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ANALYSIS OF THE NAPHTHALENE VAPOUR ABSORPTION BANDS AT 3200 Å

II. NAPHTHALENE *d*-8

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The absorption spectrum of octadeuteronaphthalene near 3200 Å has been measured and partially analyzed. The origin is at $32138{\cdot}2\,\mathrm{cm}^{-1}$, $118\,\mathrm{cm}^{-1}$ higher than that of naphthalene *h*-8. The analysis of the spectrum shows a nearly complete similarity to naphthalene *h*-8, with differences only in the relative ability of non-totally symmetrical vibrations to induce absorption along the shorter in-plane molecular axis. In naphthalene this ability is largely confined to two b_{3g} vibrations of $438\,\mathrm{cm}^{-1}$ and $911\,\mathrm{cm}^{-1}$ in the upper state; in naphthalene *d*-8 the b_{3g} vibration of $422\,\mathrm{cm}^{-1}$ behaves analogously to $438\,\mathrm{cm}^{-1}$ and induces the strongest bands in the system, but there are several higher b_{3g} frequencies giving false origins, indicating important changes in the vibrational modes on deuteration. As in naphthalene, long-axis polarized bands show single maxima and short-axis polarized bands two maxima spaced by 2 to $3\,\mathrm{cm}^{-1}$. The band group with principal head $490\,\mathrm{cm}^{-1}$ below the origin shows a structure unique in the whole system: it is proposed that this is due to Coriolis coupling of the a_g fundamental $493\,\mathrm{cm}^{-1}$ to a newly identified b_{3g} fundamental $490\,\mathrm{cm}^{-1}$. Several upper-state fundamentals are reported for the first time.

Sponer & Nordheim (1950) measured the wavelengths of two of the absorption bands of octadeuteronaphthalene vapour, but aside from this no other measurements or analysis of the vapour spectrum have been reported. The work of McClure (1956) on the spectrum of octadeuteronaphthalene embedded in a single crystal of durene does, however, provide much information that is relevant to the free molecule spectrum, and a comparison of it with the vapour bands confirms McClure's claim of 'oriented gas' behaviour in the mixed crystal. The two spectra thus in a sense belong together, and will be compared later in this paper. The main purpose is to report the vapour absorption bands, and to interpret the spectrum in relation to that of naphthalene described in the preceding paper (Craig, Hollas, Redies & Wait 1961). Our analysis of the naphthalene *d*-8 spectrum is incomplete, but the bands principally relevant to the assignment of the transition are

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identified, and a number of ground- and excited-state frequencies confirmed or reported for the first time. Assignments of a number of the other bands are proposed.

The spectrum of naphthalene *d*-8 has, like naphthalene *h*-8, a continuous background due to the onset of the much stronger 2750 Å system. This background, which gets stronger towards higher frequencies, is more intense in *d*-8 and obscures many of the bands at the high-frequency end of the spectrum, and fewer band maxima could be measured. The absence of progressions in the naphthalene *h*-8 spectrum has been discussed already in the previous paper. Totally symmetrical vibrations appear once only in combination with the true and false origins except in a single example of a two-quantum combination. These bands are always much weaker than the origin concerned, showing that the molecule undergoes only a very small dimensional change upon electronic excitation. Exactly the same features are apparent in naphthalene *d*-8, with even less intensity in the combination bands compared with the appropriate origin. The complexity of the spectrum is reduced on this account but the assignment of band groups is made difficult because of the very small number of combination bands observed, which reduces the chance of identifying particular fundamentals, and of distinguishing fundamentals from combinations and overtones.

Experimental

Octadeuteronaphthalene was obtained from Merck and Co. (Canada) and used as received. The isotopic purity was higher than the makers' claimed 99 %, according to the intensity of absorption by $C_{10}D_7H$ which was the only isotopically impure species detected. The spectrum was photographed in the 20 ft. Ebert grating spectrograph with the use of the White cell described in the preceding paper. The frequencies of band heads were measured and common differences identified using an electronic computer.

Results

A complete list of band heads (or maxima) found is given in the appendix. The search for common differences gave the following (averaged) difference frequencies, which appear in well-developed sequences, or in difference bands: 9·3, 49·0, 55·1 and 4·7 cm^{-1} in order of decreasing intensity. Additional, less strongly developed, difference frequencies occur in about 72, 90, 110 and 139 cm^{-1}. Elimination of sequence and difference bands involving these frequencies leaves a set of principal bands for assignment. These are listed in table 1, with visual estimates of intensity and assignments where these are known.

Structure of the band groups

As mentioned in the preceding paragraph, the absorption bands are grouped in sets, related to a principal band by difference frequencies occurring either as sequences or seen only in one difference band. Sequences in 9·3 and 49·0 cm^{-1} occur with up to 5 members. The differences 4·7, 72, 90 and 139 cm^{-1} appear only once in association with each principal head and are never strong, but they can be seen in each of the cases where they are expected (i.e. in association with strong principal bands, and when not obscured by a stronger band) and therefore seem definite. The lower difference frequencies are clearly related to the lower differences in naphthalene itself, both because of close-lying values and because of their similar intensities. The following pairs are related in this way (naphthalene *h*-8 value first): 5·9, 4·7 (26% drop); 10·0, 9·3 (8% drop); 55·5, 49·1 (13% drop); 64, 55 (16% drop). The 55 cm^{-1} difference band is more strongly developed in *d*-8 than is the 64 cm^{-1} in *h*-8, and might have been expected to appear in a second sequence band 110 cm^{-1} from each principal band. In fact a difference band is seen in

