

Symmetry breaking in water molecule interactions

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We discuss the phenomenon of symmetry breaking observed in minimum-energy structures for water dimers. Based on two explicit representations of the intermolecular pair potential, the ST2 and PKC forms, lowest energy dimers are evaluated as a function of oxygen-oxygen separation, and it is concluded that a critical distance R_c exists which separates mechanically stable dimers of differing symmetries. For small distances, the familiar linear hydrogen bond is manifested, while for large distances dipole-dipole forces promote alignment of the molecular axes. At R_c , eight equivalent small-distance minima of low symmetry and four large-distance high-symmetry configurations undergo confluence. Thorough investigation of constrained minima illustrates how this transition occurs and invites comparison with the theory of critical phenomena. The second-order phase transition of the Ising ferromagnet provides a useful analogy to the structural symmetry breaking of the water dimer. Finally, we consider the relation of the present case to the larger issue of interactions in condensed phases, and to the interaction of more complex molecular pairs; one thereby discovers analogs for (a) Ising models in external fields, (b) upper and lower consolute points in liquid mixtures, and (c) first-order phase transitions.

I. INTRODUCTION

Substantial research effort has recently been expended in attempting to understand the interactions between water molecules. This activity has comprised both direct quantum-mechanical studies,¹⁻⁸ as well as semi-empirical approaches to determine closed form approximations to the potential.⁹⁻¹² At present, a consensus seems to have been reached concerning at least the qualitative character of water molecule interactions: At small distances, linear hydrogen bonds tend to form between neighbors, while at large distances the interaction between permanent molecular dipole moments dominates.

This paper focuses attention on one special aspect of the water-molecule pair potential which seems to have received little attention thus far. Eight equivalent linear hydrogen bond structures exist for a molecular pair at small separation, with the optimal geometry exhibiting only a single symmetry plane. On the other hand, dominant dipole-dipole forces at large separation would cause alignment of molecular symmetry axes, so that only four equivalent optimal pair structures arise, each with *two* symmetry planes. The manner in which the former transforms into the latter as intermolecular distance increases is not obvious. We illustrate that transformation by citing concrete numerical results for two published water-molecule potential functions. For both, we conclude that upon bringing two molecules together from infinite distance, a critical distance is reached at which a spontaneous change in symmetry occurs for the minimum-energy structure.

The first pair potential examined (Sec. II) is the "ST2" potential, which was devised for use in the simulation of liquid water by molecular dynamics.^{11,13-15} This potential is to be interpreted as an "effective pair potential"¹⁶ whose form incorporates the principal structural effects of potential nonadditivity.

The second pair potential used in the present study (Sec. III) was suggested by Popkie, Kistenmacher, and Clementi.⁸ It represents an analytical fit to their ac-

curate and extensive Hartree-Fock calculations for the ground-state energy hypersurface for two (rigid) water molecules. Although this "PKC" potential differs from "ST2" in several quantitative details, calculations presented in the next two sections show that both lead to the same type of singular but continuous symmetry breaking at finite intermolecular distance. This agreement probably indicates that the exact water-molecule pair potential shares identical behavior.

Section IV stresses the analogy between spontaneous symmetry breaking in the present context, and that encountered in the statistical mechanics of phase transitions. At the very least, this analogy provides an elementary mechanical model in terms of which critical phenomena and phase transitions may be partially understood.

The basic mechanism for occurrence of spontaneously broken symmetry is already present with hypothetical point molecules possessing permanent dipole and axial quadrupole moments. Details are provided in the Appendix. However, this level of simplicity is not appropriate for description of water molecules.

II. ST2 INTERACTION

The ST2 interaction is based upon a rigid four-point-charge model for each water molecule. Figure 1(a) shows the relevant geometrical structure. The point charges are located along four directions emanating from the oxygen nucleus, each pair of which occurs at the ideal tetrahedral angle 109.47° . Two of the point charges are positive ($+q$) and can be identified as protons; they are placed 1 Å from the oxygen nucleus. The two negative charges ($-q$) are present for charge neutrality; they reside 0.8 Å from the oxygen nucleus.

