

Far-IR Vibration–Rotation–Tunnelling Spectroscopy of the Water Trimer

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Tunable far-infrared laser vibration–rotation–tunnelling spectroscopy (FIRVRTS) has been used to measure several intermolecular vibrations in the water trimer. Together with *ab initio* and group theoretical results, these data characterize the structure and especially the tunnelling dynamics of this system in considerable detail.

Much effort has been directed toward obtaining a quantitative description of the hydrogen-bonding interactions among water molecules. Both the intermolecular pair potential and the non-pairwise interactions have been subjects of numerous experimental and theoretical studies. Many empirical potentials^{1–4} (e.g. TIP3P/TIP4P, ST2, and SPC/SPC/E) have been devised for use in simulations of condensed-phase properties and biological systems. These generally employ simple pairwise rigid-body forms which implicitly incorporate the many-body effects in the parameters, but some models have recently appeared which incorporate polarization and monomer flexibility.^{5–7} None of these potentials can successfully account for more than a few properties of liquid water and this certainly limits the reliability of results obtained by computer simulations.

We have undertaken a study of small water clusters by FIRVRTS, with the goal of first extracting the water–water pair potential from spectra of the dimer, and then characterizing the many-body interactions in studies of larger clusters. The general approach and the results accumulated by the groups active in this area for a number of simple prototype systems is described in a recent review.⁸ Pugliano and Saykally⁹ reported the first definitive measurement of an intermolecular vibration in the water dimer as well as the first detailed spectroscopic study of the water trimer.¹⁰ Since the publication of that work, we have measured six new intermolecular vibrations in the non-deuteriated and deuteriated forms of the dimer, as well as several new VRT transitions in the trimer. We describe the latter results in this paper.

Water Trimer

Pugliano and Saykally¹⁰ (P–S) reported the measurement of a water trimer VRT band obeying c-type selection rules near 89.6 cm⁻¹ in the deuteriated isotopomer. The FIRVRT spectrum confirmed the chiral cyclic structure predicted early by *ab initio* calculations¹¹ and shown in Fig. 1. This band displayed a strongly perturbed near-symmetric-top rotational pattern with each rovibrational transition split into a quartet. Crude estimates of the O–O distances were made by assuming three point masses of 20 u and adjusting their separations for optimal agreement with the reported rotational constants. The spectral splittings were interpreted as resulting from isomerization tunnelling among 96 identical frameworks (48 pairs of enantiomers) *via* three low-barrier pathways: (1) ‘flipping’ of a single free hydrogen from one side of the ring to the

