Intermolecular dynamics of deuterated benzene

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Of the 24 distinct intermolecular modes of deuterated benzene, with wave vectors corresponding to the four highest symmetry points R, U, S, and T at the surface of the Brillouin zone, 23 have been observed and identified by means of coherent neutron inelastic scattering experiments. These results complement the zero wave vector data (18 normal mode frequencies) obtained previously by far infrared and Raman scattering methods, and provide a more comprehensive test of any theoretical model of the intermolecular forces in this simplest of aromatic compounds. The results are interpreted in terms of a particular force model involving pairwise interatomic forces, specified by three Buckingham 6-exponential potential functions for $C...C$, $C...D$, and $D...D$ pairs respectively, between atoms on *different* molecules (so-called nonbonding interactions). The agreement between theory and experiment, as regards both the normal mode frequencies and eigenvectors, is reasonably satisfactory, but the existence of more than one set of numerically suitable parameters casts considerable doubt on the uniqueness of the model.

I. INTRODUCTION

Benzene is one of the simplest aromatic hydrocarbons and its chemical and molecular structures are prototypes from which many more complex hydrocarbons are derived. Consequently, a knowledge of the intermolecular forces in benzene is important in understanding the properties of a very large number of organic materials. There have been many experimental measurements made on benzene in an effort to specify its intermolecular and interatomic forces and it has frequently been used as a "test" molecule for theoretical calculations of these forces. All these measurements have been of normal modes of zero wave vector (zone center). In the present paper we report measurements of the intermolecular mode frequencies at the high symmetry, zone boundary points $R, U, S,$ and T in fully deuterated benzene (C_6D_6), made by the technique of coherent inelastic neutron scattering. Several low frequency branches of the dispersion relation have also been outlined for the [010] and [101] directions. These experimental measurements, together with the zone center mode results, are then used to refine the parameter values for intermolecular force models based on nonbonded atom–atom potentials.

Benzene has no solid–solid phase transitions at normal pressures. Its crystal structure has been determined by x-ray[1] and neutron[2] diffraction methods. The crystal lattice is orthorhombic, space group $P\,bca$ (D_{2h}^{15}), and there are four planar molecules in the unit cell. Two projections of the unit cell are shown in Fig. 1. The high symmetry points and lines of the Brillouin zone are shown in Fig. 2. The optically active normal mode frequencies at Γ have been measured in C_6H_6 by both far-infrared[3–6] and Raman[8–12] scattering techniques and similar measurements have been made in d-benzene.[7,9] The assignment of the observed modes is fairly well established, although some ambiguities in the interpretation of the Raman active internal modes remain. Neutron scattering measurements have been made on h-benzene.[13,14] These measurements were made on polycrystalline samples and utilized the large *incoherent* neutron scattering cross section of hydrogen. The spectra thus obtained are related to the frequency distribution function for the normal modes, albeit in a rather complicated manner. The spectra were compared with those expected from the calculated phonon frequency distribution and reasonable agreement was found. However, no detailed measurements of the intermolecular frequencies could be made in these incoherent scattering experiments. The temperature dependence of the elastic constants of h-benzene has also been measured.[15]

The first complete calculation of the vibrational spectrum of benzene[16] used an extension of Wilson's method. The experimentally measured optic mode frequencies at Γ have been compared with calculations[17,18] based on a wide variety of atom–atom potentials. The Williams

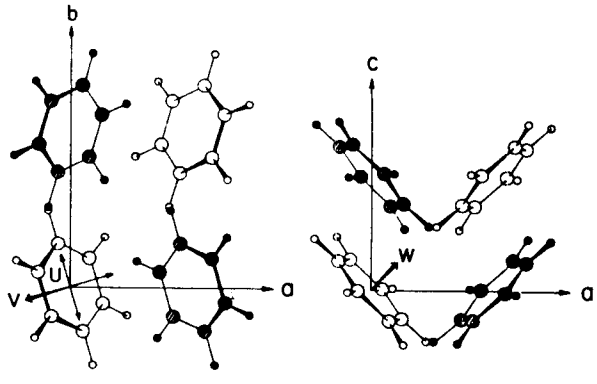

FIG. 1. Two projections of the unit cell of benzene. The shaded molecules are one half the unit cell dimension above the plane. U, V, and W indicate the principal axes of inertia of the molecule.