The ST2 potential consists of two principal parts:

$$V^{(2)}(\text{ST2}) = V_{LJ}(R_{12}) + S(R_{12}) v_{el}(1, 2). \quad (2.1)$$

The first, V_{LJ} , is a Lennard-Jones 12-6 potential acting between the oxygen nuclei, whose separation has been denoted by R_{12} . The second part contains the total

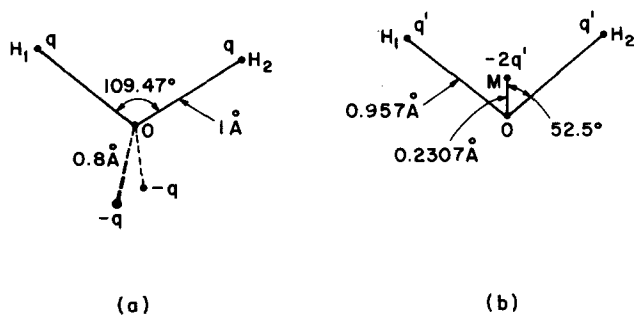


FIG. 1. Geometric arrangement of point charges used to define water-molecule pair interactions; (a) ST2 effective pair potential, (b) analytical fit to Hartree-Fock calculations constructed by Popkie, Kistenmacher, and Clementi.

electrostatic interaction v_{e1} , sixteen terms in all, for point charges on the two different molecules. This electrostatic contribution is modulated by a cubic spline function of the oxygen-oxygen distance R_{12} :

$$S(R_{12}) = 0, \quad (0 \leq R_{12} \leq R_L) \\ = \frac{(R_{12} - R_L)^2 (3R_U - R_L - 2R_{12})}{(R_U - R_L)^3}, \quad (R_L \leq R_{12} \leq R_U) \\ = 1 \quad (R_U \leq R_{12}). \quad (2.2)$$

Including the Lennard-Jones parameters ϵ and σ , the ST2 potential utilizes the following quantities:

$$q = 0.2357 e, \\ \epsilon = 7.5750 \times 10^{-2} \text{ kcal/mole}, \\ \sigma = 3.1000 \text{ \AA}, \\ R_L = 2.0160 \text{ \AA}, \\ R_U = 3.1287 \text{ \AA}. \quad (2.3)$$

In order to specify the relative configuration for two rigid water molecules, six coordinates are required. These can be chosen to be the distance R_{12} , and five angles describing the relative orientation of the molecules. The ST2 interaction provides an approximate value for the intermolecular interaction for any given set of the six relative coordinates.

Figure 2 shows schematically the structure of the minimum-energy dimer implied by the ST2 function. The single hydrogen bond is obvious (proton H_2 donated to acceptor oxygen O_2). This dimer possesses a re-

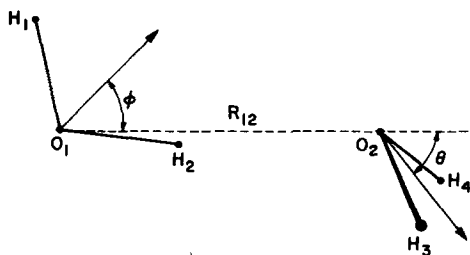


FIG. 2. Minimum-energy dimer structure. The plane containing the proton donor molecule ($H_1O_1H_2$) serves as a reflection symmetry plane.

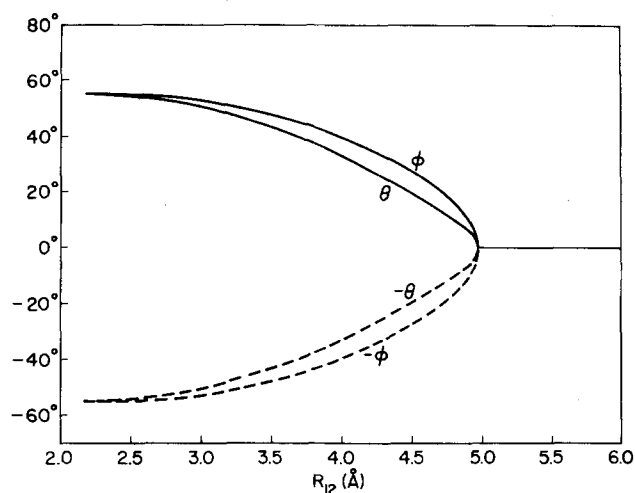


FIG. 3. Values of angles θ and ϕ (see Fig. 2) which provide constrained energy minima for the ST2 potential.

flexion symmetry in the plane containing the proton donor molecule and the symmetry axis of the acceptor molecule. The dimer is prevented from twisting out of this reflection-symmetric arrangement in part by proton-proton repulsions.