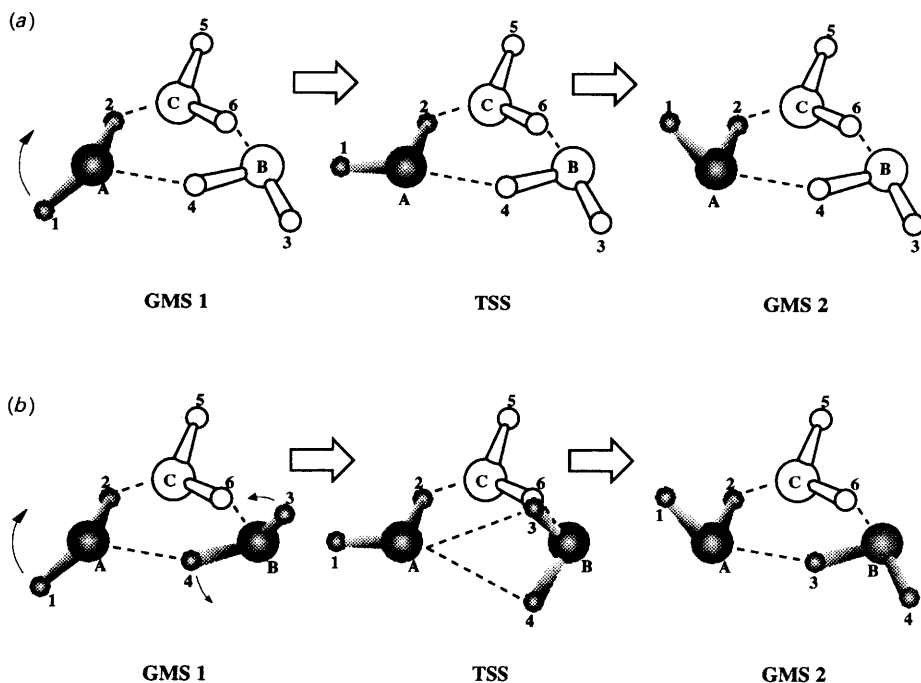


Fig. 1 (a) Structure and proposed 'flipping' pathway for the water trimer. The theoretical equilibrium geometry of the water trimer is a hydrogen-bonded ring in which each water acts as a donor and as an acceptor. Two of the free hydrogens lie above the ring and one below. 'Flipping' is accomplished by rotating one water monomer (shaded) about its donated hydrogen bond. The pathway connects a given global minimum structure (GMS 1) to an enantiomeric form (GMS 2). The transition-state structure (TSS) corresponds to two free hydrogens on opposite sides of the ring and the third approximately in the plane of the ring. In the early work of Owicki *et al.*,¹¹ this energy barrier was estimated to be very low: -0.04 kcal mol⁻¹ for (H₂O)₃ and 0.12 kcal mol⁻¹ for (D₂O)₃ after the zero-point correction. (b) The proposed 'donor tunnelling' pathway.¹⁶ This is a mechanism for one of the possible rearrangements that exchange the hydrogen-bonded and the free hydrogens on one water monomer, any of which could give rise to the observed quartet splittings in the spectra. Considering only the monomer pair highlighted in the diagram, 'donor tunnelling' in the water trimer is analogous to 'donor tunnelling' in the water dimer. In the trimer, 'donor tunnelling' involves two water units having their free hydrogens on opposite sides of the ring. The free 'donor' hydrogen moves into the bonded hydrogen and the latter moves to the other side of the ring. This exchange is accompanied by 'flipping' of the free 'acceptor' hydrogen. The TSS corresponds to the 'acceptor' molecule in the plane of the ring and the 'donor' molecule perpendicular to and bisected by that plane.

other; (2) a motion that effectively results in a C_2 rotation of a single monomer about its symmetry axis; and (3) a concerted motion that reverses the sense ('clockwise' or 'counterclockwise', *i.e.* $O_A-H \cdots O_B-H \cdots O_C-H \cdots O_A$ or $O_A-H \cdots O_C-H \cdots O_B-H \cdots O_A$) of the hydrogen-bonding network around the ring.

This work precipitated a number of sophisticated theoretical calculations of the trimer structure, vibrational frequencies and interconversion tunnelling dynamics.¹²⁻¹⁷ All high level *ab initio* calculations agree that the lowest-energy structure is a hydrogen-bonded ring in which two of the free hydrogens lie above the ring and one below, as shown in Fig. 1, and that the 'flipping' motion is nearly free; moreover, all disagree with the P-S crudely estimated O—O distances. Wales¹⁶ treatment of the tunnelling dynamics identified three low-energy reaction paths on the 12-dimensional inter-

molecular potential-energy surface (IPS) and estimated the associated splittings within a high barrier approximation. Schütz *et al.*¹⁷ carried out a detailed treatment of just the three ‘flipping’ coordinates, giving special attention to the implications of the very low barrier to the ‘flipping’ dynamics. A pseudo-rotation model was invoked to account for the observed $(\text{D}_2\text{O})_3$ band, as described below.

We have recently measured three new VRT bands for two isotopomers of the water trimer. The tunable far-infrared laser spectrometer used for these experiments has been fully described previously.^{8,18} The band origins are approximately 87.1 cm^{-1} [$(\text{H}_2\text{O})_3$], 98.1 cm^{-1} and 82.5 cm^{-1} [$(\text{D}_2\text{O})_3$]. Representative spectra are shown in Fig. 2 and 3. Line positions in the first two bands (87.1 and 98.1 cm^{-1}) correspond rigorously to symmetric rotor formulae, indicating a high degree of vibrational averaging. The

