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Elliot R. Bernstein	(303) 491-6347	

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NORMAL MODE ANALYSIS

OF VAN DER WAALS VIBRATIONS

S. Li, E. R. Bernstein

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ABSTRACT

Two alogrithms are presented for calculation of the van der Waals modes of weakly bound clusters. Both methods rely on the harmonic normal mode approximation and a chosen intermolecular potential. These calculational techniques differ specifically in the form of the force field employed: one method uses the total (both intra- and inter- molecular) force field for the cluster and the other uses only the intermolecular force field. Both methods require rather elaborate coordinate transformation and their first and second partial derivatives; these are provided in detail. The two calculations generate eigenvalues and eigenvectors that are in complete agreement with one another for a given potential. The methods insure that the van der Waals modes are calculated at the proper cluster equilibrium configuration for which all torques and forces on molecules and/or atoms are effectively zero. Examples are presented for $(H_2O)_2$ (n= 2, ..., 7), benzene clustered with water, methane, and ammonia, and a number of different intermolecular potentials. Some of the observed heterogeneous cluster van der Waals modes are reassigned in light of these new results.

I. INTRODUCTION

The accurate calculation of cluster van der Waals vibrational modes based on empirical potentials is of central importance for a number of purposes: 1. assignment of spectroscopically identified cluster vibrations; 2. determination and validation of various potential energy models of cluster interactions; 3. determination of the structure of both large and small clusters; and 4. estimation of the effect of the mixing of molecular internal modes with cluster intermolecular van der Waals modes. In this report we discuss two different methods for the proper and accurate calculation of van der Waals modes of clusters: one method calculates van der Waals modes for fixed molecular geometries, and the other calculates van der Waals modes following a distortion (relaxation) of molecular geometry brought about by the intermolecular potential energy. We refer to these algorithms as the external force field (EFF) method and the total force field - relaxed molecule (TFF-RM) method, respectively.

Systematic study of intermolecular motions in crystals can be traced back to the early studies of Halford[1], Horning[2], and Shimanouchi[3]. Bernstein[4] calculated the modes of a benzene crystal based on these earlier studies and Warshel and Lifson[5] gave general formulas for crystal normal mode calculations with periodic boundary conditions. Scheraga and co-workers have presented several calculations[6-7] of van der Waals modes of clusters. More recently Menapace, and Bernstein[8] extended this approach to calculate the van der Waals vibrational modes of heterogeneous clusters (i.e., $C_6H_6(H_2O)_1$, $C_6H_6(Ar)_1$, $C_6H_6(CH_4)_1$, $C_6H_6(NH_3)_1$, etc.). Jortner et al[9-11] calculated a limited subset of cluster normal modes using an empirical potential and an approximate Schrödinger equation. Watts et al[12-13] have studied the structure and vibrations of the water dimer employing a number of different approaches. Janda et al[14] have studied the ethylene dimer and ethylene rare gas systems. With the exception of the quantum mechanical treatments[9-14] the above studies employ the GF matrix method of Wilson[15] considering both inter- and intra-molecular interactions (force fields) simultaneously. In all of these instances the original molecular geometry is employed in the calculation - any molecular distortion due to the intermolecular

interaction within the cluster or crystal is (implicitly) ignored. We term this approach, without molecular structure relaxation, the total force field-unrelaxed molecule (TFF-UM) approach.

Cluster normal mode analyses employing the GF matrix method involve (implicitly or explicitly) the overall cluster translational and rotation degrees of freedom. The TFF-UM approach to this calculation does not necessarily set these modes to zero energy, as of course a correct calculation must. Indeed, if the intermolecular interactions are strong, this approach gives significantly large cluster overall translational and rotational energies and causes extensive mixing between cluster van der Waals, translational and rotational modes.

Nonetheless, the GF matrix diagonalization is an effective method for determination of the harmonic normal modes of van der Waals clusters; how to generate appropriate cluster F (force field) and G (reciprocal mass) matrices is the concern of this report. We discuss two algorithms for the generation of correct G and F matrices for cluster normal modes of vibration. The total force field-relaxed molecule (TFF-RM) method involves both inter- and intra-molecular force fields. The external force field (EFF) method involves rigid molecules and the intermolecular force field only. The results of both calculations are essentially identical and most significantly uniquely dependent on the chosen intermolecular potential only.

In the ensuing discussion we describe the potentials and concomitant geometries employed in these calculations. General descriptions of the two calculational algorithms (TFF-RM and EFF) are then presented. In the third section the details and manipulations associated with both calculational methods are given. The results and conclusions are presented in the final sections of this report.

II. GENERAL DESCRIPTION OF THE TECHNIQUES

A. Intermolecular Potentials and Cluster Geometries

Cluster intermolecular potential energy is calculated from several empirical intermolecular potential forms. Most frequently and generally the atom-atom Lennard-Jones 6-12-1 potential, adapted from the work of reference 16,

$$E = \Sigma\ \varepsilon_{ij} = \Sigma\ [A_{ij}/r_{ij}^{12} - C_{ij}/r_{ij}^{6} + e_i e_j / r_{ij}], \qquad (1)$$

is employed. In eq. (1) the summation is over all atom pairs for different molecules, parameters A_{ij} and C_{ij} are given in reference 8, r_{ij} are the interatomic distances of the atoms in different molecules, and e_i is the partial change on atom i. The e_i can be obtained from the work of Scheraga[17-18] and also from MOPAC 5[19-20] calculation using an appropriate Hamiltonian.

A potential employed for water clusters is somewhat different and is adopted from the work of Jorgensen:[21]

$$E = \Sigma\ \varepsilon_{ij} = \Sigma\ [d_{ij}/r_{ij}^{12} + c_{ij}/r_{ij}^{6} + b_{ij}/r_{ij}^{3}] + \Sigma' e_i e_j / r_{ij}. \qquad (2)$$

The parameters d_{ij}, c_{ij} and b_{ij} are given in reference 21. The summation for the Coulombic term in the potential (denoted by Σ') is over all the charge pairs in different molecules, and the Lennard-Jones summation (denoted by Σ) is over all atom pairs for atoms in different molecules. Each water molecule in this interaction form has four charges. This water molecule is thus five centered: two hydrogen atoms with their partial charges and one oxygen atom with two partial charges located at approximate lone pair positions. This potential form gives the experimentally suggested water dimer geometry.[22]

A potential form proposed for benzene-water clusters is an atom-atom Lennard-Jones 1-4-6-9-12 potential adopted from the work of Jonsson et al:[23]

$$E = \Sigma\ \varepsilon_{ij} = \Sigma\ [A_{ij}/r_{ij} + B_{ij}/r_{ij}^{4} + C_{ij}/r_{ij}^{6} + D_{ij}/r_{ij}^{9} + E_{ij}/r_{ij}^{12}] \qquad (3)$$

in which the parameters are detailed in reference 23.

Cluster geometries are calculated from an energy minimization routine with fixed (rigid) molecule structures: in the routine, the molecules comprising the cluster are randomly placed in space and the molecules are translated and rotated toward the cluster structure of lower energy. All molecules are eventually trapped in a local cluster potential energy minimum. An energy minimum geometry is defined as that cluster geometry for which all forces and torques on a **molecule** are less than ca. 10^{-14} dynes and dyne-angstroms, respectively, and all molecular displacements up to roughly 0.1Å generate higher energy cluster structures.

B. Total Force Field - Relaxed Molecule Method

This approach to the calculation of the normal modes of clusters considers both the inter-and intra-molecular force fields; that is, the total cluster force field. The full 3n x 3n force field matrix F in Cartesian coordinate representation, with n the total number of atoms in the cluster, is developed and employed.

The intramolecular force field is adopted from the literature. For example, the general force fields for ammonia, water, methane, etc. are given by Herzberg[24] and the general force field for benzene is given by Whiffen.[25] The intermolecular force field is directly calculated from one of the intermolecular potential energy forms (i.e., eq. (1) or (3)) by analytical calculation of second partial derivatives.