Direct calculation¹¹ shows that the dimer energy minimum exhibits the following geometric parameters (see Fig. 2):

$$R_{12} = 2.852 \text{ \AA}, \\ \theta = 51.8^\circ, \\ \phi = 53.6^\circ. \quad (2.4)$$

The ST2 energy at this minimum is -6.839 kcal/mole.

Equivalent minima may be generated by any combination of the following operations:

- rotate the acceptor molecule 180° about its symmetry axis;
 - rotate the donor molecule 180° about its symmetry axis;
 - exchange roles of donor and acceptor molecules.
- In all, eight distinct structures arise from these independent operations.

The molecular arrangement shown in Fig. 2 is also qualitatively correct for *constrained* energy minima, in which R_{12} has a preassigned value not necessarily equal to that shown in Eq. (2.4) for a global minimum. Of course, the angles θ and ϕ would then exhibit displaced values.

Figure 3 shows computed values of $\theta(R_{12})$ and $\phi(R_{12})$, the angles which provide constrained minima, versus R_{12} . As R_{12} increases from the distance 2.852 \AA corresponding to the global minimum, these minimizing angles decline monotonically and continuously to zero. As a result of these declines, the molecular symmetry axes become more and more nearly aligned with the oxygen-oxygen axis. Suddenly, at the critical distance

$$R_c(\text{ST2}) = 4.964 \text{ \AA}, \quad (2.5)$$

the alignment becomes complete. When R_{12} exceeds this value, no further change in the angles θ and φ is required; the molecular symmetry axes remain rigorously aligned.

It is clear from Fig. 3 that the rates of change of $\theta(R_{12})$ and $\varphi(R_{12})$ become infinitely rapid as R_{12} approaches R_c from below.

The values for $-\theta(R_{12})$ and $-\varphi(R_{12})$, indicated as broken curves in Fig. 3, correspond to donation of proton H_1 to oxygen O_2 in Fig. 2. This is one of the other equivalent dimer minima. Evidently this pair of minima suffers confluence at R_c . For larger R_{12} the eight minima therefore reduce to four, each of which has $\theta = \varphi = 0$. In these aligned dimers, the molecular planes remain perpendicular to each other, and both serve as reflection symmetry planes.

III. HARTREE-FOCK INTERACTION

Popkie, Kistenmacher, and Clementi based their analytical fit to Hartree-Fock dimer energies on the four-center model shown in Fig. 1 (b); note that this model uses OH bond length 0.957 \AA and HOH bond angle 105° . Three of the centers are located at the hydrogen and oxygen nucleus positions. The fourth center (M) lies in the molecular plane, 0.2307 \AA ahead of the oxygen nucleus along the molecular symmetry axis. Electrostatic charges

$$q' = 0.6704 e \quad (3.1)$$

are assigned to each of the hydrogens. The oxygen force center is regarded as uncharged, while center M carries charge $-2q'$.

The analytical fit function, $V^{(2)}$ (PKC), consists of the electrostatic interaction for the nine charge pairs in the two different molecules under consideration, augmented by exponential repulsion terms acting between the pairs of nuclei ($\alpha, \beta = \text{O, H}$):

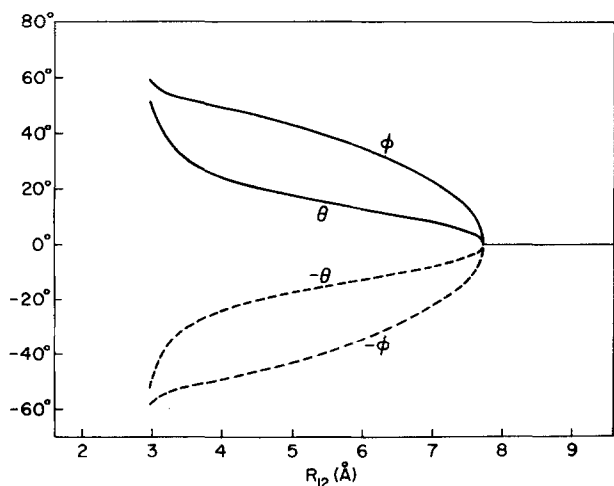


FIG. 4. Angles θ and φ describing the constrained energy minimum for the water dimer, subject to $V^{(2)}$ (PKC). Notice the differing energy scales for ST2 (left) and PKC (right).