TABLE 1. PRINCIPAL BAND HEADS AND ASSIGNMENTS (CM^{-1})

band*	frequency (head splitting)	separation from 0–0 band	intensity	assignment	Δ
b	31 252·6 (2·4)	880·6	vvw	0 − 880·6	—
e	31 388·5	749·7	vw	0 − 749·7	—
d	31 438·4	699·8	vw	0 − 699·8	—
c	31 445·9	692·3	vw	0 − 692·3	—
a	31 648·2†	490·0	m	0 − 490·0	—
b	32 119·5	18·7	—	$C_{10}D_7H$	—
a	32 127·3	10·9	—	$C_{10}D_7H$	—
A	32 138·2	0	mw	origin	—
B	32 484·4	346·2	w	(0 + 2 × 173)	—
A	32 543·8 (2·4)	405·6	w	—	—
B	32 560·1 (2·5)	421·9	vs	0 + 421·9	—
C	32 589·8 (2·4)	451·6	w	—	—
C	32 621·7	483·5	w	0 + 483·5	—
D	32 702·6	564·4	vvw	—	—
E	32 776·6	638·4	vw	0 + 638·4	—
F	32 784·2	646·1	vvw	—	—
D	32 935·9 (2·5)	797·7	vvw	—	—
E	32 960·6 (2·5)	822·4	w	0 + 822·4	—
F	32 978·0 (2·4)	839·6	vw	—	—
G	32 988·6	850·5	vw	—	—
G	32 995·6 (2·4)	857·4	vw	0 + 857·4	—
Y	31 044·3 (2·5)	906·1	vvw	0 + 421·9 + 483·5	+ 0·7
H	33 151·2 (2·4)	1 013·0	vw	—	—
I	33 156·5 (2·5)	1 018·3	vw	—	—
J	33 195·8 (2·4)	1 057·6	w	0 + 421·9 + 638·4	+ 2·7
K	33 219·5 (2·6)	1 081·3	w	—	—
L	33 348·6 (2·4)	1 210·4	vw	—	—
H	33 377·3	1 239·1	vvw	—	—
I	33 379·2	1 241·0	vvw	—	—
J	33 383·9	1 245·7	vvw	—	—
M	33 403·1 (2·3)	1 264·9	w	—	—
K	33 421·1	1 282·9	w	0 + 1 282·9	—
N	33 449·5 (2·3)	1 311·3	vw	—	—
L	33 548·7	1 410·5	w	0 + 1 410·5	—
O	33 731·4 (2·3)	1 593·2	w	0 + 1 593·2	—
P	33 916·2 (2·4)	1 778·0	vw	—	—
Q	33 968·6 (2·0)	1 830·4	vw	—	—
R	33 969·7 (2·2)	1 831·5	vw	0 + 421·9 + 1 410·5	+ 0·9
S	33 998·4 (2·3)	1 860·2	vvw	—	—
N	34 031·4	1 893·2	vw	0 + 438·5 + 1 410·5	+ 0·8
T	34 059·3 (2·4)	1 921·1	vw	—	—
O	34 147·3	2 009·1	vvw	—	—
U	34 347·1 (2·2)	2 208·9	vvw	0 + 1 410·5 + 797·7	− 0·7
V	34 375·9 (2·2)	2 237·7	vvw	0 + 822·5 + 1 410·5	− 4·7
W	34 406·3 (2·2)	2 268·1	vvw	0 + 857·4 + 1 410·5	− 0·2
P	34 560·6	2 422·4	vvw	—	—
X	34 577·5 (2·7)	2 439·3	vvw	—	—
Q	34 953·7	2 815·5	vvw	0 + 2 × 1 410·5	+ 5·5

* Bands in italics have double-headed structure, others are single-headed.

† The principal head is not split; certain sequence members are. See text.

many band groups at about this spacing which may be 2×55: the evidence on this point is conflicting, but we think that there is probably a distinct 110 cm^{-1} difference stronger than, and overlying, the second member of the 55 cm^{-1} sequence. The evidence for this interpretation is that in one group, the *B*-band group, the measured 55 cm^{-1} difference is exceptionally high, at 57·2 cm^{-1}, while the 110 cm^{-1} difference is exceptionally low at 106·6 cm^{-1}. It is unlikely that this would occur if both were members of one sequence. Then, in two other band groups *A* and *a* the 110 cm^{-1} difference band appears at more than twice the frequency of the 55 cm^{-1}. Moreover, the 110 cm^{-1} difference corresponds to the 99 cm^{-1} difference in *h*-8 to which, otherwise, there would be no analogue in *d*-8.

TABLE 2. AVERAGED SEQUENCE INTERVALS IN NAPHTHALENE *h*-8 AND *d*-8 (CM^{-1})

naphthalene *h*-8			naphthalene *d*-8		
band group	10 cm^{-1} sequence	55 cm^{-1} sequence	band group	9 cm^{-1} sequence	49 cm^{-1} sequence
$0-936$	10·0	54·6	—	—	—
$0-760$	9·8	55·4	$0-692$	9·0	47·4
$0-506$	10·3	55·4	$0-490$	9·1	48·3
$0-0$	10·0	55·1	$0-0$	9·0	48·4
$0+438$	10·0	56·2	$0+422$	9·7	51·5
$0+501$	8·9	55·8	$0+438$	7·9	48·3
$0+702$	9·9	53·3	$0+638$	9·0	47·7
$0+911$	10·0	55·1	$0+857$	—	48·4

The averaged sequence spacings differ from one band group to another, and do so more than in naphthalene *h*-8. Table 2 lists values of the 9 and 49 cm^{-1} sequence in several band groups of *d*-8, in comparison with the 10 and 55 cm^{-1} sequences of *h*-8, in band groups which are analogous in the two spectra, i.e. which involve essentially the same accompanying vibrations. The 9 and 10 cm^{-1} sequence intervals show some interesting regularities. The interval is nearly the same when accompanied by a given vibrational mode in ground and upper states: 760 cm^{-1} and its upper state partner 702 cm^{-1} have intervals 9·8 and 9·9 cm^{-1} in *h*-8, 692 and 638 cm^{-1} have intervals 9·0 and 9·0 cm^{-1} in *d*-8. Similar near equalities occur for the pairs 936, 911 and 506, 438 in *h*-8. Also the exceptionally low value of 8·9 cm^{-1} for the 501 cm^{-1} a_g upper-state vibration in *h*-8 is matched by an exceptionally low value 7·9 cm^{-1} for the corresponding 438 cm^{-1} vibration of *d*-8. Not too much should perhaps be made of these regularities, because the mean sequence intervals in one or two cases depend on averaging as few as three measured values; but they do suggest that in the lower frequencies the dynamical forms of what we regard as corresponding vibrations (i.e. those with similar activity in the u.v. absorption spectrum) are similar as between upper and lower electronic states, and between *h*-8 and *d*-8. Rather larger variations occur in the 49 cm^{-1} sequence of *d*-8, and do not offer simple regularities of the same types.