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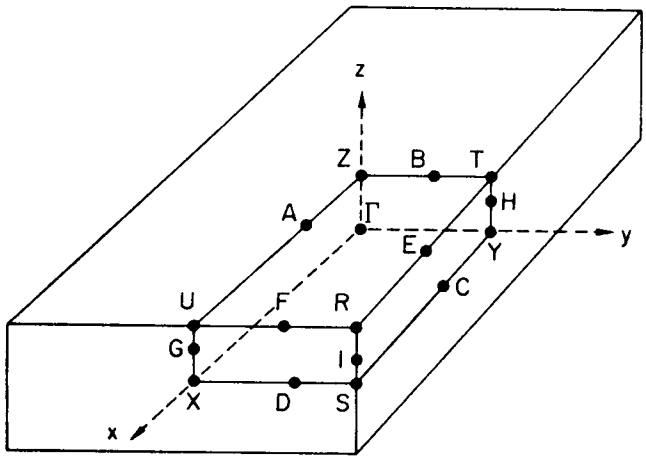

FIG. 2. High symmetry points and lines in the Brillouin zone for benzene.

parameters[19] were used in an extensive calculation[20] of these modes in both *h*-benzene and *d*-benzene, and also of the complete phonon dispersion relation for *h*-benzene.[21] It is this latter model which has been developed further in the present work, in order to make comparisons not only with the intermolecular mode frequencies at several points in the Brillouin zone, but also with the normal mode eigenvectors as manifested by the neutron coherent inelastic scattering intensities (the "inelastic" structure factors) observed in our experiments.

II. EXPERIMENTAL

In the present experiment several intermolecular mode frequencies in *d*-benzene have been measured by the technique of coherent, inelastic neutron scattering. Because of the large incoherent scattering cross section of hydrogen, coherent scattering measurements can be made far more easily on fully deuterated benzene than on the hydrogenous material. Single crystals of 98% deuterated benzene were grown by slow cooling of liquid benzene. In the course of the experiment three different crystals were grown, each with a volume about 4 cm^3. Different crystal orientations were used for each specimen to enable measurements to be made at all the special points in the zone *R*, *U*, *S*, and *T* (see Fig. 2). All the measurements were made on triple-axis crystal spectrometers operated in their constant momentum transfer mode[22] at the NRU and NRX reactors, Chalk River. Since *d*-benzene has four molecules in the unit cell, there are 24 distinct intermolecular modes for a general wave vector in the Brillouin zone. Because of the relatively low symmetry of benzene there are few points or directions in the zone at which this number is reduced by the symmetry operations. There is, for example, no reduction at the Γ point (zone center). However, at the points *R*, *U*, *S*, and *T*, and along the lines *I*, *E*, and *F* (see Fig. 2) symmetry reduces the number of distinct intermolecular frequencies to 6, each being four-fold degenerate. At the points *R*, *U*, and *S* we have measured all six frequencies while at *T* we have observed only five of the six distinct modes. The intermolecular frequencies at *R* and *U* were measured at 105 K and those at *S*, *T* were measured at 98 K. For the measurements at *R* and *U* the monochromator and analyzer were the Be (002) and Cu (002) reflections, respectively, while Si (113) and Cu (002) were utilized for the measurements at *S*, *T*. Four typical scattered neutron distributions are shown in Fig. 3. In addition, sev-