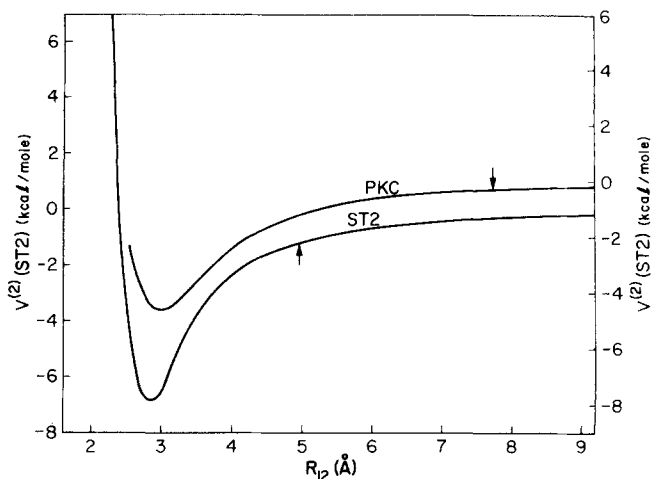


FIG. 5. Minimum dimer energies achieved at each distance R_{12} . The arrows locate the respective critical points R_c .

$$a_{\alpha\beta} \exp(-b_{\alpha\beta} r_{\alpha\beta}). \quad (3.2)$$

The six parameters used in these exponential repulsions were assigned the following values:

$$\begin{aligned} a_{\text{OO}} &= 3.65501 \times 10^5 \text{ kcal/mole}, \\ a_{\text{OH}} &= 3.43368 \times 10^3 \text{ kcal/mole}, \\ a_{\text{HH}} &= 90.2576 \text{ kcal/mole}, \\ b_{\text{OO}} &= 4.76328 \text{ \AA}^{-1}, \\ b_{\text{OH}} &= 3.65973 \text{ \AA}^{-1}, \\ b_{\text{HH}} &= 2.30881 \text{ \AA}^{-1}. \end{aligned} \quad (3.3)$$

The generic dimer configuration illustrated in Fig. 2 is relevant to the global energy minimum for $V^{(2)}$ (PKC). The computed geometric parameters are found to be

$$\begin{aligned} R_{12} &= 3.000 \text{ \AA}, \\ \theta &= 48.2^\circ, \\ \varphi &= 57.6^\circ. \end{aligned} \quad (3.4)$$

The corresponding energy is -4.598 kcal/mole . Consistent with the previous ST2 case, the structure implied by (3.4) involves a single nearly linear hydrogen bond. Once again there are eight equivalent minima in the full six-dimensional relative configuration space.

For different R_{12} choices, constrained energy minima for $V^{(2)}$ (PKC) were determined numerically. The results are plotted in Fig. 4. The pattern is similar to that shown earlier for ST2 (Fig. 3), with $\theta(R_{12})$ and $\varphi(R_{12})$ declining toward zero as R_{12} increases. Once again a critical distance R_c is reached beyond which molecular symmetry axes rigorously align, but this distance is substantially larger than before:

$$R_c(\text{PKC}) = 7.73 \text{ \AA}. \quad (3.5)$$

The characterization of this critical distance as the point of confluence for pairs of energy minima continues to hold true.

Figure 5 shows the energies of the constrained dimer minima, versus R_{12} , for both the ST2 and PKC interac-