The same essential features of sequences and difference bands appear in all the band groups except in $0-490$, which has some unusual features to be discussed later. As in naphthalene *h*-8, we have to explain the occurrence of two long sequences; these are due to population of the low frequencies 160 and 180 cm^{-1} corresponding to 175 and 191 cm^{-1} of naphthalene *h*-8 (Luther, Feldman & Hampel 1955).

Polarization of the bands

The bands in all the groups except 0—490 have maxima either definitely single, or definitely double, with two peaks separated in most examples by 2·2 to 2·5 cm^{-1}. The single bands have heads, weakly degraded to the red; of the two peaks in doubled bands that at higher frequency is a head, weakly degraded to the red, and the lower frequency peak is nearly symmetrical.

The arguments concerning the relation between band contour and polarization given for naphthalene (preceding paper) will not be repeated. We shall accept that single-headed bands are long-axis polarized and the others short-axis polarized. This, as will be shown, agrees with the absorption spectra of naphthalene *d*-8 in durene crystals.

The hot bands

Five principal band heads were measured to long wavelengths of the origin, differing from it by 490·0, 692·3, 699·8, 749·7 and 880·6 cm^{-1}. The last records itself in a double-headed band, and we assign it as a b_{3g} fundamental. Its activity in the spectrum is analogous to 936 cm^{-1} of naphthalene *h*-8, which suggests that it corresponds to a similar nuclear motion. However, Raman spectra, re-interpreted with the help of a careful re-examination of the problem of the normal vibrations of naphthalene (Freeman & Ross 1961; Scully & Whiffen 1961), show that the frequency 784 cm^{-1} is the second of the b_{3g} vibrations and is therefore the analogue of 936 cm^{-1} in naphthalene *h*-8. There is no evidence of this frequency among the hot bands, although it would appear in a clear part of the spectrum. Thus the roles of the b_{3g} frequencies 784 and 881 cm^{-1} are reversed relative to their *h*-8 analogues in the u.v. spectrum. It is interesting to note, however, that 936 cm^{-1} of *h*-8 and 881 cm^{-1} of *d*-8 change similarly on electronic excitation. 936 cm^{-1} drops to 911 cm^{-1} in the upper state (97·4 %). In *d*-8 there is a strong upper state b_{3g} frequency at 857 cm^{-1} (97·4 % of 881 cm^{-1}). One must conclude that the motion in the 784 cm^{-1} *d*-8 vibration differs substantially from that in 936 cm^{-1} of *h*-8, to make it inactive in perturbing the forbidden u.v. transition. The third of the Raman b_{3g} frequencies now recognized, namely 875 cm^{-1}, agrees fairly well with our 880·6 cm^{-1}.

The hot band displaced by 692·3 cm^{-1} from the origin belongs to the strongly Raman active a_g vibration 694 cm^{-1} and is clearly the analogue of the prominent frequency 760 cm^{-1} observed in naphthalene *h*-8. The two bands 699·8 and 749·7 cm^{-1} from the origin have single heads; the frequencies are thus totally symmetrical: they are combinations which, like two corresponding intervals in naphthalene *h*-8 of 769·8 and 837·6 cm^{-1}, are unassigned.

The most interesting of the hot band groups belongs to the principal head 490·0 cm^{-1} from the origin. This band group shows the existence of gross perturbations, which make it unique in the whole spectrum, analogous in this respect to the 0—506 band group of *h*-8. We shall, in fact, propose that 490·0 cm^{-1} is the lowest b_{3g} vibration of naphthalene *d*-8, just as 506·0 cm^{-1} is of naphthalene *h*-8. The first few bands of this group are shown in figure 1. The principal band is single headed, and is followed 3·8 cm^{-1} to the red by an (apparently) exceptionally strong difference band also of single-headed structure, but successive members of the 9·3 cm^{-1} sequence show a change from single to doubled structure, the fifth member being clearly doubled with a head spacing of 0·5 cm^{-1}. In the 49 cm^{-1} sequence the first member is split by 1·1 cm^{-1}, the second by 1·4 cm^{-1}, and the third by 2·1 cm^{-1}; and bands built on these with other sequence intervals, show similar splittings. The difference bands, in 55, 73, 90 and 138 cm^{-1} have single heads and, except in the last and weakest, they have rather strong 4 cm^{-1} difference bands associated with them. The general nature of these perturbations can be understood as Coriolis coupling effects, although it does not yet seem possible to give a detailed account of them. In naphthalene *h*-8 the b_{3g} 506 cm^{-1} and the a_g 512 to 516 cm^{-1} lie between 6 or 10 cm^{-1} apart, and the $0-506$ band shows a perturbed double-headed structure. If this perturbation is due to Coriolis coupling between the a_g and b_{3g} motions, we may expect coupling also in *d*-8 with a strength depending inversely on the separation of the corresponding a_g and b_{3g} vibrations. The frequency 490 cm^{-1} in the u.v. spectrum corresponds to the