In order to obtain meaningful harmonic force constants for the cluster based on the analytical second derivatives of a chosen potential form, the residual force (**f**) on all the atoms must be zero. Since the energy minimization procedure moves rigid **molecules** as a whole, the force residue on each **atom** does not necessarily get minimized as the force residue on the **molecule** is minimized. Thus the cluster structure is no longer at a potential minimum when the internal force field is subsequently involved. Force residues on the atoms are of the magnitude 10^{-5} to 10^{-6} dynes, compared to the initial force and torque residues on each **molecule** of 10^{-14} dynes and dyne-angstroms, respectively, at a cluster rigid molecule equilibrium geometry. Thus, if an accurate reliable harmonic force field is to be evaluated, all the molecular structures in the cluster have to be "relaxed" in accord with the intra- and inter-molecular potentials employed to insure that

a true potential minimum for the atoms in the cluster has been achieved. Higher order non-harmonic corrections to these intermolecular force fields also depend essentially on the establishment of a true cluster equilibrium geometry in the presence of all forces, torques and interactions.

In the calculations discussed below, the Newton-Raphson method is used to displace each atom in the cluster to find its new equilibrium position. Normal mode analysis is applied only after the force residue on each atom is less than 10^{-14} dynes. van der Waals mode energies are then found by diagonalization of the GF matrix. The internal molecular modes and the six cluster translational and rotational zero energy modes are then identified and the remaining modes are the van der Waals vibrational modes of the cluster. Eigenvectors are calculated to identify and confirm the character of all the generated modes of the cluster.

The quality of the calculational algorithm can in part be judged by the calculated "zero energy" translational and rotational cluster modes. Of course, the harmonic assumption is also made by the very nature of the calculation. The overall quality of the theoretical results for van der Waals modes of clusters (as judged by comparison with experiments) depends on this above separation, the harmonic approximation and on the quality of the chosen intermolecular potential.

C. External Force Field Method

The external force field method considers each (non-linear) polyatomic molecule as a rigid body with only six degrees of freedom. The degrees of freedom for the van der Waals clusters are reduced, with respect to those needed for the TFF-RM method first discussed, from 3n-6 to 6m-6, with n the number of atoms in the cluster and m the number of molecules in the cluster.

Within the EFF calculational approach, no internal force field is involved. The force and torque residues for the molecules in the cluster are as originally calculated, ca. 10^{-14} dynes or dyne-angstroms, respectively. The mixing between the van der Waals modes and the cluster translational and rotational modes caused by these residual first derivative terms is negligible. The originally obtained cluster geometries can be used directly without further

modification. The 6m x 6m GF matrix can be diagonalized and the van der Waals modes of the cluster are generated along with the six zero energy modes of overall cluster translations and rotations. The problem posed for the EFF method is the 3n to 6m coordinate transformation and its associated first and second order derivatives: these are discussed in detail below.

III. ALGORITHMS AND COMPUTATIONAL PROCEDURES

In this section the formulas used in both the TFF-RM and EFF calculational methods are derived. Several coordinate systems are required for these calculations and they will be briefly defined first.

A. Coordinate Systems and Coordinates

We will use and refer to the following coordinate systems: 1. cluster Cartesian coordinate system; 2. molecular internal coordinate system, involving the bond lengths, bending angles, etc. in terms of which the molecular internal motions are described; 3. a molecule Cartesian coordinate system with its origin fixed at the molecular center of mass and its axes parallel to those of the cluster Cartesian coordinate system; and 4. a molecule principal axis system (in which the molecular moment of inertia tensor is diagonal). Atoms are located by 3 atomic coordinates (x, y, z,) and molecules are located by six coordinates in the cluster Cartesian system.

B. Total Force Field-Relaxed Molecule Method

A function $g(\mathbf{x})$ is at a minimum at some point $\mathbf{x}_0$ if and only if its first derivative $\partial g(\mathbf{x})/\partial \mathbf{x}$ is zero and its second partial derivative matrix $\partial^2 g(\mathbf{x})/\partial x_i \partial x_j$ (for all i, j = 1, ..., n) is positive definite at this point $\mathbf{x}_0$. In other words, a true cluster potential minimum, with zero force residue $\mathbf{f}(\mathbf{x}) = \partial E/\partial \mathbf{x}$, will yield a semi-positive definite force field matrix F and the eigenvalues of the F matrix (or the GF matrix) will thereby be all positive or zero. The cluster force field must be calculated at the equilibrium position of each particle in the cluster to obtain physically meaningful (non-negative, both zero and positive) normal mode energies.

The readily available and adopted forms for the intermolecular and intramolecular interactions and force fields are distinctly different. Intermolecular interactions are represented in

the form of a potential energy function dependent on the atomic position (Cartesian) coordinates. The intermolecular forces and the intermolecular force fields are obtained from this function as the sets of first and second derivatives (evaluated at the equilibrium configuration chosen), respectively.

On the other hand, the intramolecular force fields are given in the molecular internal coordinate system in terms of the internal **displacement** coordinates. The molecular internal potential energy and restoring forces can only be calculated from molecular distortions by assuming the molecular internal force fields to be harmonic. Let E, **f**, and F denote cluster energy, force residue vector, and force field, respectively. Both E and **f** have contributions from the intermolecular (external) interactions and the intramolecular (internal) interactions, such that

$$\begin{aligned} E &= E_{ext} + E_{int} \\ \mathbf{f} &= \mathbf{f}_{ext} + \mathbf{f}_{int} \end{aligned} \tag{4}$$

with

$$E_{int} = \frac{1}{2}\ \Delta S F_{int}(S)\ \Delta S^{t}$$

and

$$\mathbf{f}_{int,x}(x) = \Delta S F_{int}(S)(\partial \Delta S^{t}/\partial x).$$

In eq. (4) the subscripts ext and int denote contributions from the intermolecular interaction and the molecular distortions, respectively, ΔS denotes the internal displacement coordinate vector, x or S in parenthesis indicates the coordinate system (cluster Cartesian or molecular internal) with respect to which the matrix or function is presented, the x subscript indicates the force element in the x-direction, and superscript t indicates the transpose vector.

The force field F, the second derivative of the potential E, in atomic Cartesian coordinate representation can be written as:

$$F(x) = F_{ext}(x) + F_{int}(x)$$

with

$$F_{int,\,xy}(x) = (\partial\Delta S/\partial x)\; F_{int}(S)\; (\partial\Delta S^t/\partial y)$$
$$+\;\; \Delta S\; F_{int}(S)(\partial^2\Delta S^t/\partial x\partial y). \qquad (5)$$

The partial derivatives $(\partial\Delta S/\partial x)$ and $(\partial^2\Delta S/\partial x\partial y)$ must be calculated. Table I gives definitions of the internal coordinates (bond stretching, angle bending, out of plane wagging, and torsion) used in this work. Others can be generated as required. Most of these definitions appear in reference 15, but a few of the coordinates are redefined in order to remove potential singularities.

The first partial derivatives of molecular internal coordinates with respect to atomic Cartesian coordinates (expressed in either the cluster or molecule Cartesian coordinate system - the elements of the "B-matrix") are deduced and tabulated in reference 15. The analytical second partial derivatives of the molecular internal coordinates with respect to atomic Cartesian coordinates have not been previously presented. While these derivatives are straightforward to obtain, their presentation in vector form is useful for computations: the full deduction of the requisite first and second partial derivatives in vector form is presented in Table II.

The calculation procedure is as follows: 1. cluster energy E, force residue **f**, and force field matrix F are calculated in atomic Cartesian coordinate representation for a given geometry; 2. if the magnitude of **f** is greater than 10^{-14} dynes, a Newton-Raphson method is employed to find atomic displacements toward a lower cluster potential energy; 3. the total molecular distortion is updated in molecular internal coordinates for each molecule of the cluster; 4. E, **f**, F are recalculated as above; 5. termination occurs when the magnitude of **f** is appropriately small (ca. 10^{-14} dynes) and the current F matrix is then used to construct the GF matrix product for normal mode analysis.