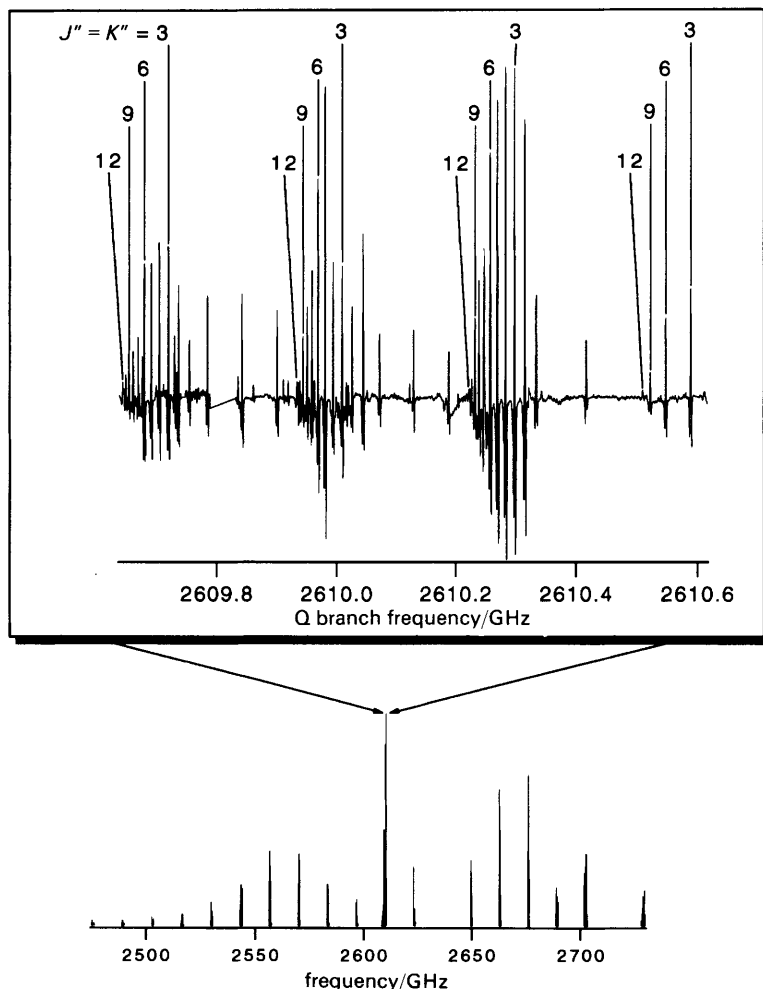


Fig. 2 FIRVRT spectrum of $(\text{H}_2\text{O})_3$. The insert is the Q branch of $J = K_c$ sub-band. The transitions with $K_c = 3, 6, 9,$ and 12 are labelled. The quartet spacing is 289 MHz . One of the quartet components has missing transitions when $K_c \neq 3n$ because of their vanishing statistical weights. This confirms that the appropriate molecular symmetry group for the water trimer is G_{48} . The quartet splitting is believed to arise from the donor proton exchange tunnelling. One example of this tunnelling pathway is shown in Fig. 1(b).