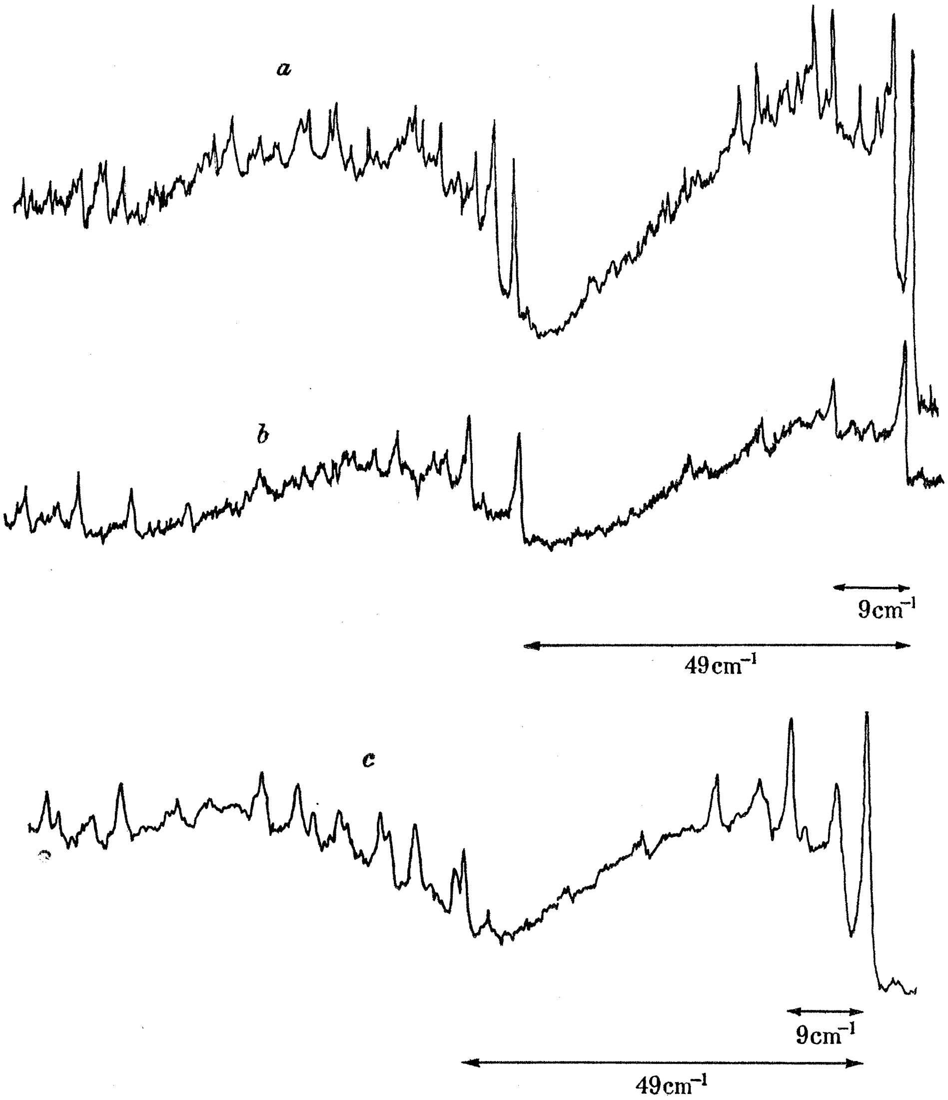

FIGURE 1. Comparison of the perturbed band contour of the $0-490$ band (*c*) with the normal short-axis polarized band contour (*a*) and long axis (*b*). At the first 49 cm^{-1} sequence member the doubling of the heads can be seen in the perturbed contour. Frequency increases from left to right.

506 b_{3g} frequency of *h*-8, and the a_g frequency measured in the Raman spectrum (Mitra & Bernstein 1959) is about 491 cm^{-1}. The Coriolis coupled frequencies are thus much closer in *d*-8 than in *h*-8, and the perturbations can be expected to be much more severe. They should have two effects, one on the energies of the rotational lines forming the band, resulting in a changed contour, and the other on the intensities, permitting the spectrally inactive vibration to gain some intensity at the expense of the active one. We might expect to observe the normally inactive frequency if the interaction were strong enough. The interpretation of the observed spectrum of naphthalene *d*-8 along these lines is that the principal band 0 — 490 would, in the absence of Coriolis effects, be double headed but that on account of the perturbation it has a contour with a single maximum. The intensity loss accompanying this change of band contour is gained by the a_g vibration of about the same frequency, and this vibration appears at 31 645·4 cm^{-1}, 3·8 cm^{-1} to the red of the b_{3g} induced band, and overlying the usual 4 cm^{-1} difference band. We thus arrive at a value 493·8 cm^{-1} for the lowest a_g frequency of naphthalene *d*-8, though this is unlikely to be precise, on account of the perturbation of the line positions. The true value is somewhat less than the measured 3·8 cm^{-1}. When, as in the members of the 49 cm^{-1} sequence, the sequence intervals for the two vibrations are different, the separation may increase, and the perturbation decrease, leading to the appearance of double-headed structure increasingly along the sequence, accompanied by the disappearance of the a_g vibration sequence members.

Another possibility to account for the strong band at 31 644·4 cm^{-1} is that the 4 cm^{-1} sequence interval is smaller for the a_g frequency than for the b_{3g} 490 cm^{-1}, leading to a closing of the interval between them in higher sequence members and increased Coriolis coupling. In this case the 31 644·4 cm^{-1} band is the usual 4 cm^{-1} sequence band with enhanced intensity, and the a_g fundamental remains unobserved, as in naphthalene *h*-8. This view has serious difficulties. The effect of Coriolis coupling should be to decrease the intensity of the spectrally active partner, not to increase it. Also the effect should be quite general in all appearances of the 4 cm^{-1} sequence, but in fact is never so marked as in the first case and often is not observed at all. For example, although the first 9 cm^{-1} sequence member shows single-headed structure, its 4 cm^{-1} sequence band is not unusually strong.

Long-axis polarized band groups

As in naphthalene *h*-8, there is a set of single-headed long-axis polarized bands, including the origin band at 32138·2 cm^{-1}, and others separated from it by totally symmetrical frequencies or combinations. Some are readily identified by their resemblance to corresponding bands in naphthalene *h*-8. Thus, the ground-state fundamental of about 516 cm^{-1} in *h*-8 drops in the upper state to 500 cm^{-1}, a change of 3 %; we expect to find in the upper state of naphthalene *d*-8 a fundamental 3 % less than the corresponding ground state 492 cm^{-1}, namely, at about 478 cm^{-1}. The band group C at 32621·7 cm^{-1} is separated by 483·5 cm^{-1} from the origin; the frequency 483·5 cm^{-1} is clearly an upper state a_g fundamental analogous to 501 cm^{-1} in *h*-8. Similarly, the 8·4 % drop from the ground state a_g fundamental 760 cm^{-1} in *h*-8 to upper state 702 cm^{-1} suggests that there should be an upper state *d*-8 fundamental about 8·4 % less than the ground state 692 cm^{-1}, at 638 cm^{-1}. The observed band E at 32776·6 cm^{-1} falls at 638·4 cm^{-1} from the origin, allowing this interval to be identified with a second a_g upper state fundamental. Both of these occur weakly in combination with the false origin $0+422$. A third a_g fundamental of 1410·5 cm^{-1} occurs in combinations with $0+422$, $0+483$, $0+822$, $0+857$ and possibly in two quanta $0+2\times 1410{\cdot}5$ (calc. − obs. = 5·6 cm^{-1}); it thus resembles in spectral activity the a_g fundamental 1435 of *h*-8, although the closeness of the frequencies precludes a very close dynamical resemblance.