Note that the molecular distortion in internal coordinates ΔS must be explicitly calculated and saved in order to calculate the molecular restoring force. ΔS cannot be approximated as $(\partial \Delta S/\partial x)\bullet\Delta x$ as the atomic displacements become large (ca. 0.1Å).

An eigenvalue shift routine is also employed to ensure rapid approach to a true potential energy minimum position. Care must be taken to reduce computer rounding errors in these calculations because the requirements on zero cluster translational and rotational residual forces are quite stringent. These force residues are made to go to zero.

C. External Force Field Method

In the external force field method, only the intermolecular interaction energy is considered; that is, $E = E_{ext}$. The cluster intermolecular potential energy is given originally as a function of the cluster Cartesian coordinates $\mathbf{x}$ of the atoms and any charges not located at atomic positions. The intermolecular interaction energy must thus be transformed into a function of molecular coordinates $\mathbf{Q}_j$ for the j^{th} molecule of the cluster - the index j runs over all m molecules of the cluster. In order to get both F and G matrices in this molecular displacement coordinate representation,

$$E = E_{ext}(\mathbf{x}) = E_{ext}(\mathbf{x}(\mathbf{Q})), \tag{6}$$

the appropriate coordinate transformation must be obtained. The vector $\mathbf{Q}$ is of the form $\mathbf{Q} = (\mathbf{Q}_1, \mathbf{Q}_2, ..., \mathbf{Q}_m)$, with $\mathbf{Q}_j$ given below.

1. The G matrix[15]

For each molecule, the molecular displacement coordinates involve three rotations $(\phi_\alpha, \phi_\beta, \phi_\gamma)$ along the three principal axes of the molecules and three translations (X, Y, Z) along the cluster Cartesian coordinate system axes. One can then write:

$$\mathbf{Q}_j = (X_j, Y_j, Z_j, \phi_{j\alpha}, \phi_{j\beta}, \phi_{j\gamma})$$
$$dX_j = \Sigma\, m_i dx_i / \Sigma m_i$$
$$d\phi_{j\alpha} = \Sigma\, m_i\ (\beta_i d\gamma_i - \gamma_i d\beta_i)/I_{j\alpha\alpha} \qquad (7)$$

in which m_i and x_i are the mass and x coordinate of atom i (in a particular molecule j), $I_{j\alpha\alpha}$ is the molecule moment of inertia along the α-axis, and α_i, β_i, γ_i are the atomic Cartesian coordinates of the i^{th} atom in the j^{th} molecule principal coordinate system. Cyclic permutation of the variables produces the other required relations. Based on these relations, the molecular B-matrix ($\partial \mathbf{Q}_j/\partial \mathbf{x}$) can now be formed. The G_j matrix is thereby given as,[15]

$$G_j = B_j M_j^{-1} B_j^t, \qquad (8)$$

in which M_j is the (diagonal) molecular atomic mass matrix. Eq. (8) yields the correct diagonal molecular G matrix, with the inverse of the molecular mass as the entry for the molecular translational motions, and the inverse of the corresponding moment of inertia for the molecular rotational motions.

Since the translational and rotational degrees of freedom of one molecule are independent of those of another, the molecular displacement coordinates of one molecule are orthogonal to those of another. The B matrix of the whole cluster is thus block diagonal and the G matrix of the cluster is diagonal.

2. The F matrix[15]

To find the force field matrix F in the same coordinate system we return to eq. (6) to find

$$\partial E/\partial Q = (\partial E/\partial x)\bullet(\partial x/\partial Q) \qquad (9)$$

and one element of F(Q) for a given molecule is,

$$\partial^2 E/\partial Q_\nu \partial Q_\mu = (\partial x/\partial Q_\nu)\bullet(\partial^2 E/\partial x \partial y)\bullet(\partial y/\partial Q_\mu) + (\partial E/\partial x)\bullet(\partial^2 x/\partial Q_\nu \partial Q_\mu) \qquad (10)$$

in which Q, Q_ν or Q_μ indicates any of the molecular coordinates X_j, Y_j, Z_j, $\phi_{j\alpha}$, $\phi_{j\beta}$, $\phi_{j\gamma}$ for all j.

Since $\partial E/\partial x$ is the force **f** on atoms and not necessarily zero in the EFF approach, both $(\partial x/\partial Q)$ and $(\partial^2 x/\partial Q_\nu \partial Q_\mu)$ are required to calculate F(Q). Note that the $(\partial x/\partial Q)$ cannot be obtained from inversion of the B matrix as B is singular. The analytical determination of these first and second derivatives is discussed in the ensuing presentation.

Atomic displacements **dx** in one molecule are independent of molecular displacements **dQ** of another molecule and the matrices $(\partial x/\partial Q)$ and $(\partial^2 x/\partial Q_\nu \partial Q_\mu)$ are thereby block diagonal in terms of molecules in the cluster. We thus drop any notation and indices referring to a particular molecule.

For a rigid molecule, an atomic transitional displacement is just the molecular translational displacement and thus,

$$\partial x_i/\partial X = 1, \partial x_i/\partial Y = 0 \text{ and } \partial^2 x_i/\partial X \partial Q_\mu = 0 \qquad (11)$$

in which x_i are atomic coordinates of the i^{th} atom, X and Y are the molecular x- and y-coordinates, respectively, and Q_μ can be any molecular translational or rotational coordinate. Other derivatives are found by cyclic permutation of the coordinates in eq. (11).

The derivatives of eq. (9) and (10) must be found only for the molecular rotational coordinates (ϕ_α, ϕ_β, ϕ_γ). The derivatives can be explicitly generated by first considering the general rotation matrix R(θ) for a rotation about an arbitrary direction in space. Let (a_1, a_2, a_3) be a unit vector along that direction and let θ be the rotation angle about this direction. The rotation matrix R(θ) is then, [26]

$$R(\theta) = \begin{pmatrix} \cos\theta + a_1^2(1-\cos\theta) & a_1a_2(1-\cos\theta) - a_3\sin\theta & a_1a_3(1-\cos\theta) + a_2\sin\theta \\ a_1a_2(1-\cos\theta) + a_3\sin\theta & \cos\theta + a_2^2(1-\cos\theta) & a_2a_3(1-\cos\theta) - a_1\sin\theta \\ a_1a_3(1-\cos\theta) - a_2\sin\theta & a_2a_3(1-\cos\theta) + a_1\sin\theta & \cos\theta + a_3^2(1-\cos\theta) \end{pmatrix} . \quad (12)$$

This rotation matrix is derived as a product of three successive rotations: a rotation of the z axis to the direction (a_1, a_2, a_3); a rotation of the coordinate system around the new z axis (a_1, a_2, a_3) by an angle $-\theta$; and a rotation of the z axis back to its original direction.