FIRVRTS of the Water Trimer

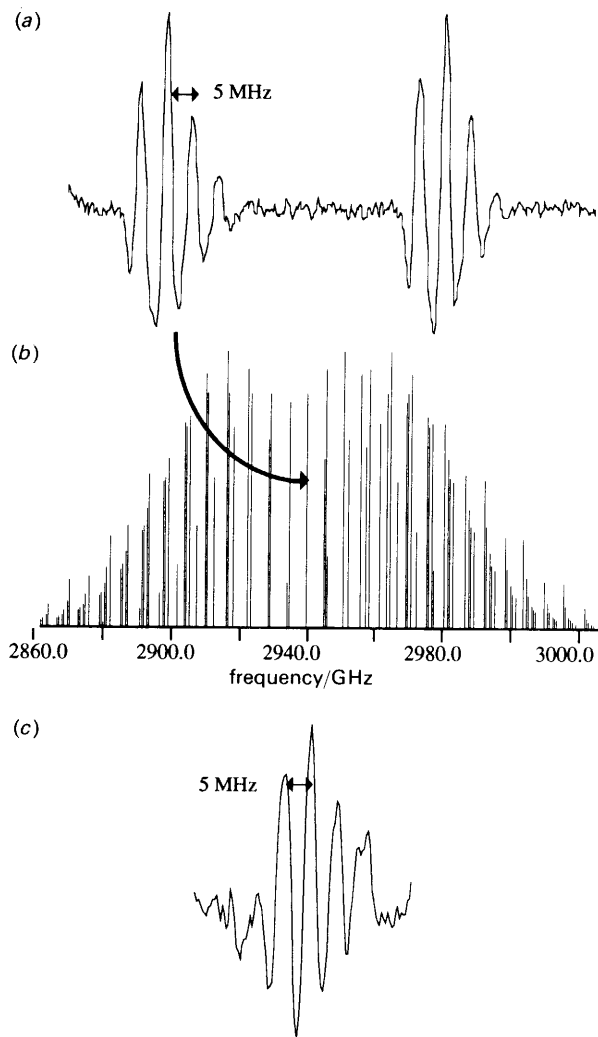


Fig. 3 (a) The $2_1 \leftarrow 2_0$ and $1_1 \leftarrow 1_0$ transitions of the 98.1 cm^{-1} band of $(\text{D}_2\text{O})_3$ showing the characteristic 5 MHz quartet splittings. (b) Calculated a-type rotational spectrum of $(\text{D}_2\text{O})_3$ at $T_{\text{rot}} = 4 \text{ K}$. Both the 82.5 cm^{-1} and 98.0 cm^{-1} bands reported were a-type bands of this form. (c) Typical transition from the 82.5 cm^{-1} band with approximately the same quartet spacing as that reported for the 98.1 cm^{-1} band. The 82.5 cm^{-1} band is approximately twice as weak as the 98.1 cm^{-1} band and has not been fully analysed. The symmetry assignment for $(\text{D}_2\text{O})_3$ was based in part on careful measurements of relative intensities of the quartet components of the 98.0 cm^{-1} band and that reported by P-S.

82.5 cm^{-1} band of $(\text{D}_2\text{O})_3$, is not yet completely analysed. Molecular parameters for each of these bands are given in Table 1.

The 87.1 cm^{-1} $(\text{H}_2\text{O})_3$ band consists of 337 measured VRT transitions obeying c-type selection rules. Every rovibrational transition was split into a quartet of equally spaced (289 MHz) lines, with an intensity pattern that is consistent with proton statistical weights calculated from the PI group G_{48} , as discussed later. The fact that one of the transitions in the quartet is missing when $K_c \neq 3n$ is a definitive signature of the molecular symmetry group. Because this is a c-type band, like that initially observed for $(\text{D}_2\text{O})_3$ by P-S, only the difference between c'' and c' can be determined.

Table 1 Molecular parameters of the observed trimer bands^a (MHz)

		(H ₂ O) ₃	(D ₂ O) ₃
transition type		c-type	a-type
band origin	ν_0	2609774.63 (20)	2940935.80 (61)
ground state	$A'' = B''$	6649.94 (2)	5796.19 (17)
	C''		3088.46 (15)
	D''_j	0.0414 (1)	0.0257 (29)
	D''_{JK}	-0.0619 (6)	-0.0281 (27)
excited state	$A' = B'$	6626.16 (2)	5786.19 (17)
	C'		3089.69 (16)
	$C'-C''$	0.82 (1)	
	D'_j	0.0400 (2)	0.0243 (29)
	D'_{JK}	-0.0604 (6)	-0.0236 (33)
quartet splitting	$\Delta\nu$	289.4 (11)	5
			6
			5

^a The assigned transitions were fitted to a symmetric-top Hamiltonian including only the listed constants. The standard deviations in the last digits are given in the parentheses. For (H₂O)₃, all four quartet components were fitted individually. Only slight differences were found in their rotational constants, which are listed here for only one component. For (D₂O)₃, only the most intense component was included in the fit. Note that for the c-type band observed for (H₂O)₃ as well as the (D₂O)₃ band observed by P-S, only the difference between the C'' and C' can be determined, while for the new (D₂O)₃ a-type band, these constants can be determined independently for each vibrational state. ^b Approximate band origins. Accurate rotational constants are not reported here because no definitive assignments have been made.

The 98.1 cm⁻¹ (D₂O)₃ band consists of 57 transitions assigned to an a-type band. A quartet splitting pattern was again observed, but the spacing was much smaller (5 MHz). Because of this small splitting, relative intensities can be determined reliably and the statistical weights predicted for the G₄₈ symmetry group were rigorously confirmed. Neither of the vibrational states was involved in the transition reported by P-S.