Of the other totally symmetrical intervals, 346·2 cm^{-1} can best be assigned to an overtone of one of the low out-of-plane vibrations. This band was not observed in the low temperature mixed-crystal spectrum by McClure (1956), but it cannot be fitted to a difference of any known ground and excited-state vibrations. There is no a_g fundamental of the upper state unaccounted for and the assignment to an overtone seems most likely. The fundamental is thus of about 173 cm^{-1}; it must be one of two frequencies concerned in forming the long sequences in the spectrum, and is therefore either 9 or 49 cm^{-1} lower in frequency than its ground-state analogue. The former would give it a ground-state value 182 cm^{-1} close to the 180 cm^{-1} proposed by Mitra & Bernstein (1959) for the lowest b_{2g} fundamental. The stronger of the remaining totally symmetrical intervals are 850·5, 1245·7 and 1282·9 which may be fundamentals.

Bands based on the false origin 0 + 422 cm^{-1}

The false origin $0+422$ cm^{-1} and its progression and sequence members include the strongest bands of the system, and are all double-peaked bands of similar band contour, with spacing of 2·2 to 2·5 cm^{-1}. There is a strong resemblance in spectral activity to $0+438$ of naphthalene *h*-8; also the drop on electronic excitation from 493 to 422 cm^{-1} (16·8 %) is close to that in *h*-8 from 506 to 438 (15·5 %) confirming the dynamical similarity of the motions. Bands separated from $0+422$ by the totally symmetrical intervals 483·5, 638·4 and 1410·5 occur, all much weaker than the false origin itself.

The false origin 0 + 857·4 cm^{-1}

One of the most striking differences between the spectra of naphthalene *h*-8 and *d*-8 lies in the changed prominence of the several false origins. In *h*-8 most of the double-headed bands can be related to the false origins $0+438$ and $0+911$ and their progressions and sequences. In *d*-8 the false origin $0+422$, clearly the analogue of $0+438$, is itself the strongest band of the system, but the bands clearly related to it by a_g intervals are few and weak. The false origin $0+857$ is comparatively weaker than the corresponding band $0+911$ of *h*-8 and only the band related by the a_g interval 1410·5 has been identified. A number of other false origins have been observed that contribute relatively more to the total intensity than do similar bands in *h*-8.

Other double-headed band groups

The other double-headed bands in *d*-8 are unrelated to either of the two false origins $0+422$ and $0+857$ by recognized a_g intervals. All must therefore be considered as new false origins, differing from the true origin by a b_{3g} fundamental, or are due to isotopic impurities, particularly naphthalene *d*-7, which will be mentioned later: it is clear in any case that only the strongest bands of the *d*-7 molecules will be seen, namely, the prominent false origin, and possibly the true origin and the bands corresponding to 0−490 of naphthalene *d*-8. The stronger bands of naphthalene *d*-8 unaccounted for in relation to the origins 0+422 and 0+857 are 0+822·4, 0+1013·1, 0+1018·3, 0+1081·3, 0+1210·4, 0+1264·9, 0+1593·2, 0+1778·0 and 0+1830·4. Not all of these intervals can measure b_{3g} fundamentals; undoubtedly some do.

Bands due to isotopic impurities

The electronic origin of naphthalene *h*-8 is 32020·2 and that of *d*-8 32138·2 cm^{-1} a shift to higher frequencies of 118 cm^{-1}. Garforth, Ingold & Poole (1948) showed that in benzene with a blue shift on complete deuteration of 200 cm^{-1}, the shift on partial deuteration is approximately proportional to the number of deuterium atoms present. We may expect therefore that the shift per deuterium atom in naphthalene will be about 15 cm^{-1}. Relative to *d*-8 the origin of naphthalene *d*-7 will be red-shifted, and the shift will be different for α- and β-protio naphthalene *d*-7. Thus the two single-headed bands at 32127·3 and 32119·5 cm^{-1}, red-shifted by 10·9 and 18·7 cm^{-1}, respectively, from the *d*-8 origin may reasonably be ascribed to the two isotopic isomers of *d*-7, and mark the electronic origins of the corresponding transitions. In the false origins the isotopic shift will be the summed effect of the change in electronic origin and in the vibration frequency concerned. In the lower-frequency modes, substitution of protium for deuterium will raise the frequency, so that the false origin will be less red-shifted than the true origin. No other bands have been identified in the spectrum fitting these requirements. The region in which bands of *d*-7 would fall analogous to 0+422 of *d*-8 is crowded, and the weak *d*-7 bands would not be detected. Isotopic substitution also lowers the molecular symmetry and permits the appearance of bands forbidden in *h*-8 and *d*-8. The double-headed bands at 32543·8 and 32589·8 cm^{-1} may be due to such transitions of naphthalene *d*-7; alternatively they may be due to combinations of *d*-8 vibrations of symmetry b_{3g} of frequencies 405·6 and 457·6 cm^{-1}, respectively. The latter value is in fact close to the combination $b_{1g} \times b_{2g} = b_{3g}$, of 180+270 = 450 cm^{-1} given by Mitra & Bernstein (1959); however, the corresponding combination in *h*-8 is not observed.

Comparison with solid-state spectra

The polarizations and frequencies found in the vapour spectrum are, in general, in very good agreement with McClure's (1956) measurements of the absorption and fluorescence by naphthalene *d*-8 embedded in crystalline durene. The sole important difference in McClure's analysis of his spectra, and that of ours, is removed when the ground state frequency 492 cm^{-1}, which McClure took as a_g, is assigned b_{3g}. This explains the fact that the origin band is stronger along the *b* axis (mainly long-axis polarized) in McClure's spectrum while 0−492 is stronger in the *c′* spectrum (mainly short-axis polarized). McClure found, as we do, that in absorption the main part of the intensity is due to short-axis polarized bands, with b_{3g} frequencies of 419, 817, 852, 1269 and 1580 cm^{-1} providing perturbations of the pure electronic transition. The activity of a_g vibrations is also similar with frequencies (vapour values bracketed): 483 (483), 641 (638), 842 (850), 1398 (1410), 1237 (1246). McClure's fluorescence spectrum shows that the low perturbing frequencies of the ground state are: 492 (490) and 879 (880) and the totally symmetrical 689 cm^{-1} corresponds to the vapour 692 cm^{-1}. According to our interpretation of the vapour spectrum, there is a near coincidence of the lowest a_g and b_{3g} frequencies, respectively, about 493 and 490 cm^{-1}. The upper-state analogues of these frequencies, 483 and 422 cm^{-1}, appear in combination in the weak band at 33044·3 cm^{-1}. A useful confirmation of the ground-state frequencies would be obtained if the corresponding combination were observed. McClure's fluorescence spectrum shows a band 984 cm^{-1} to the red of the origin stronger in c' polarization than in b, and therefore differing from the origin by b_{3g} symmetry. The assignment of this as the required combination 490+493 seems secure. The corresponding combination in naphthalene h-8 coincides with an a_g fundamental 1024 cm^{-1} but no such confusing superposition occurs in this case.

