00
160.00
200.00
240.00
280.00
320.00
360.00
FREQUENCY (CM-1) $\times 10^1$

DENSITY OF STATES
WITH SYMMETRY
E_{1U}

FIGURE 13




DENSITY OF STATES
WITH SYMMETRY
E_{2U}
FIGURE 14
DENSITY (PER CM-1)
0.00
8.00
16.00
24.00
32.00
40.00
48.00
0.00
40.00
80.00
120.00
160.00
200.00
240.00
280.00
320.00
360.00
FREQUENCY (CM-1) $\times 10^1$

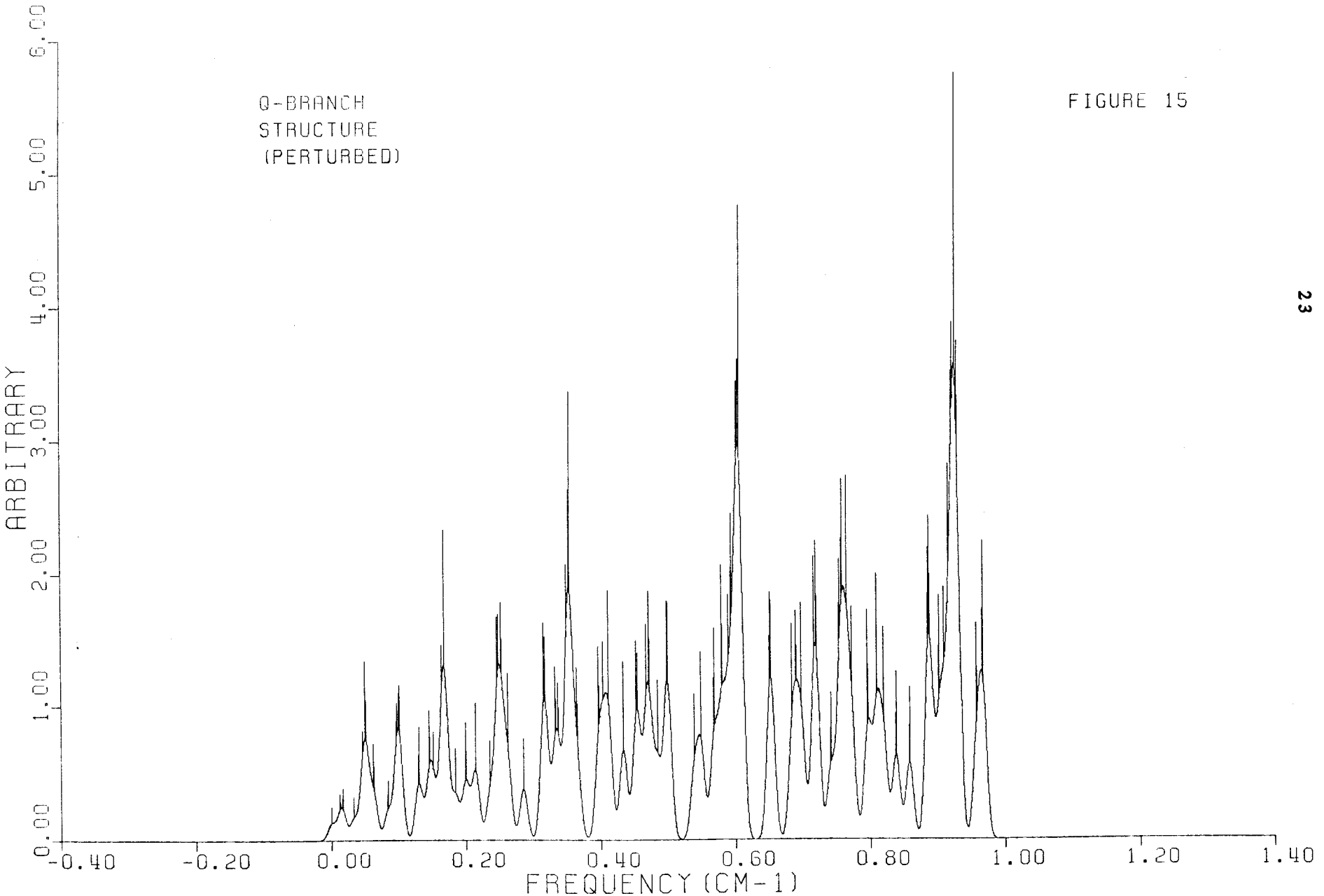

Q-BRANCH
STRUCTURE
(PERTURBED)
ARBITRARY
0.00
1.00
2.00
3.00
4.00
5.00
6.00
-0.40
-0.20
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
FREQUENCY (CM-1)