Based on this general rotation matrix form, an ordered set of rotation matrices $R_\alpha(\phi_\alpha)$, $R_\beta(\phi_\beta)$, $R_\gamma(\phi_\gamma)$ for each atom (i) in the molecule can be defined as,

$$\mathbf{r}^t = R_\alpha(\phi_\alpha)R_\beta(\phi_\beta)R_\gamma(\phi_\gamma)\mathbf{r}_o^t . \quad (13)$$

In eq. (13) R_α, R_β, and R_γ are the matrix representations of rotations along the molecular principal axes α, β, and γ, respectively, $\mathbf{r}_o$ are the unrotated and $\mathbf{r}$ the rotated atomic coordinate vectors in the molecular Cartesian coordinate system. With this definition, we have for each atom in a molecule,

$$\begin{aligned} \partial\mathbf{r}^t/\partial\phi_\alpha &= dR_\alpha(\phi_\alpha)/d\phi_\alpha R_\beta(\phi_\beta)R_\gamma(\phi_\gamma)\mathbf{r}_o^t \\ \partial^2\mathbf{r}^t/\partial\phi_\alpha^2 &= d^2R_\alpha(\phi_\alpha)/d\phi_\alpha^2 R_\beta(\phi_\beta)R_\gamma(\phi_\gamma)\mathbf{r}_o^t \\ \partial^2\mathbf{r}^t/\partial\phi_\alpha\partial\phi_\beta &= dR_\alpha(\phi_\alpha)/d\phi_\alpha dR_\beta(\phi_\beta)/d\phi_\beta R_\gamma(\phi_\gamma)\mathbf{r}_o^t . \end{aligned} \quad (14)$$

When evaluated at $\phi_\alpha = \phi_\beta = \phi_\gamma = 0$, these derivatives are,

$$\partial \mathbf{r}^t/\partial\phi_\alpha = \begin{pmatrix} 0 & -a_{13} & a_{12} \\ a_{13} & 0 & -a_{11} \\ -a_{12} & a_{11} & 0 \end{pmatrix} \mathbf{r}_o^t \qquad (15a)$$

$$\partial^2 \mathbf{r}^t/\partial\phi_\alpha^2 = \begin{pmatrix} a_{11}^2 - 1 & a_{11}a_{12} & a_{11}a_{13} \\ a_{11}a_{12} & a_{12}^2 - 1 & a_{12}a_{13} \\ a_{11}a_{13} & a_{12}a_{13} & a_{13}^2 - 1 \end{pmatrix} \mathbf{r}_o^t \qquad (15b)$$

$$\partial^2 \mathbf{r}^t/\partial\phi_\alpha\partial\phi_\beta = \begin{pmatrix} a_{11}a_{21} & a_{12}a_{21} & a_{13}a_{21} \\ a_{11}a_{22} & a_{12}a_{22} & a_{13}a_{22} \\ a_{11}a_{23} & a_{12}a_{23} & a_{13}a_{23} \end{pmatrix} \mathbf{r}_o^t$$

$$= \mathbf{a}_\beta^t \ (\mathbf{a}_\alpha \bullet \mathbf{r}_o)$$

The other derivative forms not explicitly stated in eq. (15) can be obtained by cyclic permutation of the indices. In these equations $\mathbf{a}_\alpha = (a_{11}, a_{12}, a_{13})$, $\mathbf{a}_\beta = (a_{21}, a_{22}, a_{23})$ and $\mathbf{a}_\gamma = (a_{31}, a_{32}, a_{33})$. The $\mathbf{a}_\nu$ are the three unit vectors along the three molecule principal axes represented in the original cluster Cartesian coordinate system. Their components are simply the direction cosines of the molecular principal axes in the cluster Cartesian coordinate system if the rotation is a proper rotation. The rotation matrix formed by these vectors,

$$\mathbf{P} = (\mathbf{a}_\alpha^t, \mathbf{a}_\beta^t, \mathbf{a}_\gamma^t) = \begin{pmatrix} a_{11} & a_{21} & a_{31} \\ a_{12} & a_{22} & a_{32} \\ a_{13} & a_{23} & a_{33} \end{pmatrix} \qquad (16)$$

can be gotten from the orthogonal matrix which diagonalizes the molecular moment of inertia tensor.

One can readily demonstrate that the rotation order (order of the matrices in eq. (13)) is of no consequence for the final F (Q) provided that: the same rotation order is maintained for all atoms in a molecule; the molecule has no net torque; and the rotation is an infinitesimal one. Moreover, the rotation matrix P in eq. (16) may be either proper or improper (i.e., $|P| = \pm 1$). Of course, all the rotation matrices for all the molecules in the cluster must be simultaneously proper or improper.

3. Eigenvectors

To visualize the resulting eigenvectors of the GF matrix in the EFF method, transformation of these eigenvectors into the cluster Cartesian coordinate system is quite helpful. We discuss this procedure below.

Three successive small rotations $(\phi_\alpha, \phi_\beta, \phi_\gamma)$ of a molecule around its three molecular principal axes are equivalent to a single rotation ϕ around the axis pointing in the direction $(\phi_\alpha, \phi_\beta, \phi_\gamma)$ for which ϕ is the norm of the vector $(\phi_\alpha, \phi_\beta, \phi_\gamma)$. Rotation of a molecule through $(\phi_\alpha, \phi_\beta, \phi_\gamma)$ in the molecular principal coordinate system is equivalent to rotation of the molecule about $(\phi_\alpha, \phi_\beta, \phi_\gamma)$ P in the molecular coordinate system with axis parallel to those of the original cluster Cartesian coordinate system.

For three infinitesimal rotations $\phi_\alpha, \phi_\beta, \phi_\gamma$ around the three molecular principal axes, eq. (15a) gives,

$$\mathbf{r}^t = (\mathbf{r}_o + \mathbf{dr})^t = \begin{pmatrix} 1 & -\phi'_\gamma & \phi'_\beta \\ \phi'_\gamma & 1 & -\phi'_\alpha \\ -\phi'_\beta & \phi'_\alpha & 1 \end{pmatrix} \mathbf{r}_o^t \qquad (17)$$

in which $(\phi'_\alpha, \phi'_\beta, \phi'_\gamma) = (\phi_\alpha, \phi_\beta, \phi_\gamma)$ P.

Let the eigenvector coefficients for a molecule j be $(X'_j, Y'_j, Z'_j, \phi_{j\alpha}, \phi_{j\beta}, \phi_{j\gamma})$. The equivalent but unnomalized eigenvector coefficients for each atom i in molecule j are,

$$\begin{pmatrix} 0 & -\phi_{j\gamma}' & \phi_{j\beta}' \\ \phi_{j\gamma}' & 0 & -\phi_{j\alpha}' \\ -\phi_{j\beta}' & \phi_{j\alpha}' & 0 \end{pmatrix} \mathbf{r}_i^t + \begin{pmatrix} X_j' \\ Y_j' \\ X_j' \end{pmatrix} \qquad (18)$$

in which again $(\phi'_{j\alpha}, \phi'_{j\beta}, \phi'_{j\gamma}) = (\phi_{j\alpha}, \phi_{j\beta}, \phi_{j\gamma})\, P_j$, and $\mathbf{r}_i$ is the atomic coordinates of atom i in the molecular coordinate system with axes parallel to those of the original cluster Cartesian coordinate system.

4. Summary of EFF Method

The EFF computational procedure is summarized as follows: 1. calculate the intermolecular force vector **f** and force field F in atomic coordinates based on the cluster geometry of the local energy minimum with rigid molecular structure; 2. find the molecular moment of inertia tensor for every molecule in the cluster and diagonalize it; 3. the molecular mass and principal moments of inertia are saved as the inverse entry of the usual G matrix; 4. the orthogonal matrices which do this diagonalization are determined to be proper or improper and are saved as the rotation matrices P in eq. (16); 5. the matrices of the first partial derivatives $\partial x/\partial Q$ and second partial derivatives $\partial^2 x/\partial Q_\nu \partial Q_\mu$ are calculated based on eq. (11) and (15); 6. the GF matrix is formed in the molecular coordinate representation and diagonalized; and 7. the eigenvectors are transformed back to atomic coordinates for visualization according to eq. (18).

IV. RESULTS AND DISCUSSION

A. Homogeneous Clusters

Table III contains the results of calculations of the van der Waals modes of the water dimer by several different techniques: TFF-UM, TFF-RM, EFF, and MOPAC 5 algorithms. Different potential forms are employed as well for the two methods advocated in this work.

Unfortunately, no experimental results are available for comparison. The cluster geometries associated with these potentials are given in Figure 1. The "relaxed" geometry obtained for this dimer (TFF-RM) is not distinguishable from that of the original one presented. The results for the two methods discussed in detail (TFF-RM and EFF) are virtually indistinguishable - this demonstrates the detailed correctness of both calculational methods. The residual non-zero rotational and translational energies are due almost entirely to round-off errors in the computer calculation.

