

Vibrational Assignment and Thermodynamic Properties of Naphthalene

A. L. McClellan and George C. Pimentel

Citation: [The Journal of Chemical Physics](#) **23**, 245 (1955); doi: 10.1063/1.1741948

View online: <http://dx.doi.org/10.1063/1.1741948>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/23/2?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Thermodynamic properties of normal and deuterated naphthalenes](#)

J. Phys. Chem. Ref. Data **8**, 527 (1979); 10.1063/1.555602

[1,2-Difluorobenzene: Chemical Thermodynamic Properties and Vibrational Assignment](#)

J. Chem. Phys. **38**, 532 (1963); 10.1063/1.1733691

[4-Fluorotoluene: Chemical Thermodynamic Properties, Vibrational Assignment, and Internal Rotation](#)

J. Chem. Phys. **37**, 867 (1962); 10.1063/1.1733176

[Vibrational Spectra and Assignment of Naphthalene and Naphthalene-d-8](#)

J. Chem. Phys. **23**, 238 (1955); 10.1063/1.1741947

[The Vibrational Assignment and Thermodynamic Properties of N-Dimethylaminodiborane](#)

J. Chem. Phys. **22**, 762 (1954); 10.1063/1.1740183

A promotional banner for AIP Applied Physics Reviews. The background is a dark blue gradient with abstract, light blue, wavy patterns. On the left, there is a small image of a book cover for 'AIP Applied Physics Reviews' featuring a diagram of a crystal structure. The text 'NEW Special Topic Sections' is prominently displayed in large, white, sans-serif font. Below this, the text 'NOW ONLINE' is in yellow, followed by 'Lithium Niobate Properties and Applications: Reviews of Emerging Trends' in white. The AIP Applied Physics Reviews logo is in the bottom right corner.

NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP Applied Physics Reviews

Vibrational Assignment and Thermodynamic Properties of Naphthalene

A. L. MCCLELLAN* AND GEORGE C. PIMENTEL

Department of Chemistry and Chemical Engineering, University of California, Berkeley, California

(Received June 2, 1954)

A complete vibrational assignment of naphthalene and naphthalene- d_8 is presented. This assignment is in substantial agreement with the experimental thermodynamic properties, the product rule and the spectroscopic data. The assigned frequencies are used to calculate the thermodynamic properties of naphthalene, S^0 , C_p^0 , $(H^0 - E_0^0)/T$, and $-(F^0 - E_0^0)/T$ from 273.16° to 1500°K.

RECENTLY, several studies of the infrared and Raman spectra of naphthalene and naphthalene- d_8 have appeared.¹⁻⁴ These data, combined with the measured thermodynamic properties of naphthalene,⁵ permit a more reliable vibrational assignment than that proposed earlier by the present authors.⁵

Lippincott and O'Reilly¹ give a complete assignment for naphthalene without an attempt to fit the thermodynamic properties exactly. Partial assignments of the Raman-active fundamentals were given by Kohlrausch and Seka,⁶ Nedungadi,⁷ and Luther.⁸ Mannebach⁹ considered the planar skeletal vibrations.

VIBRATIONAL ASSIGNMENT

The symmetry of a number of vibrations can be assigned on the basis of the band contours in the spectra of gaseous naphthalene.² Coupled with the infrared^{1,2,10} and Raman^{1,3} spectra of naphthalene- d_8 , these assignments provide a firm basis for determining approximate spectral locations of the characteristic vibrational modes of naphthalene. Table I lists the bands for which symmetry assignment and frequency shift on deuteration are definitely known. The deuteration frequency shift is expressed as R , the ratio $\nu(\text{C}_{10}\text{H}_8)/\nu(\text{C}_{10}\text{D}_8)$.

From the data presented in Table I, the vibrational assignment of benzene and a simple normal coordinate analysis of the out-of-plane skeletal vibrations, we have determined probable spectral ranges for each characteristic vibration type of naphthalene. The results are quite similar to the spectral regions and guide values of R derived independently by Lippincott and O'Reilly.¹

* Present address: California Research Corporation, Richmond, California.

¹ E. R. Lippincott and E. J. O'Reilly, Jr., J. Chem. Phys. **23**, 238 (1955). Hereafter this paper will be called I.