TABLE 3. LOW IN-PLANE VIBRATIONS OF NAPHTHALENE d-8 (CM^{-1})

species a_g		species b_{3g}	
ground state	excited state	ground state	excited state
493	483	490	422
692	638	881	857

Table 3 contains a list of the lowest a_g and b_{3g} frequencies of naphthalene d-8, with their upper-state analogues as observed in the vapour spectrum. In this, as in all important respects, there is an excellent agreement between the vapour and mixed crystal spectra.

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APPENDIX

The following is a complete list of measured maxima, referred to as 'heads' hereafter. Assignments, where proposed, refer to the principal heads in table 1, and give the sequence intervals between the head concerned and the principal head. Thus

$$B^{1200}_{000}$$

differs from the principal band head A by one sequence interval in 9 cm^{-1}, and by two in 49 cm^{-1}. The superscripts in order from the left refer to the sequence intervals of about 9, 49, 55, 72 and the subscripts to 5, 90 and 139 cm^{-1}, respectively. Roman letters refer to single-headed bands and italics to double-headed bands. The higher-frequency head of doubled bands is used for measurement; the lower head is recorded with ϵ added to the designation. Thus

$$B^{1200}_{000} \quad \text{and} \quad B^{1200}_{000}\epsilon$$

form a double-headed band. The designation 'wing' refers to rotational structure associated with the named band, usually a very weak unresolved flat maximum to the red of the main maxima in doubled bands. Frequencies marked with an asterisk were measured from enlargements and are believed accurate ±0·1 cm^{-1}. Others were read from the plates and are believed accurate ±0·05 cm^{-1}.

Doubtful assignments are bracketed.