Since no five-center water molecule internal force field is available, mixing of the eq. (2) intermolecular force field and any three-center intramolecular force field in any TFF approach causes non-zero cluster translational energies. This potential then can only be employed within the EFF method.

The TFF-UM approach with any intra- and inter- molecular potential, generates large, residual forces on the atoms and thereby large non-zero (negative) eigenvalues for the overall translational and rotational modes of the clusters. This is seen in Table III.

One might anticipate that by increasing the internal force field and thereby making the molecule more rigid, one could force these negative eigenvalues to zero. The results presented in Table IV do not support this position. Two reasons can be cited for the failure of this approach: 1. the force residue, from which these negative eigenvalues derive, is neither reduced nor balanced by increasing the internal force field; and 2. the disparity between the sizes of the two force fields eventually causes the matrix diagonalization routine to fail.

The first column of Table IV gives the calculated energies for the water dimer geometry given in Figure 1c. This structure is at a saddle point on the intermolecular potential surface described in eq. (1). Cluster geometries at true energy minima ($\mathbf{f} = 0$ and $|F|$ semi-positive definite) must have six zero energy translational and rotational modes, and no negative vibrational energies. Cluster geometries at saddle points may also have six zero energy modes but additionally have negative energy vibrational modes due to the negative curvature of the potential surface at the saddle point in some direction. Non-zero residual forces will cause non-zero

translational and rotational energies. Thus a van der Waals mode analysis can be used to check for true minimum energy or saddle point cluster structures. These results (Table III and IV) suggest that the geometries observed from the energy minimization analysis are indeed at local energy minima.

Larger water clusters [$(H_2O)_m$, n = 3, ..., see Figure 2] represent a very difficult calculation for the TFF-UM approach due to the strong intermolecular interactions. Thus, mixing of the van der Waals modes with both the internal modes of water and the overall rotational and translational motions of the cluster (**f** > 0) can be quite extensive. Table V, along with Tables III and IV, provides an example of this problem. Clearly the normal modes of even the simplest clusters can be reliably calculated only after the residual forces in the cluster are zeroed (by TFF-RM, EFF, or some other technique).

The difference between mode energies calculated by the TFF-RM and EFF methods is greatest for the high energy modes due to the mixing of the van der Waals modes with the internal modes: the TFF-RM high energy modes are lower in energy than the comparable EFF modes as is to be expected. The two methods yield nearly identical results for the low energy modes. The requisite relaxed geometry calculated for the TFF-RM method is different from that of the original energy minimization result by typically less than 0.1 Å (see Figure 2).

B. Heterogeneous Clusters

van der Waals energies calculated by the TFF-UM, TFF-RM, and EFF methods for various different potentials (eq. (1) and eq. (3)) are presented in Table VI for $C_6H_6(H_2O)_1$, $(NH_3)_1$ and $(CH_4)_1$. These results are compared to the earlier calculations of reference 8. The maximum cluster translational and rotational energies for each calculation are given in parenthesis. All the corresponding cluster geometries, based of course on the various potentials, are depicted in Figure 3.

The calculational results for heterogeneous clusters presented in Table VI are nearly identical for both the TFF-RM and EFF methods. Apparently little internal mode-external mode coupling takes place in these clusters. Clearly cluster geometry (i.e., $C_6H_6(NH_3)_1$) and cluster

intermolecular potential are the major determining factors for normal mode energies in these clusters if the calculations are performed at an appropriate equilibrium position.

Based on these new calculations we can attempt to reassign the observed van der Waals modes for the clusters presented in Table VI and Figure 3. The right-hand column contains the experimentally observed van der Waals mode energies. Only the fundamentals that seem reasonably intense and well characterized are included in this listing. If the molecular structures are not properly relaxed (TFF-UM) to drive **f** to zero, the low frequency van der Waals modes mix with the cluster translational and rotational motions. The extent of mixing not only depends on the magnitude of the force residues, but also on the nature of the internal force field. This latter point can be seen in the first two columns of Table VI for the TFF-UM calculation: the comparison is for the data of reference 8 and the calculations presented herein using a more complete and accurate force field for both molecules of the heterogeneous cluster.

The eigenvectors calculated by both the TFF-RM and EFF methods are identical for a given potential function; the form of the eigenvectors and the mode energies are, of course, highly dependent on the chosen intermolecular potential. This can be seen in Figure 4 quite clearly.

C. TFF-RM or EFF?

While the EFF method of calculating cluster normal modes of vibration does not yield the internal-external mode mixing and concomitant mode splittings and shifts, it does provide a simple effective method that yields quite reasonable results, especially if the external and internal modes are well separated in energy. For large clusters we recommend the EFF method (with the above caveats) for the following reasons: 1. only the intermolecular potentials are required; 2. reminimization of the cluster energy is not required; 3. since each molecule is described by only six coordinates much less computer memory is needed for this method compared to the TFF-RM method; and 4. the TFF-RM method can be applied only to atom-atom interaction potentials with point charges located at atomic mass positions.

V. CONCLUSIONS

Two methods for the calculation of van der Waals modes of molecular clusters are presented. One uses both internal and external force fields to calculate all the vibrational eigenvectors and eigenvalues for a given cluster. The other employs the intermolecular force field only and thus obtains only van der Waals mode eigenvectors and eigenvalues. Both techniques ensure that modes are calculated for equilibrium structures of the cluster only. Both approaches give excellent separation between van der Waals modes and overall cluster (zero energy) translational and rotational degrees of freedom and give no negative eigenvalues.

The TFF-RM method, employing both internal molecular and intermolecular force fields, shows small mixing between the lower energy molecule modes and the high energy cluster modes. The two methods, TFF-RM and EFF, yield virtually identical results for van der Waals modes below 150 cm^{-1}, for the clusters and potential energy forms considered herein. In general, the calculation seems to be in good agreement with the sparse experimental data. The TFF-RM method also generates "exchange or exciton" type interactions between the internal molecule modes of the clusters.

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Table I. Definitions of Internal Coordinates

Internal Mode	Variable, definition, and Formula Expression
Bond Stretching	r_{ij} (distance between atom i and j) $r_{ij} = \lvert \mathbf{r}_{ij} \rvert = \lvert \mathbf{r}_i - \mathbf{r}_j \rvert$
Angle Bending I	θ_{ijk} (angle between bond $\mathbf{r}_{ij}$ and $\mathbf{r}_{kj}$) $\cos(\theta_{ijk}) = \mathbf{r}_{ij} \cdot \mathbf{r}_{kj} / r_{ij} r_{kj}$
Angle Bending II	θ_H (angle created by bond r_{ij} bending with respect to the bisector of the k-j-l angle) $\theta_H = (\theta_{ijk} - \theta_{ijl})/2$.
Out of plane Wagging	γ_{ijkl} (angle between r_{ik} and the plane determined by j, k and l atoms) $\sin(\gamma_{ijkl}) = \mathbf{r}_{ik} \cdot (\mathbf{r}_{jk} \times \mathbf{r}_{kl}) / r_{ik} \lvert \mathbf{r}_{jk} \times \mathbf{r}_{kl} \rvert$
Torsion[a]	Φ_{ijkl} (angle between bonds r_{ij} and r_{kl}, viewed along r_{jk} bond) $\sin(\Phi_{ijkl}) = ((\mathbf{r}_{ij} \times \mathbf{r}_{jk}) \mathbf{r}_{kl})\, r_{jk} / \lvert \mathbf{r}_{ij} \times \mathbf{r}_{jk} \rvert \lvert \mathbf{r}_{jk} \times \mathbf{r}_{kl} \rvert$.

[a]This definition of Φ_{ijkl} is valid only about $\Phi \sim 0$ and $\sim \pi$. At $\Phi \sim \frac{\pi}{2}$ and $\sim \frac{3\pi}{2}$ this definition yields a singularity for the necessary derivatives and a new relation is required.

Table II. Derivatives of Vector Quantities

a, b, c, d are vectors, and a, b, c, d are their lengths.