² Person, Pimentel, and Schnepf, J. Chem. Phys. **23**, 230 (1955). Hereafter this paper will be called II.

³ Goubeau, Luther, Feldman, and Brandes, Chem. Ber. **86**, (2), 214-26 (1953).

⁴ Pimentel, McClellan, Person, and Schnepf, J. Chem. Phys. **23**, 234 (1955).

⁵ G. M. Barrow and A. L. McClellan, J. Am. Chem. Soc., **73**, 573 (1951).

⁶ K. W. F. Kohlrausch and R. Seka, Deut. Chem. Gel. Ber. **71**, 1551 (1938).

⁷ T. M. K. Nedungadi, Proc. Indian Acad. Sci. **15A**, 387 (1942).

⁸ H. Luther, Z. Elektrochem. **52**, 210 (1948).

⁹ C. Mannebach, J. chim. phys. **46**, 49-57 (1949).

¹⁰ G. C. Pimentel and A. L. McClellan, J. Chem. Phys. **20**, 270 (1952).

Only the estimates of the lower bounds for the skeletal distortions are significantly different from their Table III. We estimate that the lowest out-of-plane skeletal bend has a frequency between 100 and 200 cm^{-1} , and the lowest in-plane distortion has a frequency around 400 cm^{-1} .

The selection rules for naphthalene (molecular symmetry D_{2h}) have been given earlier.^{1,10} The classes are taken up in the order of certainty of the assignment. The Raman frequencies listed here are average values based on twenty-one investigations.

A_g (9 FUNDAMENTALS)

The choice of the fundamental frequencies of this class is greatly simplified by the use of the polarization data.^{6,11-13} The Raman shifts observed at 512, 762, 778, 880, 943, 1024, 1324, 1379, 1460, and 3058 cm^{-1} have been reported as polarized. In agreement with I, frequencies at 512, 762, 1024, 1379, and 3058 cm^{-1} are chosen as fundamentals. Furthermore, the argument presented in I, attributing a totally symmetric mode to the unpolarized line at 1576 cm^{-1} in preference to the polarized line at 1460 cm^{-1} , is accepted. The second hydrogen stretching motion of this class is assigned at 3001 cm^{-1} . Because it is more intense and has a lower

TABLE I. Naphthalene bands of known symmetry and deuteration shift.

Frequency		Class	R	Vibrational mode
C_{10}H_8	C_{10}D_8			
475 cm^{-1}	408 cm^{-1}	B_{1u}	1.16	op† skeletal bend
512	491	A_g	1.04	ip‡ skeletal distortion
620	595	$B_{2u}^?$	1.04	ip skeletal distortion
762	694	A_g	1.10	ip skeletal distortion
1379	1379	A_g	1.00	ip skeletal stretch
1601	1440	B_{2u}	1.11	ip skeletal stretch
780	628	B_{1u}	1.24	op hydrogen bend
956	790	B_{1u}	1.21	op hydrogen bend
1012	830	B_{3u}	1.22	ip hydrogen bend
1024	862	A_g	1.19	ip hydrogen bend
1125	885	B_{2u}	1.27	ip hydrogen bend

† op = out-of-plane.
‡ ip = in-plane.

¹¹ B. D. Saksena, Proc. Indian Acad. Sci. **8A**, 73 (1938).

¹² Benel, Kastler, and Rousset, Compt. rend. **211**, 595 (1940).

¹³ Braun, Spooner, and Fenske, Anal. Chem. **22**, 1074 (1950).

value of ρ^{13} , the line at 943 cm^{-1} was selected instead of the line at 880 cm^{-1} . The line at 778 cm^{-1} is not considered because of its proximity to the more intense line at 762 cm^{-1} .

On the basis of intensities, the assignment of the corresponding C_{10}D_8 lines is fairly definite; 491, 694, 862, 1380, 2268, 1548, 2257, and 752 cm^{-1} . The C_{10}D_8 line at 829 cm^{-1} is omitted from this class because of proximity to the stronger line at 862 cm^{-1} .