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frequency	assnmt.
34 953·67*	Q^{0000}_{000}
34 577·45*	X^{0000}_{000}
74·73*	$X^{0000}_{000}\ \epsilon$
68·80*	—
66·77*	—
60·57*	P^{0000}_{000}
34 406·28	W^{0000}_{000}
04·83	—
04·05	$W^{0000}_{000}\ \epsilon$
34 396·31	W^{1000}_{000}
93·96	$W^{1000}_{000}\ \epsilon$
75·87*	V^{0000}_{000}
73·65	$V^{0000}_{000}\ \epsilon$
47·11	U^{0000}_{000}
44·96	$U^{0000}_{000}\ \epsilon$
34 147·33*	O^{0000}_{000}
36·75*	O^{1000}_{000}
34 059·25*	T^{0000}_{000}
56·89*	$T^{0000}_{000}\ \epsilon$
31·38	N^{0000}_{000}
23·25	N^{1000}_{000}
14·98	N^{2000}_{000}
33 998·41	S^{0000}_{000}
96·09	$S^{0000}_{000}\ \epsilon$
82·12	N^{0100}_{000}
73·88*	N^{1100}_{000}
69·69	R^{0000}_{000}
68·59	Q^{0000}_{000}
67·48	$R^{0000}_{000}\ \epsilon$
66·61	$Q^{0000}_{000}\ \epsilon$
63·35	$(R^{0000}_{100}\ \epsilon)$
61·09	$(Q^{0000}_{100}\ \epsilon)$
59·87	R^{1000}_{000}
58·70	Q^{1000}_{000}
57·58	$R^{1000}_{000}\ \epsilon$
56·30	$Q^{1000}_{000}\ \epsilon$
48·55	Q^{2000}_{000}
16·20	P^{0000}_{000}
13·82	$P^{0000}_{000}\ \epsilon$
06·13	P^{1000}_{000}
33 892·20	—
33 731·41	O^{0000}_{000}
29·09	$O^{0000}_{000}\ \epsilon$
25·68	$O^{0000}_{000}\ \alpha$
23·42	$O^{0000}_{100}\ \epsilon$
21·90	O^{1000}_{000}
19·54	$O^{1000}_{000}\ \epsilon$
33 682·11	O^{0100}_{000}
79·89	$O^{0100}_{000}\ \epsilon$
72·85*	O^{1100}_{000}
70·28	$O^{1100}_{000}\ \epsilon$
33 550·89	M^{0000}_{000}
49·73	—
48·71	L^{0000}_{000}
43·66	L^{0000}_{100}
41·21	M^{1000}_{000}
39·28	L^{1000}_{000}
30·02	L^{2000}_{000}
20·95*	L^{3000}_{000}
33 499·40	L^{0100}_{000}
92·05	L^{0010}_{000}
89·93	L^{1100}_{000}
82·62*	L^{1010}_{000}
80·59*	L^{2100}_{000}
73·24*	—
70·09	—
64·75	—
61·66	—
49·96	—
49·47	N^{0000}_{000}
47·15	$N^{0000}_{000}\ \epsilon$
43·92*	N^{0000}_{100}
33 442·32*	—
40·03	N^{1000}_{000}
38·43	L^{0020}_{0000}
32·68	—
30·39	—
26·94	—
23·78	—
21·06	K^{0000}_{000}
17·20	—
16·56	—
16·05	—
14·86	K^{0000}_{100}
13·66	—
11·79	K^{1000}_{000}
04·65	—
04·33	—
03·10	M^{0000}_{000}
01·38	—
00·83	$M^{0000}_{000}\ \epsilon$
33 397·26	M^{0000}_{100}
96·25	—
95·66	—
94·46	M^{1000}_{000}
93·22	—
89·29	—
88·12	—
83·87	J^{0000}_{000}
81·48	—
80·41	—
79·19	I^{0000}_{000}
77·27	H^{0000}_{000}
75·33*	—
33 373·80*	J^{1000}_{000}
70·08*	I^{1000}_{000}
67·78	H^{1000}_{000}
58·46	M^{0100}_{000}
56·16	$M^{0100}_{000}\ \epsilon$
48·61	L^{0000}_{000}
46·20	$L^{0000}_{000}\ \epsilon$
44·36	—
43·39	—
39·21	L^{1000}_{000}
36·71	$L^{1000}_{000}\ \epsilon$
30·18	I^{0100}_{000}
24·06	—
20·95	—
13·31	—
33 297·80	L^{0100}_{000}
95·40	$L^{0100}_{000}\ \epsilon$
19·45	K^{0000}_{000}
16·88	$K^{0000}_{000}\ \epsilon$
08·51	K^{1000}_{000}
05·96	$K^{1000}_{000}\ \epsilon$
33 198·42	K^{2000}_{000}
95·76	J^{0000}_{000}
93·38	$J^{0000}_{000}\ \epsilon$
86·13	J^{1000}_{000}
83·83	$J^{1000}_{000}\ \epsilon$
71·16	K^{0100}_{000}
68·71	$K^{0100}_{000}\ \epsilon$
66·00*	K^{0010}_{000}
63·60*	$K^{0010}_{000}\ \epsilon$
56·52	I^{0000}_{000}
54·07	$I^{0000}_{000}\ \epsilon$
51·23	H^{0000}_{000}
48·82	$H^{0000}_{000}\ \epsilon$
39·86	—
39·14	—
08·71*	K^{0020}_{000}
05·82*	$K^{0010}_{000}\ \epsilon$
03·07*	H^{0100}_{000}
00·18*	$H^{0100}_{000}\ \epsilon$
33 044·28*	Y^{0000}_{000}
41·75*	$Y^{0000}_{000}\ \epsilon$
32 995·59	G^{0000}_{000}
93·20	$G^{0000}_{000}\ \epsilon$
88·64	G^{0000}_{000}
87·38	—
85·99	G^{1000}_{000}
84·58	—
83·69	$G^{1000}_{000}\ \epsilon$
78·03	F^{0000}_{000}
75·64	$F^{0000}_{000}\ \epsilon$
60·60	E^{0000}_{000}
58·06	$E^{0000}_{000}\ \epsilon$
32 954·09	$(E^{0000}_{100}\ \epsilon)$
51·55	E^{1000}_{000}
49·15	$E^{1000}_{000}\ \epsilon$
48·66	—
47·17	G^{0100}_{000}
44·80	$G^{0100}_{000}\ \epsilon$
42·25	—
40·11	G^{0100}_{000}
35·92	D^{0000}_{000}
33·43	$D^{0000}_{000}\ \epsilon$
25·91*	D^{1000}_{000}
24·55*	—
23·38*	$D^{1000}_{000}\ \epsilon$
11·43	E^{0100}_{000}
09·04	$E^{0100}_{000}\ \epsilon$
04·99	—
32 898·84*	G^{0200}_{000}
96·45*	$G^{0200}_{000}\ \epsilon$
62·50	E^{0200}_{000}
60·08	$E^{0200}_{000}\ \epsilon$
32 784·24	F^{0000}_{000}
76·62	E^{0000}_{000}
72·12	E^{0000}_{100}
67·61	E^{1000}_{000}
62·92*	E^{1000}_{100}
58·63	E^{2000}_{000}
29·73*	—
28·92*	E^{0100}_{000}
22·07*	—
02·61	D^{0000}_{000}
32 692·89	D^{1000}_{000}
83·97	—
21·66	C^{0000}_{000}
17·67	C^{0000}_{100}
13·94	C^{1000}_{000}
13·39	—
05·97	C^{2000}_{000}
32 597·97	C^{3000}_{000}
89·76	C^{0000}_{000}
87·38	$C^{0000}_{000}\ \epsilon$
85·09	C^{0000}_{100}
82·56	$C^{0000}_{100}\ \epsilon$
78·88	C^{1000}_{000}
76·50	$C^{1000}_{000}\ \epsilon$
73·34	C^{0100}_{000}
68·95	C^{0100}_{100}
65·62	C^{1100}_{000}
60·60	B^{0000}_{000} (wing)
60·07	B^{0000}_{000}
58·40	$B^{0000}_{000}\ \epsilon$ (wing)
57·61	$B^{0000}_{000}\ \epsilon$
55·44	B^{0000}_{100}
53·12	B^{0000}_{100}