FIGURE 15

contribution to the spectrum shown.

For comparison, the experimental spectra of ref. 1 are shown in figure 16. (Note the different energy scales.) The qualitative agreement with the calculated spectra of figures 1 and 15 is good.

(b) Predictions for Other Transitions

One prediction our model makes is that if this phenomenon were observed in other transitions with weaker Coriolis coupling, there might be some rotational structure for low K even when that for larger K is obscured, since the strength of the Coriolis interaction is proportional to K.

Another prediction this model can make is whether this type of rotational structure is to be expected in other transitions, assuming the primary state is not itself strongly coupled to a non-radiative manifold. Of the stronger two-photon transitions in benzene[3] with symmetry b_{2u}, this structure might be observable in the $15^1_0 1^2_0$ transition at 2995 cm^{-1}, with a harmonic density of b_{1u} states around 3 per cm^{-1}, but would probably not be seen for the $14^1_0 11^2_0$ transition at 2599 cm^{-1}, with a harmonic density around 1 per cm^{-1}.

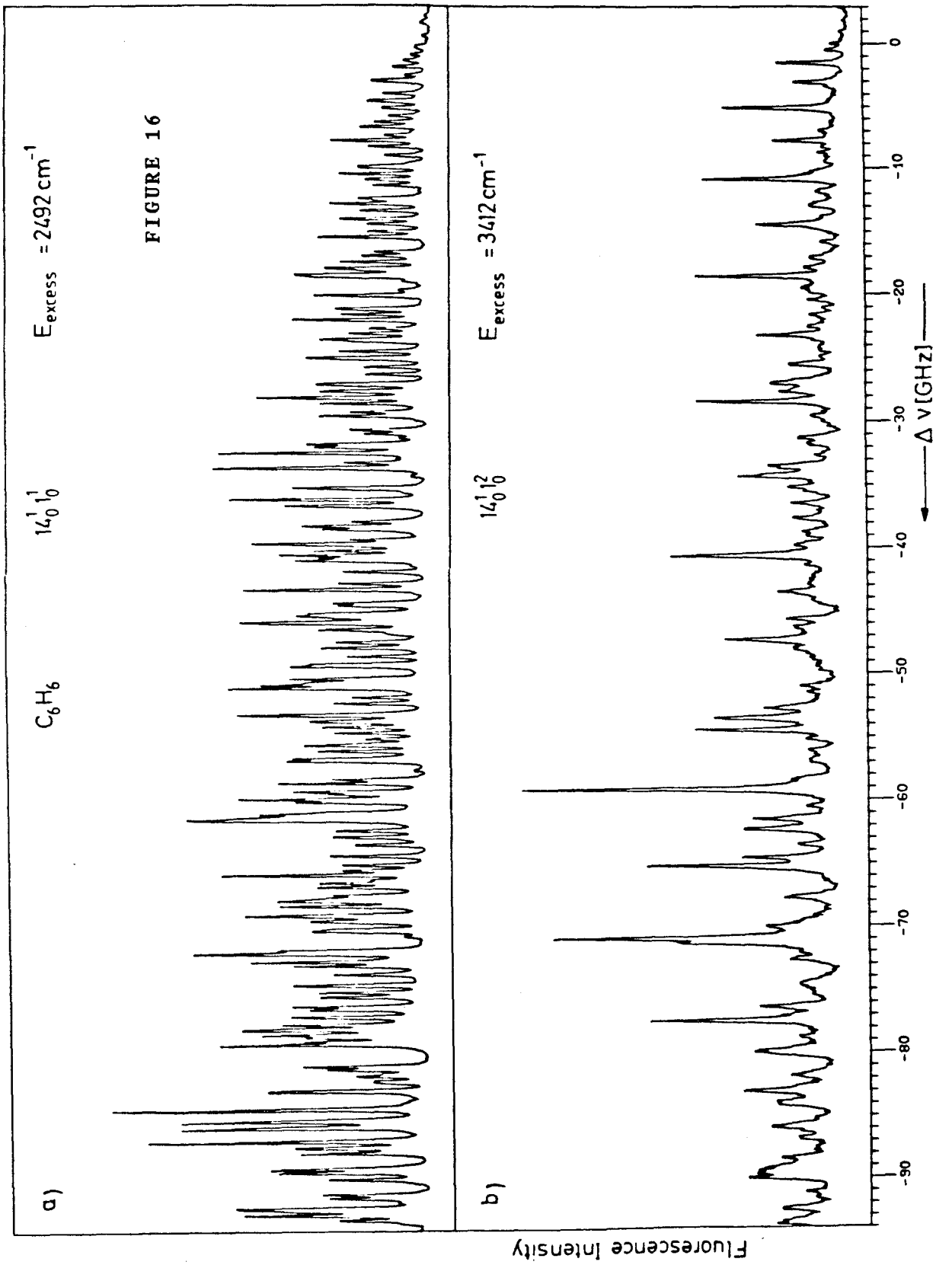

a)
C_6H_6
$14_0^1 1_0^1$
$E_{excess} = 2492\,cm^{-1}$
b)
$14_0^1 1_0^2$
$E_{excess} = 3412\,cm^{-1}$
Fluorescence Intensity
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
Δ ν [GHz]

FIGURE 16

Of the transitions with symmetry e_{1u}, which couple to other states of the same symmetry, the structure might be observable in the $18_0^1 1_0^2$ transition at 2770 cm^{-1}, with a harmonic density around 7 per cm^{-1}, but would probably not be seen for the $14_0^1 1_0^1 6_1^1$ transition occurring at 2391 cm^{-1}, with a harmonic density around 2 per cm^{-1}.

Conclusions

We have performed some calculations confirming the qualitative reasonableness of a suggestion by Riedle *et al*[1] to explain their recent observations of the rotational structure in the Q-branches of the $14_0^1 1_0^n$ vibrational progression in the S_0 to S_1 excitation spectrum of benzene.