The one A_g vibrational mode remaining, a hydrogen bending motion, is assigned to 1240 cm^{-1} (C_{10}H_8) and 1006 cm^{-1} (C_{10}D_8). The polarized C_{10}H_8 line at 1324 cm^{-1} is rather close to the intense polarized absorption at 1379 cm^{-1} and it can be associated with the combination between the two B_{3u} frequencies 742 and 581 cm^{-1} .

The values of R associated with this complete assignment of the A_g class suggest that the skeletal breathing mode absorbs at 1024 cm^{-1} but involves considerable interaction with the symmetric hydrogen bending motions. The high intensities of the 1024 – 862 cm^{-1} pair are consistent with the high intensities of the breathing motions of benzene and benzene- d_6 , which provide the most intense lines observed in the respective Raman spectra.

B_{1u} (4 FUNDAMENTALS)

Three prominent bands in the infrared spectrum of gaseous C_{10}H_8 have the band contour appropriate to the B_{1u} class; 475 , 780 , and 956 cm^{-1} . The correlation of counterparts in the spectrum of C_{10}D_8 is straightforward; 403 , 628 , and 790 cm^{-1} , respectively. The remaining fundamental mode is ν_{25} , the motion identified in I as the "wing-wagging" motion. The simple normal coordinate analysis of the out-of-plane skeletal vibrations indicated that this motion should have the lowest frequency of the out-of-plane modes, and it was estimated to be between 100 and 200 cm^{-1} . The far infrared studies reported in II extend to 130 cm^{-1} and the band observed at 176 cm^{-1} is the only absorption detected below 362 cm^{-1} . This band is assigned as ν_{25} and from the product rule the C_{10}D_8 counterpart is calculated to be near 160 cm^{-1} .

B_{2u} (8 FUNDAMENTALS)

The gas phase spectra identify three B_{2u} fundamentals; 1268 and 1601 cm^{-1} for C_{10}H_8 and 885 cm^{-1} for C_{10}D_8 . Correlation of the spectra of the solids allows choice with confidence of two C_{10}H_8 – C_{10}D_8 pairs: 1601 – 1440 and 1125 – 885 cm^{-1} . The values of R , 1.11 and 1.27 show that the 1601 cm^{-1} band is associated with a skeletal stretching motion and the 1125 cm^{-1} band with a hydrogen bending motion.

Although the gas phase contour of the C_{10}H_8 band at 1385 cm^{-1} was not successfully resolved,² the investigations of the spectra of the solid phases indicate that this band has B_{2u} symmetry. The C_{10}D_8 counterpart could be the band observed at 1316 cm^{-1} or one of

the features in the region near 1258 cm^{-1} . In either case, the isotopic shift identifies this fundamental as a skeletal stretching mode. Since only two skeletal stretching modes are expected, the intense B_{2u} band of C_{10}H_8 at 1268 cm^{-1} must be the unassigned hydrogen bending motion. This argument raises the dilemma that no band of suitable intensity is observed in the infrared spectrum of C_{10}D_8 . The band at 1050 cm^{-1} is chosen despite a slight dichroism suggesting B_{1u} or B_{3u} symmetry. The selection of the band at 963 cm^{-1} as the C_{10}D_8 counterpart of the 1268 cm^{-1} fundamental frequency leads to product rule difficulties. With the pairing of 1268 cm^{-1} (C_{10}H_8)– 1050 cm^{-1} (C_{10}D_8), however, the selection of the remaining fundamentals is not difficult. The C_{10}H_8 band at 620 cm^{-1} seems to be associated with a vibration of B_{2u} symmetry, although the polarized spectra of the solid phase do not corroborate the gas phase band contour. There is a band at 595 cm^{-1} with the dichroic properties of the B_{2u} class in the spectrum of solid C_{10}D_8 . One of the skeletal distortion modes of the B_{2u} class is assigned to this 620 – 595 cm^{-1} pair. The other skeletal distortion motion is assigned to the C_{10}H_8 band at 362 cm^{-1} and the C_{10}D_8 band at 339 cm^{-1} .

The present assignment gives a satisfactory fit of the product rule and differs from I in the selection of skeletal distortion frequencies which are in better accord with the data of II.