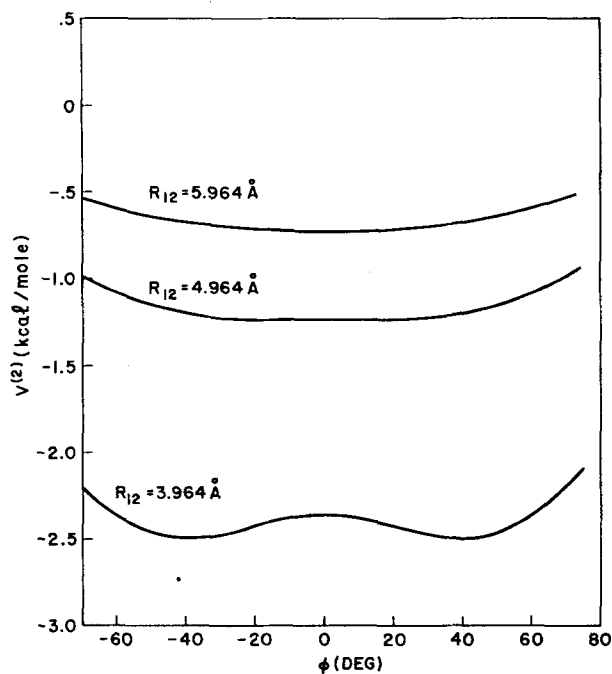


FIG. 6. Doubly-constrained energy minimum curves for the ST2 potential. Angle θ (see Fig. 2) is adjusted to minimize the interaction for each R_{12} , φ choice.

tions. The fact that the ST2 curve falls well below the PKC curve in the neighborhood of $R_{12} \approx 3 \text{ \AA}$ stems in part from the neglect of electron correlation effects in the Hartree-Fock approximation, and in part from the inclusion of nonadditive contributions in ST2 whose net effect should be increased binding.^{16,17} Since it can be argued that the correlation error in $V^{(2)}$ (PKC) affects this function's angle variations relatively little,¹⁸ we believe that the type of behavior shown in Fig. 4 is rather accurately indicative of the exact water dimer potential.

IV. RELATION TO CRITICAL PHENOMENA

The reduction in symmetry that spontaneously occurs for the constrained dimer as R_{12} decreases through R_c is analogous to the spontaneous symmetry breaking experience by an Ising ferromagnet cooled through its critical temperature T_c . The sudden but continuous change from zero of angle φ (or θ) in the former at R_c , is matched by a sudden but continuous change from zero of magnetization m in the latter at T_c .

This analogy can be pursued by examining detailed energy curves for the water dimer. In particular, Fig. 6 shows angle variation curves for the ST2 potential (PKC is qualitatively similar) at three distances, $R_c - 1.0 \text{ \AA}$, R_c , and $R_c + 1.0 \text{ \AA}$. These curves are plotted versus angle φ , and for each φ the acceptor angle θ has been adjusted so as to minimize the now doubly-constrained $V^{(2)}$ (ST2). At the smallest of the three distances, the energy curve clearly displays a pair of minima at nonzero angle, separated by a maximum at zero angle. Increasing the distance to R_c , however, causes the three extrema to flow together. Consequently, the R_c curve in Fig. 6 is very flat around zero angle,

having in fact vanishing curvature there. For distances exceeding R_c , a well-developed single minimum persists at zero angle, with positive curvature.

The family of energy curves versus φ in Fig. 6 provides the intermolecular force analog of the set of Ising model free energy curves versus magnetization.¹⁹ Thermal equilibrium requires that free energy be minimized at every temperature, so the Ising model seeks out the lowest minimum ($T \geq T_c$) or minima ($T < T_c$).

Strictly speaking, the Ising ferromagnet free energy curves to which we refer are those arising in approximate treatments such as the mean-field (Bragg-Williams) or quasichemical (Bethe-Peierls) approaches.²⁰ The common element in them is that near the critical point, the free energy F may be represented as a simple polynomial in magnetization m :

$$F(m, T) = F(0, T) + A \Delta T m^2 + B m^4, \quad (4.1)$$

$$\Delta T = T - T_c, \quad A, B > 0,$$

where for present purposes it suffices to neglect terms of order m^6 or higher. The potential energy analog to this equation would obviously be the following:

$$V(\varphi, R_{12}) = V(0, R_{12}) + C \Delta R \varphi^2 + D \varphi^4, \quad (4.2)$$

$$\Delta R = R_{12} - R_c, \quad C, D > 0.$$

Above T_c , the minimum free energy in Eq. (4.1) is just the function $F(0, T)$, while below T_c one recognizes that minima occur at

$$m = \pm (-A \Delta T / 2B)^{1/2}, \quad (4.3)$$

so that the form of the low-temperature free energy is

$$F(0, T) - [A^2 (\Delta T)^2 / 4B]. \quad (4.4)$$

Thus the equilibrium free energy in this class of approximations suffers a discontinuous second temperature derivative at T_c . The dimer potential energy analog gives $V(0, R_{12})$ when $R_{12} \geq R_c$, but owing to minima at

$$\varphi = \pm (-C \Delta R / 2D)^{1/2} \quad (4.5)$$

when $R_{12} < R_c$, the small-distance potential is

$$V(0, R_{12}) - C^2 (\Delta R)^2 / 4D. \quad (4.6)$$

The implied second R_{12} -derivative discontinuity at R_c is present in the curves of Fig. 5, though barely discernible to the eye.