We have made predictions regarding the likely rotational structure of several transitions in this spectrum. In brief, we concluded that anomalous rotational structure is likely when the density of states with the proper symmetry for Coriolis coupling to the primary state is of the order of six per wavenumber. For weaker coupling, there might be a transition from unperturbed lines for small K to the perturbed spectrum for larger K.

The plots for density of states of the different symmetries as a function of energy appear similar to that for the total density of states, apart from a scale factor. (Each of the eight nondegenerate symmetries has about 4 percent of the total number of states, and each of the four degenerate symmetries has about 17 percent.) It would be interesting to see whether this is in fact the case at high energies, and if so, whether some statistical description of these densities could be found analogous to the Whitten-Rabinovitch approximation.

One aspect of the observed spectrum that the present study does not explain is the onset of a new structure in the $14_0^1 1_0^2$ band at high values of J. One possibility is that for higher J (stronger perturbations) there is a new zeroth-order Hamiltonian. Analogies occur in spectra with double wells as the coupling between the wells increases, and in the pendulum problem as the barrier to hindered rotation decreases. It would be interesting to investigate this possibility by studying the diagonalization of a large matrix of the relevant basis states, and examining the eigenvalue sequences.

Appendix

The material in this appendix is concerned with some cubic anharmonic calculations on the upper surface of benzene which were done earlier in connection with the subject of this thesis, but which were not used in the results reported here. This material is included for the possible future reference of someone doing anharmonic calculations on benzene.