B_{3u} (8 FUNDAMENTALS)

The spectra of gaseous naphthalene indicate three B_{3u} fundamentals: 1508 and 1012 cm^{-1} for C_{10}H_8 and 830 cm^{-1} for C_{10}D_8 . The correlation of the 1012 and 830 cm^{-1} bands identifies one of the hydrogen bending motions. The band at 1508 cm^{-1} , associated with the C_{10}D_8 band at 1391 cm^{-1} , is considered to be caused by one of the two skeletal stretching motions. The other stretching motion is assigned to the 1723 – 1569 cm^{-1} pair. Just as in the B_{2u} class, the assignment of the second hydrogen bending motion is difficult. The pair 1144 – 905 cm^{-1} is selected, although the data of I indicate that much of the intensity of the C_{10}D_8 absorption near 905 cm^{-1} must be attributed to $\text{C}_{10}\text{D}_7\text{H}$ impurity. The remaining two skeletal motions are assigned to the C_{10}H_8 – C_{10}D_8 pairs 742 – 680 and 581 – 546 cm^{-1} . With reasonable choices of the two hydrogen stretching motions, the complete assignment is in accord with the data of II and the product rule.

B_{1g} (8 FUNDAMENTALS)

The investigations of Nedungadi⁷ using polarized light incident upon a single crystal of naphthalene segregate the in-plane vibrational modes from the nonplanar modes. After selection of the fundamental frequencies of the A_g class, the remaining in-plane modes can be attributed to B_{1g} motions. In agreement with Nedungadi, and Lippincott and O'Reilly,¹ we include the Raman shifts 1145 , 1439 , and 1586 cm^{-1} among the B_{1g} fundamental frequencies of C_{10}H_8 . The

absorption observed at 1625 cm^{-1} is also designated as a B_{1g} fundamental. Presumably the two frequencies, 1625 and 1586 cm^{-1} , correspond to the two skeletal stretching motions of this symmetry. These can be associated with the two C_{10}D_8 bands at 1573 and 1473 cm^{-1} . Therefore, the C_{10}H_8 bands at 1439 and 1145 cm^{-1} must be associated with hydrogen bending motions. The correlations given in I give values of R which are implausible. More acceptable selections for the C_{10}D_8 fundamentals are the Raman shifts observed at 1120 and 929 cm^{-1} .

Two B_{1g} hydrogen stretching motions and two skeletal distortion motions must be assigned on the basis of the frequency range expected and the product rule. The skeletal frequencies selected are 879 and 611 cm^{-1} for C_{10}H_8 and 777 and 569 cm^{-1} for C_{10}D_8 .

B_{2g} AND B_{3g} (3 AND 4 FUNDAMENTALS)

Little basis exists for segregation of the Raman-active out-of-plane fundamentals. The skeletal normal coordinate analysis indicates that the frequencies of the lowest nonplanar motions have the order $B_{1u} < B_{2g} < B_{3g}$. The product rule provides the only other evidence in support of any distribution of frequencies between the B_{2g} and B_{3g} classes.

Each of the C_{10}H_8 bands at 191 and 285 cm^{-1} has a counterpart in the Raman spectrum of C_{10}D_8 (at 180 and 270 cm^{-1}). Since the lowest vibrational frequency for C_{10}H_8 is thought to be the B_{1u} frequency at 176 cm^{-1} , no explanation of 191 or 285 cm^{-1} involving sum combinations is possible. In the low temperature (20°K) fluorescence spectra of solid C_{10}H_8 and C_{10}D_8 , McClure¹⁴ has observed spectral features which can be associated with the vibrational frequencies 191–180 and 285–270 cm^{-1} , thus eliminating the explanation of any of these lines as a difference combination or as an impurity absorption. It seems necessary to include both 191 and 285 cm^{-1} as fundamentals of C_{10}H_8 , and hence, the 191–180 cm^{-1} pair is assigned to the B_{2g} class and the 285–270 cm^{-1} pair to the B_{3g} class.