V. POTENTIAL OF MEAN FORCE

In a condensed phase, the potential of mean force for a pair of molecules, $W^{(2)}$, describes the distribution of relative configurations in thermal equilibrium. Specifically, the molecular pair correlation function

$$g^{(2)}(1, 2) = \exp[-W^{(2)}(1, 2)/kT] \quad (5.1)$$

is proportional to that distribution.¹⁰ By convention, $W^{(2)}$ vanishes at infinite separation so that $g^{(2)}$ reduces to unity in that limit.

The function $W^{(2)}$ contains both the direct interaction $V^{(2)}$ for the pair of molecules considered, as well as an averaged contribution owing to molecules in the sur-

rounding medium. That medium might consist of the same species as those forming the pair, but it need not. In any case, $W^{(2)}$ would sensitively reflect the nature of feasible modes of packing molecules around the given pair.²¹

It is obvious that if the density ρ of the medium tends to zero, only the direct interaction remains in $W^{(2)}$:

$$\lim_{\rho \rightarrow 0} W^{(2)}(1, 2) = V^{(2)}(1, 2). \quad (5.2)$$

While ρ is small (i.e., dilute vapor medium), $W^{(2)}$ will differ little from $V^{(2)}$ for any relative configuration. With respect to the symmetry breaking investigated in the previous Sections, but now for $W^{(2)}$ instead of $V^{(2)}$, we would expect at best a small shift in R_c , with sign dependent on details of interactions between members of the pair and the dilute surroundings. Presumably both types of R_c shift are possible, depending on the chemical structure and properties of the medium molecules.

By contrast, the difference between $W^{(2)}$ and $V^{(2)}$ would be very large if the medium were liquid. R_c could undergo major shifts, and in particular, might collapse to zero to cause disappearance of the symmetry-breaking phenomenon. This last possibility nevertheless seems remote for a pair of water molecules.

We wish to point out one speculative but particularly interesting type of $W^{(2)}$ behavior, which seems to us not to be unreasonable in liquid media. Specifically, it may happen that the broken-symmetry dimer structures which minimize $W^{(2)}$ are partially confined to an isolated interval of positive distances,

$$0 < R_{1c} < R_{12} < R_{uc}. \quad (5.3)$$

By reducing R_{12} below the lower critical distance R_{1c} , the optimal dimer arrangements would revert to the dipole-aligned higher-symmetry arrangement characteristic of large R_{12} . The confinement of spontaneous symmetry breaking to one or more distinct intervals is suggested partially by the layering of concentric neighbor shells usually observed in pair correlation functions.²²

Upper and lower critical distances R_{uc} and R_{1c} are analogous to upper and lower critical temperatures that occur in a few binary liquid solutions. The nicotine-water system offers a classic example.²³ Therefore we suggest that $W^{(2)}$ for water dimers in suitable liquid media may offer a mechanical analogy to this delicately balanced solution behavior.

VI. DISCUSSION

(a) Having raised the issue of a spontaneous symmetry-breaking phenomenon in the interaction between water molecules, it is natural to inquire about relevance to other substances. The structure of the hydrogen fluoride dimer has been determined experimentally by Dyke, Howard, and Klemperer.²⁴ A single linear hydrogen bond is involved, but the proton acceptor molecule appears to be rotated 60° – 70° off the F–H····F axis. Since the molecular dipole moments

necessarily lie along the covalent bond axes, this minimum-energy dimer configuration possesses lower symmetry than the aligned structure to be expected at large intermolecular distance. Evidently, a critical distance R_c exists at which spontaneous reduction in symmetry arises.