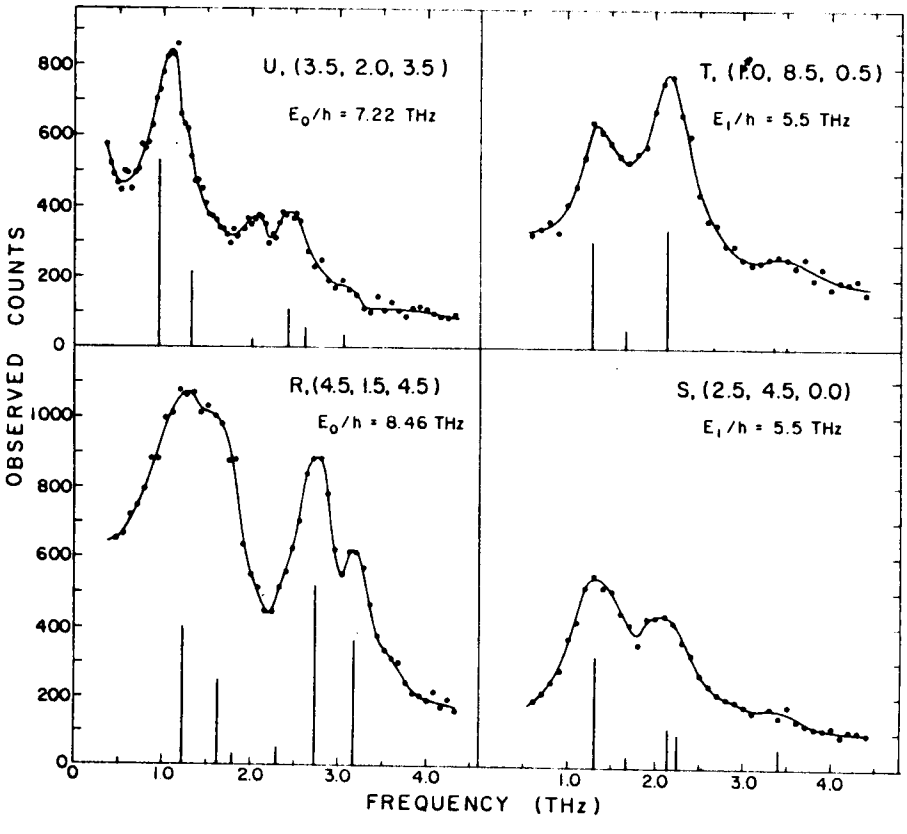

FIG. 3. Typical scattered neutron distributions corresponding to four momentum transfer vectors Q. The lines are hand drawn through the experimental data points. The vertical lines are drawn at the observed frequencies and their lengths are proportional to the calculated one-phonon structure factors. The reciprocal space coordinates are given in brackets for each momentum transfer Q and the fixed incident (E_0) or scattered (E_1) neutron energies are shown.

eral low frequency modes along the [010] and [101] directions were also measured.

At any given momentum transfer, even those corresponding to the high symmetry points, more than one intermolecular mode is observed. Consequently, the assignment of the peaks in the scattered neutron distributions to the correct intermolecular modes is a nontrivial problem. The assignment is made by comparing the integrated intensities of the observed peaks with the inelastic (one-phonon) structure factors calculated from an assumed lattice dynamical model. In the present experiments the one-phonon structure factor was calculated from the lattice dynamical model of Bonadeo and Taddei[21] (see Sec. III). In Fig. 3 the lengths of the vertical lines are proportional to the intensities calculated as described above and they are drawn at their respective observed frequencies. The calculation predicts that most of the intermolecular frequencies should have significant intensity at the momentum transfers shown. Although there is fairly good overall agreement, the calculated intensities show some discrepancies when compared with those observed, indicating that the model does not calculate the intermolecular mode eigenvectors correctly in all cases. For example, the U mode near 2 THz is observed to be more intense than expected from the model calculation, and the combined intensity of the low frequency R modes is seen to exceed that of the two highest frequency R modes, while the opposite behavior is indicated by the calculations. There is, nevertheless, substantial agreement between theory and experiment for many scattered neutron distributions such as those in Fig. 3, corresponding to each of the points R, U, S, and T. From an overall comparison between theoretical and observed intensities in all zones, the assignment of the intermolecular mode frequencies was made. The results are given in Table I. For the R, U, and S points all six distinct intermolecular frequencies are determined at each point. At the T point, however, only five of the six frequencies can be unambiguously assigned. There are indications that the T_5 mode has a frequency slightly below that of T_4, but we are unable to assign a definite T_5 mode frequency.

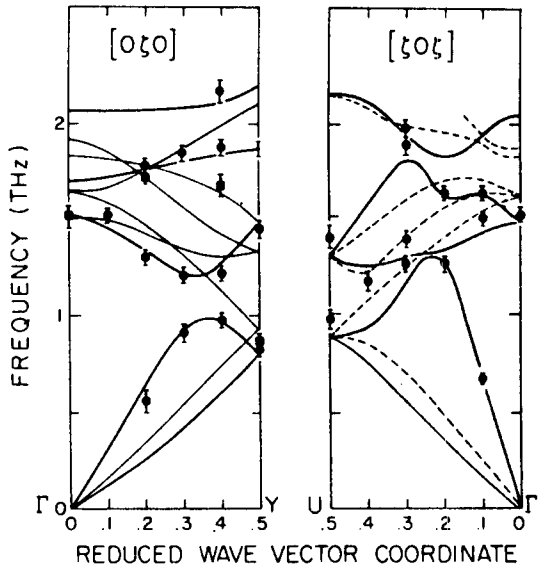

FIG. 4. Comparison of experimental and theoretical dispersion curves in C_6D_6 near 100 K. The "Williams" parameters are used in the calculations.

The analysis of the measurements of the low frequency branches along [010] and [101] directions proved to be very difficult. The calculated structure factors indicated that all of the intermolecular modes contributed to the scattered neutron distributions with rather similar intensity. However, despite this difficulty, enough modes were assigned definite frequencies to outline some of the low frequency branches. The experimental frequencies are compared with the calculated dispersion curves in Fig. 4.