The force field used for the $^1B_{2u}$ excited state was that of Ref. 7. The benzene molecule was assumed to be planar with D_{6h} symmetry, although there is recent evidence for a slight distortion from planarity in the excited state[2]. The normal modes and frequencies were calculated using Wilson's F and G matrix method[12].

We used the simplest anharmonic perturbations to this harmonic model--the contributions to the potential energy from the diagonal cubic terms in the C-C and C-H bond lengths. The perturbing Hamiltonian is

$$H' = \sum k_1(\Delta CC)^3 + \sum k_2(\Delta CH)^3 \quad .$$

(It has been observed that the diagonal terms in bond lengths are the most important contributions to both cubic and quartic anharmonic potentials[13].) We initially used the cubic force constants calculated by Pulay *et al*[14], but found that these were too large by a factor of about four

to be consistent with the 1_0^n overtones of the observed spectrum of Garforth and Ingold[15], who found good agreement with the anharmonic form

$$E = \hbar\omega(n + 1/2) - x\hbar\omega(n + 1/2)^2 \text{ , where}$$

$$\hbar\omega = 924 \text{ cm}^{-1} \quad \text{and} \quad x\hbar\omega = 0.5 \text{ cm}^{-1}.$$

Instead we used an anharmonicity consistent with these overtones. (This is discussed further below.) First-order nondegenerate perturbation theory was used to calculate the anharmonic vibrational wavefunctions. This calculation is consistent with our use of second-order perturbation theory to calculate the energies of some of the vibrational overtones. (An odd perturbation leaves the energies unchanged to first order.)

Initially we used the cubic force constants of Pulay et al[14] to calculate the anharmonic perturbations in benzene, but obtained perturbations that were far too large. (These constants were -34.0 aJ/Å^3 for the C-H stretches and -40.7 aJ/Å^3 for the C-C stretches.) As a check, we calculated the overtone frequencies for the 1_0^n (symmetric C-C stretch) progression, which are known to deviate only slightly from a purely harmonic progression[15]. The calculated frequencies were too anharmonic. New values for both constants of -9.0 aJ/Å^3 gave reasonable agreement with the first few terms of the progression[16]. (These results are relatively insensitive to the anharmonicity of

the C-H stretches since the principal motions involved are C-C stretches.)

There are several possibilities for the origin of the discrepancy with the calculation of Pulay *et al*. The published values were for the ground state, not the excited state, but it seems unlikely that this would cause a difference of half an order of magnitude since the ground state symmetric C-C stretch progression 1_n^0 in the phosphorescence spectrum of benzene is also quite harmonic[17]. The reported *ab initio* values were apparently calculated from the distortions of individual bonds, not symmetric (or antisymmetric) combinations of bond distortions. This could make a significant difference in the higher order corrections (which are, after all, relatively small). (It should be noted that the same anharmonic corrections do not necessarily apply to all distortions; rather, they are a function of the normal coordinate(s) involved.) Finally, it might be the case that an *ab initio* surface which does well for the harmonic force constants is not as accurate for higher order terms.

The cubic contributions to the wavefunctions were in the neighborhood of 1 to 8 percent.

The F and G matrix method of Wilson[12] is a time-honored method of finding frequencies and normal modes of polyatomic molecules. (Chapter 10 is devoted to a

sample calculation for benzene.) There are standard routines for doing this, but doing it oneself allows for more flexibility and makes calculating Coriolis constants fairly simple since one has the B matrix needed for the Coriolis constants as an intermediate result from generating the G matrix. ("Dummy" zero frequency modes may have to be appended to the B matrix to make it square before inversion if the zero frequency modes are initially separated out of the coordinate system.) The EISPACK eigensystem package of the NATS (National Activity to Test Software) served very well in diagonalizing the matrices, and the Givens procedure did well inverting matrices. Although we found fault with their anharmonic constants, the harmonic force field of Pulay _et al_ for the ground state of benzene[14] seems to be a good one if needed. (We actually did not use the ground state surface anywhere in these calculations since we did not explicitly compute Franck-Condon factors.) Robey and Schlag's force field for the excited state of benzene[7] seems to be the best to date. One should pay close attention to their sign conventions, which are a little confusing, but are defined in the body of the paper. One should also note that different authors use different internal coordinates or have what appear to be the same coordinates when in fact some differ by multiplicative constants. We performed the calculations in internal coordinates rather than symmetry coordinates since internal coordinates are more versatile for anharmonic