Derivatives of $u = \mathbf{a}\cdot\mathbf{b}/(ab)$

$$\partial u/\partial x = [\partial(\mathbf{a}\cdot\mathbf{b})/\partial x]/(ab) - (\partial a/\partial x)u/a - (\partial b/\partial x)u/b$$

$$\partial^2 u/\partial x\partial y = [\partial^2(\mathbf{a}\cdot\mathbf{b})/\partial x\partial y]/(ab)$$
$$- [(\partial a/\partial y)/a + (\partial b/\partial y)/b](\partial u/\partial x) - [(\partial a/\partial x)/a + (\partial b/\partial x)/b](\partial u/\partial y)$$
$$- [(\partial a/\partial x)(\partial b/\partial y) + (\partial a/\partial y)(\partial b/\partial x)]\ u/(ab)$$
$$- (\partial^2 a/\partial x\partial y)\ u/a - (\partial^2 b/\partial x\partial y)\ u/b$$

Derivatives of $v = (\mathbf{a}\cdot\mathbf{d})c/(ab)$

$$\partial v/\partial x = [\partial(\mathbf{a}\cdot\mathbf{d})/\partial x]\ c/(ab) + (\mathbf{a}\cdot\mathbf{d})(\partial c/\partial x)/(ab)$$
$$- (\partial a/\partial x)v/a - (\partial b/\partial x)v/b$$

$$\partial^2 v/\partial x\partial y = [\partial^2(\mathbf{a}\cdot\mathbf{d})/\partial x\partial y]\ c/(ab) + (\mathbf{a}\cdot\mathbf{d})(\partial^2 c/\partial x\partial y)/(ab)$$
$$+ \{[\partial(\mathbf{a}\cdot\mathbf{d})/\partial x](\partial c/\partial y) + [\partial(\mathbf{a}\cdot\mathbf{d})/\partial y](\partial c/\partial x)\}/(ab)$$
$$- [(\partial a/\partial y)/a + (\partial b/\partial y)/b](\partial v/\partial x) - [(\partial a/\partial x)/a + (\partial b/\partial x)/b](\partial v/\partial y)$$
$$- [(\partial a/\partial x)(\partial b/\partial y) + (\partial a/\partial y)(\partial b/\partial x)]\ v/(ab)$$
$$- (\partial^2 a/\partial x\partial y)\ v/a - (\partial^2 b/\partial x\partial y)\ v/b$$

Other Necessary Derivatives

$$\partial a/\partial x = \mathbf{a}\cdot(\partial\mathbf{a}/\partial x)/a$$

$$\partial^2 a/\partial x\partial y = [\ \mathbf{a}\cdot(\partial^2\mathbf{a}/\partial x\partial y) + (\partial\mathbf{a}/\partial x)\cdot(\partial\mathbf{a}/\partial y) - (\partial a/\partial x)(\partial a/\partial y)]/a$$

$$\partial(\mathbf{a}\cdot\mathbf{b})/\partial x = (\partial\mathbf{a}/\partial x)\cdot\mathbf{b} + \mathbf{a}\cdot(\partial\mathbf{b}/\partial x)$$

$$\partial(\mathbf{a}\times\mathbf{b})/\partial x = (\partial\mathbf{a}/\partial x)\times\mathbf{b} + \mathbf{a}\times(\partial\mathbf{b}/\partial x)$$

When both **a** and **b** are $\mathbf{r}_{ij}$:

$$\partial^2(\mathbf{a}\cdot\mathbf{b})/\partial x\partial y = (\partial\mathbf{a}/\partial x)\cdot(\partial\mathbf{b}/\partial y) + (\partial\mathbf{a}/\partial y)\cdot(\partial\mathbf{b}/\partial x)$$

$$\partial^2(\mathbf{a}\times\mathbf{b})/\partial x\partial y = (\partial\mathbf{a}/\partial x)\times(\partial\mathbf{b}/\partial y) + (\partial\mathbf{a}/\partial y)\times(\partial\mathbf{b}/\partial x)$$

Table III. vdW normal mode comparisons (in cm^{-1}) for $(H_2O)_2$. The entry in parenthesis in each column represents the largest non-zero energy for the cluster translational and rotational motions.

Eq. 1 TFF-RM	Eq. 1 EFF	Eq. 2 EFF	MOPAC 5	Eq. 1 TFF-UM
441.4	459.0	723.1	483.5	437.3
289.5	291.0	716.6	434.1	238.5
153.5	155.8	307.5	379.6	108.5
118.5	119.4	301.1	270.6	57.5
95.9	96.9	263.4	190.7	0.2
26.9	26.9	99.6	100.2	0.0
(0.7)	(0.1)	(0.2)	(121.0)	0.0
				-17.5
				-33.0
				-54.5
				-69.7
				-85.6

Table IV. The effect of a saddle point structure and an increased internal force field on cluster normal modes (in cm^{-1}): $(H_2O)_2$. Example for TFF-UM employing Eq. 1.

Saddle Point	Field x 10^0	Field x 10^2	Field x 10^4	Field x 10^6
438.5	437.3	456.3	458.1	1126.7
245.8	238.4	238.5	249.2	702.3
103.2	108.5	109.1	133.7	625.6
97.7	57.5	57.5	57.5	395.5
90.6	0.2	0.0	43.5	61.9
0.1	0.0	0.0	0.0	57.3
0.1	0.0	-1.9	0.0	0.0
0.0	-17.5	-17.3	-14.7	0.0
0.0	-33.0	-33.0	-23.8	-14.8
0.0	-54.5	-54.4	-46.7	-24.5
0.0	-69.7	-69.7	-56.9	-52.0
-409.2	-85.6	-85.5	-79.0	-66.2

TABLE V. van der Waals Mode Energies (cm^{-1}) for a Few Water Clusters employing the Intermolecular Potential given in Eq. 1

One of $(H_2O)_3$			One of $(H_2O)_4$		One of $(H_2O)_5$	
TFF-RM	EFF	TFF-UM	TFF-RM	EFF	TFF-RM	EFF
508.2	527.7	503.1	534.6	555.1	542.9	562.0
378.7	393.2	370.2	449.8	467.5	486.9	504.7
301.6	303.9	238.0	348.5	360.9	409.0	424.0
274.3	276.5	214.3	301.9	304.9	340.8	351.7
182.7	186.2	116.9	290.8	293.7	303.1	307.1
139.2	141.5	89.9	245.6	245.0	290.8	293.7
125.0	126.2	56.4	208.7	215.9	288.1	292.0
109.0	110.0	0.4	175.8	178.5	247.3	251.8
64.6	65.4	0.0	133.7	135.5	208.7	210.8
23.2	23.4	0.0	123.5	125.1	178.2	182.1
16.9	16.8	-19.5	113.3	114.5	168.1	172.4
13.3	13.2	-23.0	69.3	70.2	130.3	131.6
(0.18)	(0.15)	-34.8	65.0	65.9	125.7	128.4
		-37.5	20.9	21.0	115.3	116.6
		-46.2	19.9	20.0	74.4	75.3
		-69.7	14.2	14.3	67.9	68.3
		-82.6	6.7	7.6	62.0	62.9
		-87.6	1.5	1.9	24.0	25.1
			(0.83)	(0.10)	20.9	21.3
					17.8	17.8
					15.0	15.1
					8.8	8.8
					3.8	4.0
					1.2	1.0
					(0.17)	(0.10)

TABLE V. (cont'd)

One of $(H_2O)_6$		One of $(H_2O)_7$	
TFF-RM	EFF	TFF-RM	EFF
513.5	535.0	745.5	773.0
473.2	492.5	678.4	704.1
473.2	492.5	548.2	566.9
384.8	397.9	486.7	502.1
384.8	397.9	450.9	467.0
358.6	363.8	433.1	449.6
303.8	314.4	410.3	416.9
303.8	308.5	364.0	369.9
303.7	308.5	312.3	317.8
296.4	299.9	303.5	308.3
282.6	285.5	291.5	295.8
282.6	285.5	283.4	287.0
197.1	200.8	274.7	278.6
197.1	200.8	251.8	258.7
196.6	199.9	242.4	245.7
196.6	199.9	200.8	203.5
175.2	178.7	194.2	196.7
157.3	159.5	181.2	184.7
80.8	81.3	169.3	172.9
67.3	67.9	140.4	141.8
64.6	65.2	123.4	126.3
64.6	65.2	120.6	121.2
53.9	54.5	118.1	119.0
53.9	54.5	115.7	116.6
43.3	44.1	68.1	69.3
24.4	24.8	37.6	38.0
24.4	24.8	32.3	33.0
15.6	15.5	24.2	24.4
10.8	10.7	22.8	23.2
10.7	10.7	20.1	19.8
(0.56)	(0.10)	16.9	16.7
		13.7	13.9
		11.7	11.9
		6.6	6.6
		3.8	3.9
		2.8	3.0
		(0.29)	(0.10)

Table VI. Normal mode (in cm^{-1}) comparisons for inhomogeneous clusters. The structures are depicted in Figure 3. The entry in each column in parenthesis represents the largest value for the set of modes indicated.