III. THEORETICAL

In the atom–atom model[20,21] the intermolecular potential is written as

$$V_e=\frac{1}{2}\sum_{\alpha\beta}\sum_{\mu\nu}\sum_{ij} V^{\beta\nu j}_{\alpha\mu i}(r^{\beta\nu j}_{\alpha\mu i}) ,$$

where $r^{\beta\nu j}_{\alpha\mu i}$ (denoted as r_{ij} below) is the distance between

TABLE I. Frequencies (in THz) of intermolecular modes in C_6D_6 near 100 K, corresponding to certain high-symmetry points at the Brillouin zone boundary. The frequencies are calculated with the "Williams" parameters.

Mode	R_2	R_2	R_1	R_1	R_2	R_1
$R(1/2,1/2,1/2)$						
Observed	1.23±0.03	1.63±0.05	1.80±0.05	2.30±0.03	2.73±0.04	3.18±0.04
Calculated	1.23	1.50	1.79	2.33	2.80	3.28
$U(1/2,0,1/2)$						
Observed	0.96±0.06	1.35±0.05	2.02±0.03	2.43±0.05	2.62±0.05	3.06±0.06
Calculated	0.87	1.29	2.15	2.48	2.74	3.21
$S(1/2,1/2,0)$						
Observed	1.31±0.02	1.67±0.05	2.14±0.03	2.55±0.07	3.25±0.05	3.41±0.05
Calculated	1.13	1.68	2.14	2.50	3.21	3.34
$T(0,1/2,1/2)$						
Observed	1.29±0.03	1.67±0.07	•••	2.14±0.03	2.67±0.07	3.35±0.05
Calculated	1.18	1.67	2.02	2.18	2.55	3.38

atoms i and j belonging to two different molecules μ, ν within unit cells α, β. Following Williams[19] we have used atom–atom functions of the Buckingham form

$$V(r_{ij}) = A \exp(-Br_{ij}) - Cr_{ij}^{-6}$$

A set of parameters A, B and C is required to specify each of the three possible interactions between C and H (or D) atoms.

TABLE II. Observed and calculated intermolecular mode frequencies (in cm^{-1}) in C_6H_6 and C_6D_6 with the "Williams" and "Refined" parameters. (1 cm^{-1} = 0.029979 THz).

Crystal	Point in BZ	Symmetry	ν_{obs}	ν_{calc} Williams	ν_{calc} Refined
		B_{1u}	85	86	88
			73	72	72
			...	...	...
		B_{2u}	96	101	102
			66	59	60
			...	...	...
		B_{3u}	99	98	101
			54	53	53
			...	...	...
C_6H_6	Γ	A_g	92	95	95
			79	75	77
			57	54	54
		B_{1g}	128	130	129
			100	96	97
			57	60	60
		B_{2g}	...	101	103
			90	93	93
			79	83	82
		B_{3g}	128	128	127
			92	89	89
			61	67	64
		$u(R_2)$	91	94	95
			54	50	50
			41	41	42
	R	$g(R_1)$	106	109	109
			77	78	79
			60	60	58
			114	111	111
			85	83	84
	S		75	74	75
			71	71	71
			56	56	57
			44	38	39
C_6D_6			112	113	112
			89	85	85
	T		71	73	73
			...	67	68
			56	56	58
			43	40	40
			102	107	106
			87	91	92
	U		81	83	83
			67	72	71
			47	43	44
			32	29	30

TABLE III. Comparison of atom–atom potential parameters before and after fitting to zone center and zone boundary mode frequencies. Units for A, B, and C are kcal/mole $Å^{-1}$ and kcal/mole $Å^6$, respectively. 1 kcal/mole = 0.69489×10^{-20} J/bond; 1 $Å^{-1}$ = 10 nm^{-1}; kcal/mole $Å^6$ = 0.69489×10^{-80} (J/bond) m^6.

Interaction	Parameter	Williams	Refined
H–H	A	2654	1264
	B	3.74	3.74
	C	27.3	−26.5
H–C	A	8766	15475
	B	3.67	3.67
	C	125	330
C–C	A	83630	41800
	B	3.60	3.60
	C	568	10

Since the lowest lying internal mode of benzene has a frequency greater than 12 THz, there is a negligible interaction between internal and external modes,[20] and the rigid body approximation can be used. Under these conditions the dynamical problem is completely determined by the intermolecular potential and the crystal structure.