The 82.5 cm⁻¹ band of (D₂O)₃ is comparatively very weak and falls very near strong absorption from atmospheric water vapour. These factors have thus far precluded a definitive analysis, such as that presented for the other two bands. Nevertheless, 50 transitions of an a-type band have been observed and are split into quartets similar in spacing and intensity pattern to that of the other (D₂O)₃ bands. Additional work will be required to fix the origin of this band to within experimental precision and to determine if it shares any states with the other bands reported here.

New experiments performed on the original 89.6 cm⁻¹ band of (D₂O)₃ studied by P-S reveal it to originate in an excited state, as it is extremely sensitive to the supersonic jet conditions, unlike the other transitions studied in this work. This supports the model proposed by Schütz *et al.*,¹⁷ in which the 89.6 cm⁻¹ band originates in the $m = 1$ excited pseudo-rotational level. Moreover, the 89.6 cm⁻¹ band was found to be strongly perturbed, further strengthening this view. In fact, the 82.5 cm⁻¹ band may actually involve the perturbing state. Finally, we note that another band of (D₂O)₃ has been observed by Suzuki and Blake¹⁹ near 41.1 cm⁻¹. In the pseudo-rotation model, this probably corresponds to a pure $m = 0 \rightarrow 2$ pseudo-rotational transition.

A detailed group theoretical analysis has been carried out in order to analyse these spectra, and is published elsewhere.²⁰ When combined with theoretical calculations of the pathways and barriers, a characterization of the complicated structural rearrangement dynamics that occur *via* quantum tunnelling can be made. Two low-barrier pathways must be invoked in order to rationalize the observed spectra. The first, for which the calculated barrier is very near zero,¹² involves the 'flipping' motion of a single water molecule about the hydrogen bond. This 'flipping' pathway is shown in Fig. 1(a). Flip-

ping of a single water molecule rotates the A and B inertial axes by 60° about the C axis, such that six sequential flips will cause a complete rotation, indistinguishable from the true inertial motion. This is the pseudo-rotation.

The second low-barrier rearrangement pathway, also shown in Fig. 1(b), is called donor tunnelling and the calculated barrier height is $1.5 \text{ kcal mol}^{-1}$.¹² This is analogous to the donor tunnelling motion in the water dimer (barrier *ca.* $1.7 \text{ kcal mol}^{-1}$).²¹ As donor tunnelling becomes feasible, each pseudo-rotational state produced from the flipping motion splits into eight sub-levels, which appear as a quartet due to degeneracies. As described above, the patterns and relative intensities observed in the spectra agree rigorously with the statistical weights predicted²⁰ from a group theoretical analysis based on these two pathways for structural rearrangements.

We now consider the nature of the intermolecular vibrations described here. The cited theoretical studies^{12–17} include calculations of water trimer intermolecular ‘normal mode’ frequencies and IR intensities in the double-harmonic approximation. These are compared with experimental results in Table 2. The lowest-frequency modes of $(\text{H}_2\text{O})_3$ are calculated to lie between 100 and 200 cm^{-1} , 50–100% higher in frequency than the $(\text{H}_2\text{O})_3$ band we report here. However, the crudeness of the double-harmonic approximation for calculating intermolecular modes makes information on the calculated vibrational eigenvectors quite useful for matching the measured intermolecular vibrational bands with calculated normal modes. Only Schütz *et al.*¹⁷ provide such a description of their calculated vibrations. They conclude that of the 12 intermolecular trimer modes, three of the lowest-frequency vibrations are combinations of flipping motions (these have the highest IR intensity), and three are mainly intermolecular stretches. They replace their harmonic treatment of the lowest flipping vibration by the more appropriate pseudo-rotation model discussed above, using the approach of Harris *et al.* to estimate the pseudo-rotation constant.²²

The observed rotational constants in the new (unperturbed) data presented here change very little between lower and upper vibrational states; this makes the assignment of the observed bands to intermolecular stretches (where the vibrationally averaged hydrogen-bond lengths are longer, due to anharmonicity) rather unlikely. One possibility suggested by Schütz *et al.*¹⁷ is that the vibration observed by P–S is one of the other two flipping vibrational modes. Since the observed rotational constants are already ‘flipping-averaged’ in the ground state, it is reasonable to expect that they would not change much in such a vibration. Thus, such an assignment for all of the bands observed so far seems consistent with our analysis. However, until more data are accumulated, not much more can be ascertained about the nature of the measured vibrations. Moreover, we are unable to extract a more detailed structural characterization from the results presented here because of the large extent of the vibrational averaging that is so dominant in the spectra. As in the now infamous case of the ammonia dimer, such extreme non-rigidity mandates great caution and a large data set for extracting the structure of the cluster.