$C_6H_6(H_2O)_1$

Ref. 8	Eq. 1 TFF-UM	Eq. 1 TFF-RM	Eq. 1 EFF	Eq. 3 EFF	Expt.	Mode Identity (Approx.)
156	167.5	162.7	163.0	287.0		Tx
50	163.4	161.4	162.5	125.0		Ty
159	51.3	50.2	50.2	82.0		Stretch
18	30.0	29.5	29.4	39.0	30.3[a]	Bend1
14	21.1	24.1	24.2	38.8	25.5[a]	Bend2
40	40.0	4.4	4.3	5.1	5.2[b]	Tz
(?)	(6.31)	(0.49)	(0.04)	(0.05)		(Rot.)
(?)	(0.44)	(0.00)	(0.00)	(0.00)		(Tr.)

$C_6H_6(NH_3)_1$-Geometry A

Ref. 8	Eq. 1 TFF-UM	Eq. 1 TFF-RM	Eq. 1 EFF	Expt.	Mode Identity (Approx.)
152	156.1	152.0	153.1		Tx
152	156.1	152.0	153.1		Ty
97	97.7	97.8	98.4		Stretch
19	30.7	29.5	29.7		Bend1
19	30.7	29.5	29.7		Bend2
44	43.2	16.0	16.3	15.0[b]	Tz
(?)	(7.96)	(0.65)	(0.06)		(Rot.)
(?)	(0.41)	(0.00)	(0.00)		(Tr.)

Table VI (continued)

$C_6H_6(NH_3)_1$-Geometry B

Ref. 8	Eq. 1 TFF-UM	Eq. 1 TFF-RM	Eq. 1 EFF	Expt.	Mode Identity (Approx.)
44	42.2	128.3	128.7		Tz
112	109.7	106.6	107.6		Stretch
21	36.4	36.5	36.4		Bend1
125	135.2	31.4	31.9		Txy1
15	21.6	17.7	17.7	17.9[b]	Bend2
48	46.0	6.7	7.6	8.8[b]	Txy2
(?)	(6.95)	(0.06)	(0.06)		(Rot.)
(?)	(0.46)	(0.00)	(0.00)		(Tr.)

$C_6H_6(CH_4)_1$

Ref. 27	Eq. 1 TFF-UM	Eq. 1 TFF-RM	Eq. 1 EFF	Expt.	Mode Identity (Approx.)
89	93.4	90.9	91.1		Tx
89	93.4	90.9	91.1		Ty
82	82.7	82.7	82.8		Stretch
16	26.8	25.9	26.0	27.3[a]	Bend y
16	26.8	25.9	26.0	27.3[a]	Bend x
28	32.1	11.8	11.9	16.1[a]	Tz
(?)	(6.44)	(0.63)	(0.02)		(Rot.)
(?)	(0.41)	(0.00)	(0.00)		(Tr.)

[a]In the 6_0^1 region.

[b]In the origin region.

Figure Captions

Figure 1. Water dimer geometry. **a**. Geometry of the minimum energy configuration obtained from Scheraga's intermolecular potential;[16] **b**. Geometry of the minimum energy configuration obtained from Jorgensen's intermolecular potential;[21] **c**. Geometry at an energy saddle point obtained from Scheraga's intermolecular potential.[16]

Figure 2. A few geometries of minimum energy configuration of higher order water clusters obtained from Scheraga's intermolecular potential.[16] Structures on the left are generated by the energy minimization routine. Structures on the right are generated by the TFF-RM algorithm. **a**. one of the water trimers; **b**. one of the water tetramers; **c**. one of the water pentamers; **d**. one of the water hexamers; **e**. one of the water heptamers.

Figure 3. Cluster geometries of minimum energy configuration. **a**. Benzene(water)$_1$ from Scheraga's potential;[16] **b**. One of the benzene (water)$_1$ structures employing Jonsson's potential;[23] **c**. One of the benzene(ammonia)$_1$ structures employing Scheraga's potential;[16] **d**. Second benzene(ammonia)$_1$ employing Scheraga's potential;[16] **e**. Benzene(methane)$_1$ employing Scheraga's potential;[16] **f**. Second benzene(water)$_1$ structure employing Jonsson's potential.[23]

Figure 4. Normal vdW mode vibrations of the benzene(water)$_1$ cluster. **a**. TFF-RM method employing Scheraga's potential;[16] **b**. EFF method employing Scheraga's potential;[16] **c**. EFF method employing Jonsson's potential.[23] The mode energies are indicated for each pattern displayed (in cm^{-1}).