The calculation method used in the present work has been discussed in detail[20,21] and will be only outlined here. The dynamical matrix is constructed on the basis of Eckart mass-weighted molecular rotation and translation coordinates, which are reduced for translational symmetry at each point K in reciprocal space; further symmetrization and the removal of degeneracies are accomplished using the irreducible representations of $G_o(K)$. Using the calculated eigenvectors, the normal modes are transformed back to the one-molecule basis, and the complex atomic displacements are then used to calculate the structure factors. The refinement procedure is described in Refs. 21 and 23; starting with a set of trial parameters, the derivatives of the dynamical matrix elements with respect to potential parameters are calculated, reduced and symmetrized, and the Jacobian of the calculated frequencies constructed with the aid of the calculated eigenvectors. The Jacobians for the crystal lattice energy (equated to the measured heat of sublimation) and the equilibrium conditions are also evaluated, and the parameters refined with a least squares procedure. In the present work the method described in Ref. 23 has been expanded so as to be able to include not only optically active (Γ point) modes, but also frequencies at any point in the Brillouin zone.

The philosophy underlying this type of calculation has recently been criticized by Starr and Williams,[24] who point out (a) that these calculations have not been carried out at the (theoretical) minimum energy structure, (b) electrostatic contributions to the intermolecular potential have been ignored, and (c) the hydrogen interaction center has been located at the nuclear site (C–H bond length 1.09 Å) rather than at the center of the hydrogen electron distribution (a foreshortened C–H bond length of 1.027 Å). In making the calculation for the *observed* structure rather than for that corresponding

to the theoretical minimum energy, we are neglecting effects arising from the first derivative of the energy. If we were to adopt the opposite viewpoint, we would be making a more consistent calculation, but for a hypothetical "idealized" benzene crystal rather than for real benzene. Use of the foreshortened C–H or C–D bond length in conjunction with the Williams' parameters is both consistent and relatively straightforward when only static properties are considered. The location of interaction centers at points other than those at the mass centers poses awkward problems in dynamical calculations such as the one-phonon structure factors. (See Kjems and Dolling[25] for an example of these problems in the case of solid N_2.) Thus it seems reasonable to allow the hydrogen mass and interaction center to coincide in our calculations and to minimize the resulting (small) inconsistency by allowing the potential parameters to vary. Neglect of specific electrostatic interactions may also be justified at this level of approximation, with these effects being taken into account by adjustments of the existing parameters. In summary, therefore, we prefer to make use of the simpler (but numerically successful) approach of the earlier calculations[20,21] rather than to introduce the additional refinements suggested by Starr and Williams.[24]

IV. REFINEMENT OF POTENTIAL PARAMETERS

Although the overall agreement between observed frequencies and those calculated using Williams' parameters is already good, we have attempted a refinement using the data obtained in the present work for C_6D_6 and the Γ point frequencies for C_6H_6 which are known from optical experiments. The most complete assignments for the translational modes are reported in Refs. 4 and 6. We have taken the values of Wyncke and Hadni,[6] who made polarized far infrared absorption measurements at various temperatures. Frequencies corresponding to 100 K were obtained by interpolation. The assignments and frequencies of the Raman bands were taken from the single crystal measurements of Bonadeo *et al.* at 140 K, with the reinterpretation of some bands proposed by Ellenson and Nicol.[12] The columns of the Jacobian matrix for the A and B parameters of each type of interaction are found to be nearly proportional to each other, so that the parameters are not independent. This seems to be a general feature of the Buckingham form, since it also occurred in the refinements of similar force models for chlorinated[23] and brominated[26] benzenes. Therefore only the A and C parameters were refined. In Table II we show the observed frequencies together with those calculated from the initial set of Williams' parameters and from the parameters after refinement. The parameter values themselves are listed in Table III. Disconcertingly large changes are obtained for several parameters. In particular, the Van der Waals coefficient C for the H–H (or D–D) interactions changes sign, and that for the C–C interactions is very much reduced. The one-phonon structure factors calculated from the refined parameters show many quantitative differences from those obtained from the original Williams' parameters. Nevertheless, the overall agreement between theory and experiment is of substantially the same quality as that illustrated in Fig. 3, so that it is not possible to eliminate the refined model parameters by means of the observed scattered neutron intensities. The dramatic variations in some of the model parameters indicate, however, that there is probably very little physical significance to be attached to individual model parameters; furthermore, it may well be possible to find other almost equally good fits to the results, involving sets of parameter values quite different from either set listed in Table III. It would seem, therefore, that the Williams' parameters, although close to optimal, are by no means unique, and that the fitting of such model parameters to experimental results for one particular crystal is of limited value. This reinforces the conclusion reached by previous authors[17,19] that a wide variety of properties should be considered for entire classes of compounds (with the assumption that potential parameters may be transferred from one compound to another) if an intermolecular potential function of general validity is to be established.

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