frequency	assnmt.
32 550·51	B^{1000}_{000} (wing)
49·94	B^{1000}_{000}
48·85	$B^{1000}_{000}\ \epsilon$ (wing)
47·54	$B^{1000}_{000}\ \epsilon$
45·17	B^{1000}_{100}
43·79	A^{0000}_{000}
42·84	B^{1000}_{100}
41·89	—
41·36	$A^{0000}_{000}\ \epsilon$
40·81	B^{2000}_{000} (wing)
40·11	B^{2000}_{000}
37·72	$B^{2000}_{000}\ \epsilon$
32·36	$(B^{2000}_{100}\ \epsilon)$
31·95	—
30·39	B^{3000}_{000}
28·03	$B^{3000}_{000}\ \epsilon$
20·73	B^{4000}_{000}
18·48	$B^{4000}_{000}\ \epsilon$
07·98	B^{0100}_{000}
05·49	$B^{0100}_{000}\ \epsilon$
02·84	B^{0010}_{000}
00·51	$B^{0010}_{000}\ \epsilon$
32 498·27	B^{1100}_{000}
97·29	—
96·57	—
95·81	$B^{1100}_{000}\ \epsilon$
94·94	—
94·12	—
93·12	B^{1010}_{000}
92·64	—
91·91	—
88·72	B^{2100}_{000}
87·48	—
86·32	$B^{2100}_{000}\ \epsilon$
84·42	B^{0000}_{000}
83·64	B^{0001}_{000}
80·95	$B^{0001}_{000}\ \epsilon$
79·76	—
76·89	—
76·36	—
74·31	B^{1000}_{000}
73·55*	B^{1001}_{000}
73·04*	—
70·68	B^{0000}_{010}
68·18	$B^{0000}_{100}\ \epsilon$
67·06	—
66·14	—
60·71	B^{1000}_{100}
59·91	—
56·60	B^{0200}_{000}
54·12	$B^{0200}_{000}\ \epsilon$
53·49	B^{0020}_{010}
51·02	$B^{0000}_{010}\ \epsilon$
50·05	B^{0110}_{000}
32 447·69	$B^{0110}_{000}\ \epsilon$
47·10	B^{1200}_{000}
44·65	$B^{1200}_{000}\ \epsilon$
43·54	B^{1000}_{010}
41·21	$B^{1000}_{010}\ \epsilon$
37·47	B^{2200}_{000}
30·10	—
29·44	—
20·58	B^{0000}_{001}
18·90	B^{0100}_{100}
17·97	$B^{0000}_{001}\ \epsilon$
16·46*	$B^{0100}_{100}\ \epsilon$
09·47*	—
07·93	$(B^{1000}_{001}\ \epsilon)$
05·59	B^{0300}_{000}
03·25	$B^{0300}_{000}\ \epsilon$
01·82	B^{0100}_{010}
32 396·39*	B^{1300}_{000}
95·33*	—
94·09*	$B^{1300}_{000}\ \epsilon$
65·50*	—
62·97*	—
32 138·18	A^{0000}_{000}
34·02	A^{0000}_{100}
31·57	—
29·14	A^{1000}_{000}
27·31	a^{0000}_{000}
24·85	A^{1000}_{100}
20·11	A^{2000}_{000}
19·49	b^{0000}_{000}
12·84	—
11·10*	A^{3000}_{000}
02·07*	A^{4000}_{000}
32 089·46	A^{0100}_{000}
84·90	A^{0100}_{100}
83·17	A^{0010}_{000}
80·39	A^{1100}_{000}
78·62	—
75·20*	—
74·02	A^{1010}_{000}
71·25	A^{2100}_{000}
68·81*	—
67·50*	—
66·23	A^{0001}_{000}
64·96	A^{2010}_{000}
62·27	A^{3100}_{000}
56·96	A^{1001}_{000}
53·36*	$(\mathrm{A}^{4100}_{000})$
48·14*	A^{0000}_{100}
40·95	A^{0200}_{000}
34·38	A^{0110}_{000}
31·75	A^{1200}_{000}
27·79	A^{0020}_{000}
26·61	—
32 025·29	A^{1110}_{000}
24·96*	—
22·77	A^{2200}_{000}
20·42*	—
18·93*	A^{1000}_{010}
18·05*	A^{0101}_{000}
16·40*	A^{2110}_{000}
15·64*	—
14·31*	—
13·13*	—
09·64*	A^{2000}_{010}
31 999·13	A^{0000}_{001}
92·65	A^{0300}_{000}
85·90	A^{0210}_{000}
79·24*	A^{0100}_{010}
76·76*	A^{1210}_{000}
72·14*	A^{0010}_{010}
69·88*	A^{1100}_{010}
67·90*	A^{2210}_{000}
62·77*	—
60·46*	A^{2100}_{010}
48·54*	—
44·57*	A^{0400}_{000}
44·03*	—
39·57*	—
37·53*	A^{0310}_{000}
35·10*	—
30·63*	—
29·40*	—
28·17*	A^{1310}_{000}
08·28*	—
31 648·18	a^{0000}_{000}
44·39	a^{0000}_{100}
40·52	c^{0000}_{000}
39·06	a^{1000}_{000}
35·07	a^{1000}_{100}
29·98	a^{2000}_{000}
27·25	—
25·84	a^{2000}_{100}
20·87	a^{3000}_{000}
11·72	a^{4000}_{000}
02·64	a^{5000}_{000}
02·13	$a^{5000}_{000}\ \epsilon$
31 599·23	a^{0100}_{000}
98·10	$a^{0100}_{000}\ \epsilon$
94·94	a^{0100}_{100}
93·23	a^{0010}_{000}
90·20	a^{1100}_{000}
89·14	$a^{1100}_{000}\ \epsilon$
85·01	a^{1100}_{100}
84·16	a^{1010}_{000}
81·08	a^{2100}_{000}
79·31	$(a^{2100}_{000}\ \epsilon)$
74·96	a^{0001}_{000}
31 574·02	$a^{0001}_{000}\ \epsilon$
72·19	a^{3100}_{000}
68·83*	—
64·79*	(a^{1001}_{000})
63·57*	$(a^{1001}_{000}\ \epsilon)$
58·15	a^{0000}_{100}
54·89	(a^{2001}_{000})
50·70	a^{0200}_{000}
49·35	$a^{0200}_{000}\ \epsilon$
44·36	a^{0110}_{000}
41·69*	a^{1200}_{000}
40·47	$a^{1200}_{000}\ \epsilon$
37·96*	a^{0020}_{000}
35·22	a^{1110}_{000}
32·65	a^{2200}_{000}
28·57*	a^{1000}_{010}
23·49	a^{3200}_{000}
22·61	—
20·67	a^{0011}_{000}
19·53	$a^{0011}_{000}\ \epsilon$
09·53	a^{0000}_{001}, (a^{0100}_{100})
02·41	a^{0300}_{000}
00·31	$a^{0300}_{000}\ \epsilon$
31 493·35*	a^{1300}_{000}
91·78*	$a^{1300}_{000}\ \epsilon$
86·87	—
84·23*	a^{2300}_{000}
71·26	—
68·44	—
55·05	a^{0400}_{000}
45·86	c^{0000}_{000}
38·42	d^{0000}_{000}
36·74*	c^{1000}_{000}
29·77	d^{1000}_{000}
27·87*	c^{2000}_{000}
25·66*	—
31 398·47*	c^{0100}_{000}
90·75*	d^{0100}_{000}
88·53	e^{0000}_{000}
84·18*	d^{0010}_{000}
79·35*	e^{1000}_{000}
76·57*	—
75·43*	d^{1010}_{000}
71·13*	e^{2000}_{000}
39·21	e^{0100}_{000}
34·34	e^{0010}_{000}
30·43	e^{1100}_{000}
31 288·85*	e^{0200}_{000}
80·95*	e^{1200}_{000}
74·68*	—
57·61*	b^{0000}_{000}
55·25*	$b^{0000}_{000}\ \epsilon$

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