The second out-of-plane skeletal motion of the B_{3g} class is expected to absorb near 500 cm^{-1} (by comparison to the frequencies of the B_{1u} class) and the 588–541 cm^{-1} pair is selected. The C_{10}H_8 – C_{10}D_8 pair 385–339 cm^{-1} was not used since the thermodynamic properties are consistent with an assignment containing only two Raman-active frequencies at or below 400 cm^{-1} if infrared-active frequencies at 176 and 362 cm^{-1} are included. The 385–339 cm^{-1} pair can be explained as harmonics of the lines at 191 and 180 cm^{-1} , respectively. If a frequency of 385 cm^{-1} is included in the assignment, the experimental thermodynamic properties seem to necessitate the elimination of one of the low frequencies: 176, 191, 285, 362, or 400 cm^{-1} . It seems necessary to retain the assignments of 176, 191, and 285 cm^{-1} . The infrared band at 362 cm^{-1} could be eliminated by assign-

ing it to the combination of 176 cm^{-1} and 191 cm^{-1} . A final alternative is to raise the A_u frequency estimated at 400 cm^{-1} to a frequency above 500 cm^{-1} .

The hydrogen bending motions of the B_{3g} class were assigned to the Raman shifts at 774 and 1099 cm^{-1} for C_{10}H_8 , and 671 and 829 for C_{10}D_8 on the basis of intensities and the product rule.

TABLE II. The fundamental vibrational frequencies for naphthalene and naphthalene- d_8 .

Species	Freq. no.	Type of vibration	C_{10}H_8 cm^{-1}	C_{10}D_8 cm^{-1}	R
A_g	1	CH stretching	3058	2268	1.35
	2	CH stretching	3001	2257	1.33
	3	CC stretching	1576	1548	1.02
	4	CC stretching	1379	1379	1.00
	5	§ip CH bending and	1240	1006	1.23
	6	skeletal	1024	862	1.19
	7	breathing	943	752	1.25
	8	ip skeletal distortion	762	694	1.10
	9	ip skeletal distortion	512	491	1.04
$\pi(R) = 3.83\ (4.00)$					
A_u	10	op CH bending	1307		
	11	op CH bending	1094		
	12	op skeletal distortion	842		
	13	op skeletal distortion	(400)		
B_{1g}	14	CH stretching	3025	2302	1.31
	15	CH stretching	2980	2257	1.32
	16	CC stretching	1625	1573	1.03
	17	CC stretching	1586	1437	1.10
	18	ip CH bending	1439	1170	1.23
	19	ip CH bending	1145	929	1.23
	20	ip skeletal distortion	879	777	1.13
	21	ip skeletal distortion	611	569	1.07
$\pi(R) = 3.58\ (3.75)$					
B_{1u}	22	op CH bending	956	790	1.21
	23	op CH bending	780	628	1.24
	24	op skeletal bending	475	408	1.16
	25	op wing-wagging	176	(160)	1.10
$\pi(R) = 1.91\ (1.93)$					
B_{2g}	26	op CH bending	1167	875	1.33
	27	op CH bending	715	541	1.32
	28	op skeletal bending	191	180	1.06
$\pi(R) = 1.86\ (1.89)$					
B_{2u}	29	CH stretching	3034	2285	1.33
	30	CH stretching	2942	2256	1.30
	31	CC stretching	1601	1440	1.11
	32	CC stretching	1385	1258	1.10
	33	ip CH bending	1268	1050	1.21
	34	ip CH bending	1125	885	1.27
	35	ip skeletal distortion	620	595	1.04
	36	ip skeletal distortion	362	328	1.10
$\pi(R) = 3.71\ (3.85)$					
B_{3g}	37	op CH bending	1099	829	1.33
	38	op CH bending	774	671	1.15
	39	op skeletal bending	588	541	1.09
	40	op skeletal bending	285	270	1.06
$\pi(R) = 1.77\ (1.84)$					
B_{3u}	41	CH stretching	3070	2323	1.32
	42	CH stretching	2984	2271	1.31
	43	CC stretching	1723	1569	1.10
	44	CC stretching	1508	1391	1.08
	45	ip CH bending	1143	905	1.26
	46	ip CH bending	1012	830	1.22
	47	ip skeletal distortion	742	680	1.09
	48	ip skeletal distortion	581	546	1.06
$\pi(R) = 3.65\ (3.85)$					

§ ip = in-plane.
|| op = out-of-plane.

¹⁴ D. C. McClure (private communication).

TABLE III. Comparison of the experimental and calculated values of the heat capacity and entropy of naphthalene.