(b) The C_{2v} symmetry of the isolated water molecule can be reduced by chemically substituting one of the hydrogen atoms with another type of atom or functional group. In this way, one attains other nonlinear molecules with permanent dipole moments, such as hypofluorous acid (HOF), methanol (HOCH₃), and lithium hydroxide (HOLi). The respective $V^{(2)}$'s will be dominated by dipole-dipole interactions at large distance, and will probably manifest nearly linear hydrogen bonds at small distance, just as does the water dimer. However these less symmetrical molecules would not be expected to exhibit a critical distance R_c at which singular change in constrained energy minimum structure occurs. Instead, continuous deformation of the aligned-dipole structure to the hydrogen-bond structure is possible as distance decreases from infinity, owing to the inherent bias introduced by chemical substitution. For this reason the chemical substitution plays a role analogous to an external magnetic field in the Ising model, which is known to remove the phase transition.

(c) In contrast to the analog of second-order phase change provided by the water dimer, the interaction of two ammonia molecules has the character of a *first-order* transition. This difference arises from the c_{3v} symmetry of each ammonia molecule that places the nuclei at vertices of a triangular pyramid.²⁵ The NH₃ molecules in this geometry possess permanent dipole moments parallel to the threefold rotational axis. At large intermolecular distance these dipoles would be expected to align along the direction connecting the nitrogens, with a staggered arrangement of hydrogens when viewed along that mutual axis. There will be six equivalent constrained $V^{(2)}$ minima in this large-distance regime.

At small distance the preferred mode of interaction involves a single linear hydrogen bond between one of the molecules acting as proton donor, the other acting as proton acceptor.²⁶ The dimer arrangement is illustrated in Fig. 7. In all, 18 such equivalent hydrogen-bonded structures can be formed. If a continuous connection were to be identified between these structures and the more symmetric ones which obtain at large separation, triplets would have to merge at some critical distance R_c to collapse the eighteen equivalent struc-

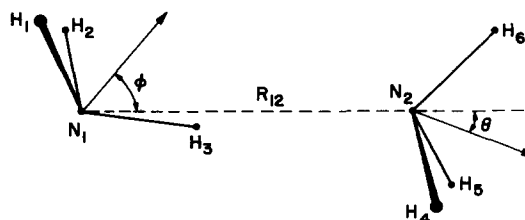


FIG. 7. Hydrogen-bonded ammonia dimer.

tures to six.

It follows from general group-theoretical arguments²⁷ that a continuous transition is *not* possible with change in symmetry elements by a factor of three. However, such a change would be required if the eighteen small-distance structures were to deform continuously into six. Instead, a discontinuous shift must occur at R_c , in which positive values of $\theta(R_{12})$ and $\varphi(R_{12})$ (see Fig. 7) suddenly jump to zero.

Such discontinuous jumps are characteristic of order parameters in first-order phase changes. A statistical-mechanical model, with threefold symmetry breaking, that exhibits exactly this type of behavior is the cubic lattice model for isotropic-nematic ordering of rigid linear molecules.²⁸

APPENDIX

Consider a pair of interacting point particles, each endowed with dipole moment μ and axial quadrupole moment Θ . Their interaction at distance R may be expressed as follows:

$$V^{(2)} = \frac{\mu^2}{R^3} F_{dd}(\theta_1, \theta_2, \varphi_{12}) + \frac{\mu\Theta}{R^4} F_{d\alpha}(\theta_1, \theta_2, \varphi_{12}) + \frac{\Theta^2}{R^5} F_{\alpha\alpha}(\theta_1, \theta_2, \varphi_{12}). \tag{A1}$$

Angle θ_i measures the deflection of the dipole direction for particle i from the direction toward the other particle. Angle φ_{12} represents the rotation along the interparticle axis required to bring the dipoles into coplanarity (and parallelism if $\theta_1 + \theta_2 = \pi$). The angle functions in (A1) have the following specific forms²⁹:

$$\begin{aligned} F_{dd} &= 2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \varphi_{12}, \\ F_{d\alpha} &= \frac{3}{2} [\cos \theta_1 (3 \cos^2 \theta_2 - 1) + \cos \theta_2 (3 \cos^2 \theta_1 - 1) \\ &\quad + 2 \sin \theta_1 \sin \theta_2 (\cos \theta_1 + \cos \theta_2) \cos \varphi_{12}], \\ F_{\alpha\alpha} &= \frac{3}{4} [1 - 5 \cos^2 \theta_1 - 5 \cos^2 \theta_2 + 17 \cos^2 \theta_1 \cos^2 \theta_2 \\ &\quad + 2 \sin^2 \theta_1 \sin^2 \theta_2 \cos^2 \varphi_{12} \\ &\quad + 16 \sin \theta_1 \cos \theta_1 \sin \theta_2 \cos \theta_2 \cos \varphi_{12}]. \end{aligned} \tag{A2}$$