Table 2 Comparison of *ab initio* intermolecular vibrational frequencies^a of the water trimer with experimental results (in cm^{-1})

	HF	MP2	experiment
$(\text{H}_2\text{O})_3$	101, 135, 146, 151, 178, 192 ^b 134, 146, 149, 167, 182, 212 ^c 111, 147, 159, 166, 192, 208 ^d	158, 173, 185, 193, 218, 235 ^b	87.1
$(\text{D}_2\text{O})_3$	83, 114, 144, 149, 153, 184 ^d		41.1 ^e , 82.5, 89.6, 98.1

^a Only the lowest six modes from calculations are listed here. ^b Ref. 13; harmonic frequencies. ^c Ref. 15; harmonic frequencies. ^d Ref. 17; the $(\text{H}_2\text{O})_3$ modes are partially mixed. ^e Ref. 19.

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References

- 1 J. R. Reimers, R. O. Watts and M. L. Klein, *Chem. Phys.*, 1982, **64**, 95, and references therein.
- 2 W. L. Jorgensen, J. Chandrasekhar, J. Madura, R. Impley and M. L. Klein, *J. Chem. Phys.*, 1983, **79**, 926.
- 3 M. Townsend, M. Morse and S. A. Rice, *J. Chem. Phys.*, 1983, **79**, 2496.
- 4 H. J. C. Berendsen, J. R. Grigera and R. P. J. Straatsma, *J. Phys. Chem.*, 1987, **91**, 6269.
- 5 P. Cieplak, P. Kollman and Lybrand, *J. Chem. Phys.*, 1990, **92**, 6755; J. Caldwell, L. X. Dang and P. A. Kollman, *J. Am. Chem. Soc.*, 1990, **112**, 9144.
- 6 S. Kuwajima and A. Warshel, *J. Phys. Chem.*, 1990, **94**, 460.
- 7 L. X. Dang and B. M. Pettitt, *J. Phys. Chem.*, 1987, **91**, 3349.
- 8 R. J. Saykally and G. A. Blake, *Science*, 1993, **259**, 1570, and references therein.
- 9 N. Pugliano and R. J. Saykally, *J. Chem. Phys.*, 1992, **96**, 1832.
- 10 N. Pugliano and R. J. Saykally, *Science*, 1992, **257**, 1937.
- 11 J. C. Owicki, L. L. Shipman and H. A. Scheraga, *J. Phys. Chem.*, 1975, **79**, 1794.
- 12 J. Fowler and H. F. Schaefer III, *J. Am. Chem. Soc.*, submitted.
- 13 S. S. Xantheas and T. H. Dunning Jr., *J. Chem. Phys.*, 1993, **99**, 8774.
- 14 J. G. C. M. van Duijneveldt-van de Rijdt and F. B. van Duijneveldt, *Chem. Phys.*, submitted.
- 15 O. Mó, M. Yáñez and J. Elguero, *J. Chem. Phys.*, 1992, **97**, 6628.
- 16 D. J. Wales, *J. Am. Chem. Soc.*, 1993, **115**, 11180.
- 17 M. Schütz, T. Bürgi, S. Leutwyler and H. B. Bürgi, *J. Chem. Phys.*, 1993, **99**, 5228.
- 18 G. A. Blake, K. B. Laughlin, R. C. Cohen, K. L. Busarow, D-H. Gwo, C. A. Schmuttenmaer, D. W. Steyert and R. J. Saykally, *Rev. Sci. Instrum.*, 1991, **62**, 1701.
- 19 S. Suzuki and G. A. Blake, in preparation.
- 20 K. Liu, J. G. Loeser, M. J. Elrod, B. C. Host, J. A. Rzepiela, N. Pugliano and R. J. Saykally, *J. Am. Chem. Soc.*, 1994, **116**, 3507.
- 21 B. J. Smith, D. J. Swanton, J. A. Pople, H. F. Schaefer III and L. Radom, *J. Chem. Phys.*, 1990, **92**, 1240.
- 22 D. O. Harris, H. W. Harrington, A. C. Luntz and W. D. Gwinn, *J. Chem. Phys.*, 1966, **44**, 3467.