T °K	C_p° cal/deg-mole		S° cal/deg-mole	
	Expt.	Calc'd	Expt.	Calc'd
451.0	48.18±0.48	48.13	96.85±0.44	96.92
522.7	54.17±0.54	54.28	104.41±0.44	104.48

The two unassigned B_{2g} hydrogen motions were selected at 725 and 1167 cm^{-1} for C_{10}H_8 and at 541 and 875 cm^{-1} for C_{10}D_8 . This choice places two C_{10}D_8 fundamentals at 541 cm^{-1} , a proposal which is consistent with the high intensity of this band.

A_u (4 FUNDAMENTALS)

Bands which could be associated with A_u motions are those observed in the infrared spectrum of solid naphthalene but absent in the spectrum of the gas. Seven bands which show this behavior are listed in reference 4. The normal coordinate analysis permits an estimate that the lowest A_u vibration is in the range 300–500 cm^{-1} . This frequency was guessed to be 400 cm^{-1} . The remaining three frequencies were selected from the seven bands listed in reference 4 with consideration of the expected spectral location and the thermodynamic properties. The final selections are 842, 1094, and 1307 cm^{-1} .

DISCUSSION

Table II summarizes the present assignment for C_{10}H_8 and C_{10}D_8 . The table includes the value of R and the presumed vibration mode. For each symmetry species, agreement with the product rule can be seen by comparing $\pi(R)$, the product of the assigned R 's, with the product calculated from the appropriate molecular parameters (given parenthetically after $\pi(R)$ in Table II).

The calculated entropy depends heavily upon the selections of the fundamental frequencies below 500 cm^{-1} . The present work utilizes two important data in the choice of these low frequency fundamentals; the observed infrared absorption at 176 cm^{-1} , and the argument in favor of assigning both 191 and 285 cm^{-1} as fundamentals.¹⁴ To establish the sensitivity of the calculated thermodynamic properties toward changes of these low frequency motions, two alternative assignments were made, omitting the Raman line at 285 cm^{-1} or the Raman line at 191 cm^{-1} . In each case, the com-

TABLE IV. Calculated values of the thermodynamic properties of naphthalene in the ideal gas state.

T , °K	C_p° cal/deg-mole	$\frac{H^\circ - E_0^\circ}{T}$	$-\frac{(F^\circ - E_0^\circ)}{T}$	S° cal/deg-mole
		cal/deg-mole	cal/deg-mole	
273.16	29.18	15.83	61.92	77.75
298.16	32.08	17.07	63.36	80.43
300	32.28	17.16	63.46	80.63
400	43.20	22.34	69.11	91.44
500	52.44	27.47	74.65	102.11
600	59.94	32.28	80.08	112.36
700	66.01	36.68	85.40	122.07
800	71.00	40.67	90.56	131.22
900	75.13	44.27	95.56	139.83
1000	78.59	47.54	100.40	147.93
1100	81.52	50.50	105.07	155.56
1200	84.00	53.19	109.58	162.77
1300	86.11	55.64	113.93	169.57
1400	87.93	57.89	118.14	176.03
1500	89.49	59.94	122.20	182.14

pensating changes required to restore agreement with the experimental thermodynamic properties were such that the calculated thermodynamic properties were unchanged within 0.3 cal/deg-mole over the temperature range 300–1500°K. These assignments suggest that alternate interpretations of the low frequency fundamentals will not radically alter the calculated thermodynamic properties.

THERMODYNAMIC PROPERTIES

Table III shows a comparison of the experimental and calculated values of the heat capacity and entropy. The calculated values are identical to those given by Barrow and McClellan⁵ except for the thermodynamic contributions by the vibrational degrees of freedom. The agreement is within the experimental error.

Table IV lists the calculated values of the thermodynamic properties of naphthalene in the ideal gas state from 273.16° to 1500°K. The calculated values are probably accurate to ± 0.5 cal/deg-mole but they are listed with more significant figures for uses where internal consistency is desired.

ACKNOWLEDGMENT

We wish to express our appreciation to the American Petroleum Institute Research Projects 44 and 50 for support of this investigation, and to Dr. E. R. Lippincott, Dr. D. S. McClure, and Dr. H. Sponer for extremely helpful discussions.