For large R , it suffices to restrict attention to small deviations from $\theta_1 = 0, \theta_2 = \pi$, one of the two dipole-aligned configurations. Therefore set

$$\theta_1 = x, \quad \theta_2 = \pi - y. \tag{A3}$$

Through quadratic order in x and y , the interaction has the following form:

$$V^{(2)} \cong (\mu^2/R^3) [-2 + 6\Gamma - 12\Gamma^2 + (x^2 + y^2 + xy \cos \varphi_{12}) - 6\Gamma(x^2 + y^2) + \frac{3}{2}\Gamma^2(11x^2 + 6y^2 - 16xy \cos \varphi_{12})], \tag{A4}$$

where

$$\Gamma = \Theta/\mu R. \tag{A5}$$

In the event that Γ is very small, as will be the case if $R \rightarrow \infty$, the resulting quadratic form in x and y ,

$$x^2 + y^2 + xy \cos \varphi_{12}, \tag{A6}$$

is positive-definite, so the dipole-aligned structure

($x = y = 0$) is mechanically stable. However, as Γ increases (R decreasing), the full quadratic form shown in Eq. (A4) can cease to be positive-definite by developing a direction with vanishing restoring force. Provided that

$$0 \leq 12\Gamma^2 < 1, \tag{A7}$$

this will happen first for $\varphi_{12} = \pi$, which we now require.

Consequently, it is necessary to examine the quadratic form:

$$Q(x, y) = x^2 + y^2 - xy - 6\Gamma(x^2 + y^2) + \frac{3}{4}\Gamma^2(11x^2 + 6y^2 + 16xy). \tag{A8}$$

Introduce polar coordinates r, α in the x, y plane:

$$x = r \cos \alpha, \quad y = r \sin \alpha, \tag{A9}$$

so that

$$Q = r^2 [1 - 6\Gamma + \frac{5}{8}\Gamma^2 - \frac{1}{2} \sin 2\alpha + \frac{3}{4}\Gamma^2(\frac{5}{2} \cos 2\alpha + 8 \sin 2\alpha)]. \tag{A10}$$

Angle α must be determined by minimizing this expression. By setting the appropriate first derivative equal to zero, one finds

$$\begin{aligned} \sin 2\alpha &= (-48\Gamma^2 + 4)/(2529\Gamma^4 - 384\Gamma^2 + 16)^{1/2}, \\ \cos 2\alpha &= -15\Gamma^2/(2529\Gamma^4 - 384\Gamma^2 + 16)^{1/2}. \end{aligned} \tag{A11}$$

By substituting these results into Eq. (A10), we find the minimum possible value of Q for given r, Γ :

$$Q_{\min} = r^2 [1 - 6\Gamma + \frac{5}{8}\Gamma^2 - \frac{1}{8}(2529\Gamma^4 - 384\Gamma^2 + 16)^{1/2}]. \tag{A12}$$

When Γ is small, the coefficient of r^2 in Eq. (A12) is certainly positive, but it decreases as Γ increases. One calculates that this coefficient function vanishes when

$$\Gamma = 0.1067475; \tag{A13}$$

the corresponding value of α , from Eqs. (A11), is

$$\alpha = 46.4169^\circ. \tag{A14}$$

At this point the quadratic restoring force on the rotatable point particles vanishes, indicating mechanical instability. For Γ larger than (A13), small deviations from dipole alignment reduce $V^{(2)}$, and precise location of the stable configuration requires extending the $V^{(2)}$ expression (A4) to include quartic terms in x and y . But evidently result (A13) locates the critical distance R_c to be

$$R_c = 9.367901 \Theta/\mu. \tag{A15}$$

For the water molecule, using its oxygen nucleus as origin, the following moments are applicable³⁰:

$$\begin{aligned} \mu &= 1.855 \times 10^{-18} \text{ esu cm}, \\ \Theta &= 0.116 \times 10^{-26} \text{ esu cm}^2. \end{aligned} \tag{A16}$$

The resulting critical radius is found to be

$$R_c = 0.586 \text{ \AA}. \tag{A17}$$

Since this is roughly an order of magnitude smaller than the distances predicted for ST2 and PKC, it is obvious that major effects must arise from higher multipole moments.

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