calculations or for extensions to substituted benzenes; the amount of CPU time needed to diagonalize a 30x30 matrix with EISPACK is negligible. There are two conventions for labeling the normal modes of benzene. The one that appears to be more common, and the one used here, is that of Pitzer and Scott[18]. (The other is that of Herzberg[19].) In the harmonic approximation for a planar molecule, the in-plane modes and out-of-plane modes separate exactly. For a particular calculation, it may be sufficient to calculate just the in-plane modes. (In the calculations reported here, the only information needed regarding the out-of-plane modes was their frequencies, which were added in an ad hoc manner.) However, there is evidence that benzene in the $^1B_{2u}$ state is slightly puckered[2]. It might be interesting to take the puckering into account; however, no dramatic changes in the Q-branch rotational lines would be expected since the molecule would still be a symmetric top.

To calculate the anharmonic wavefunctions, standard first-order nondegenerate perturbation theory was used. (Second-order theory was used to find the positions of the overtones; these were used to estimate the cubic constants.) Diagonalization of the matrix GF gives the matrix L, where S=LQ, S represents the internal coordinates, and Q the normal coordinates. The cubes of the bond length displacements may then be written as a

third order polynomial in the Q's, and the resulting integrals for the matrix elements are separable and may be performed analytically. (We found them with the aid of MACSYMA, the MIT symbolic manipulation language.) The development of anharmonic force fields is not nearly so extensive as that of harmonic force fields, especially for polyatomic molecules. Pliva[13] might serve as a useful starting point, but the literature is sparse. Estimating anharmonicity constants from overtone and combination progressions might be as good a method as any.

References

1. E. Riedle, H. J. Neusser, and E. W. Schlag, J. Phys. Chem 86, 4847 (1982).

2. E. Riedle, H. J. Neusser, and E. W. Schlag, J. Chem. Phys. 75, 4231 (1981).

3. L. Wunsch, H. J. Neusser, and E. W. Schlag, J. Chem. Phys. 66, 386 (1977).

4. L. Wunsch, H. J. Neusser, and E. W. Schlag, Z. Naturforsch. 36A, 1340 (1981).

5. W. M. McClain, Acct. Chem. Res. 7, 129 (1974).

6. E. B. Wilson, J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill 1955, p. 367.

7. M. J. Robey and E. W. Schlag, J. Chem. Phys. 67, 2775 (1977).

8. G. Herzberg, Infrared and Raman Spectra, Van Nostrand 1945, p. 126.

9. P. J. Robinson and K. A. Holbrook, Unimolecular Reactions, Wiley-Interscience 1972, p. 131.

10. Wilson, Decius, and Cross, p. 332.

11. Herzberg, p. 127.

12. Wilson, Decius, and Cross, chap. 4.

13. J. Pliva in Critical Evaluation of Chemical and Physical Structural Information, D. R. Lide and M. A. Paul (ed.), National Academy of Sciences 1974, p 289.

14. P. Pulay, G. Fogarasi, and J. E. Boggs, J. Chem. Phys. 74, 3999 (1981).

15. F. M. Garforth and C. K. Ingold, J. Chem. Soc., 417 (1948).

16. The deviations from harmonicity expected from the results of Garforth and Ingold[9] in the 1^n states for n = 1, 2, and 3 are 1.0, 3.0, and 6.0 cm^{-1}, respectively. The values which were obtained for $k_1=k_2= -9.0$ aJ/Å^3 were 1.6, 3.5, and 5.5 cm^{-1}, respectively.

17. E. R. Bernstein, S. D. Colson, D. S. Tinti, and G. W. Robinson, J. Chem. Phys. 48, 4632 (1968).

18. K. S. Pitzer and D. W. Scott, J. Am. Chem. Soc., 803 (1943).

19. Herzberg, p. 118.