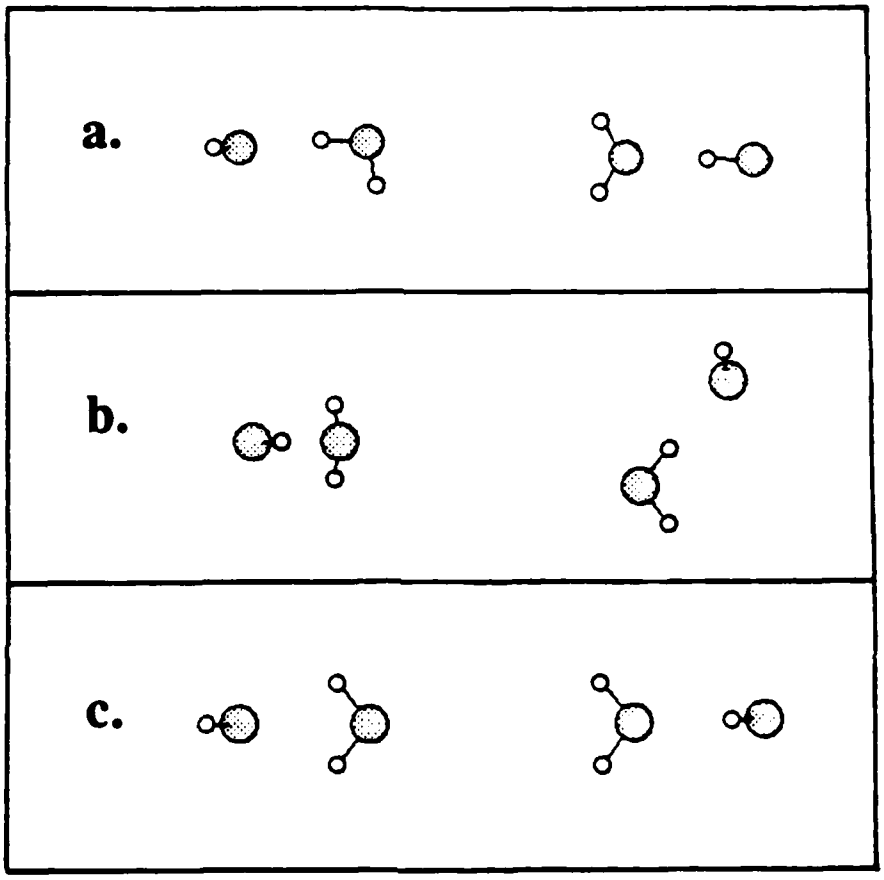

Figure 1

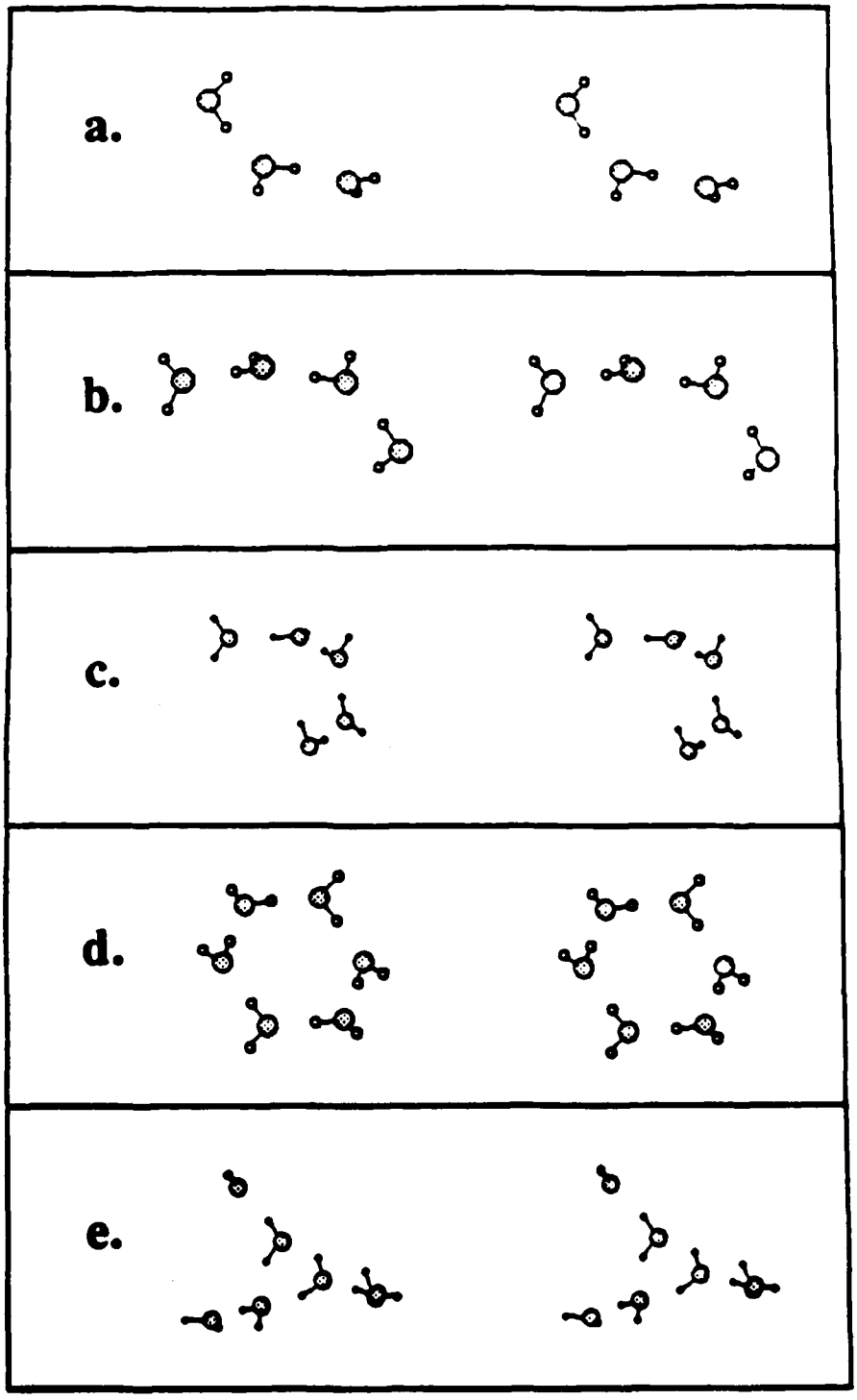

Figure 2

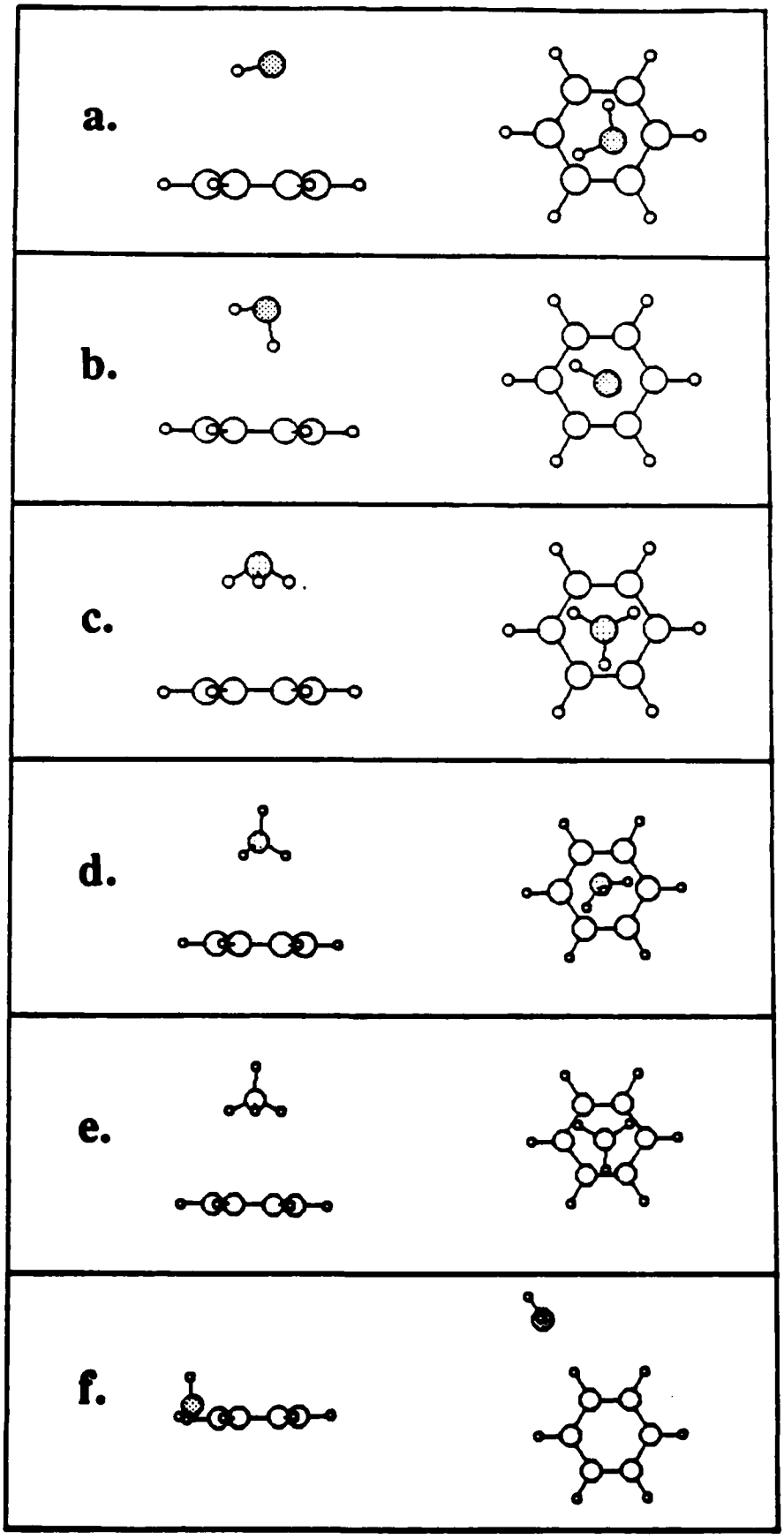

Figure 3

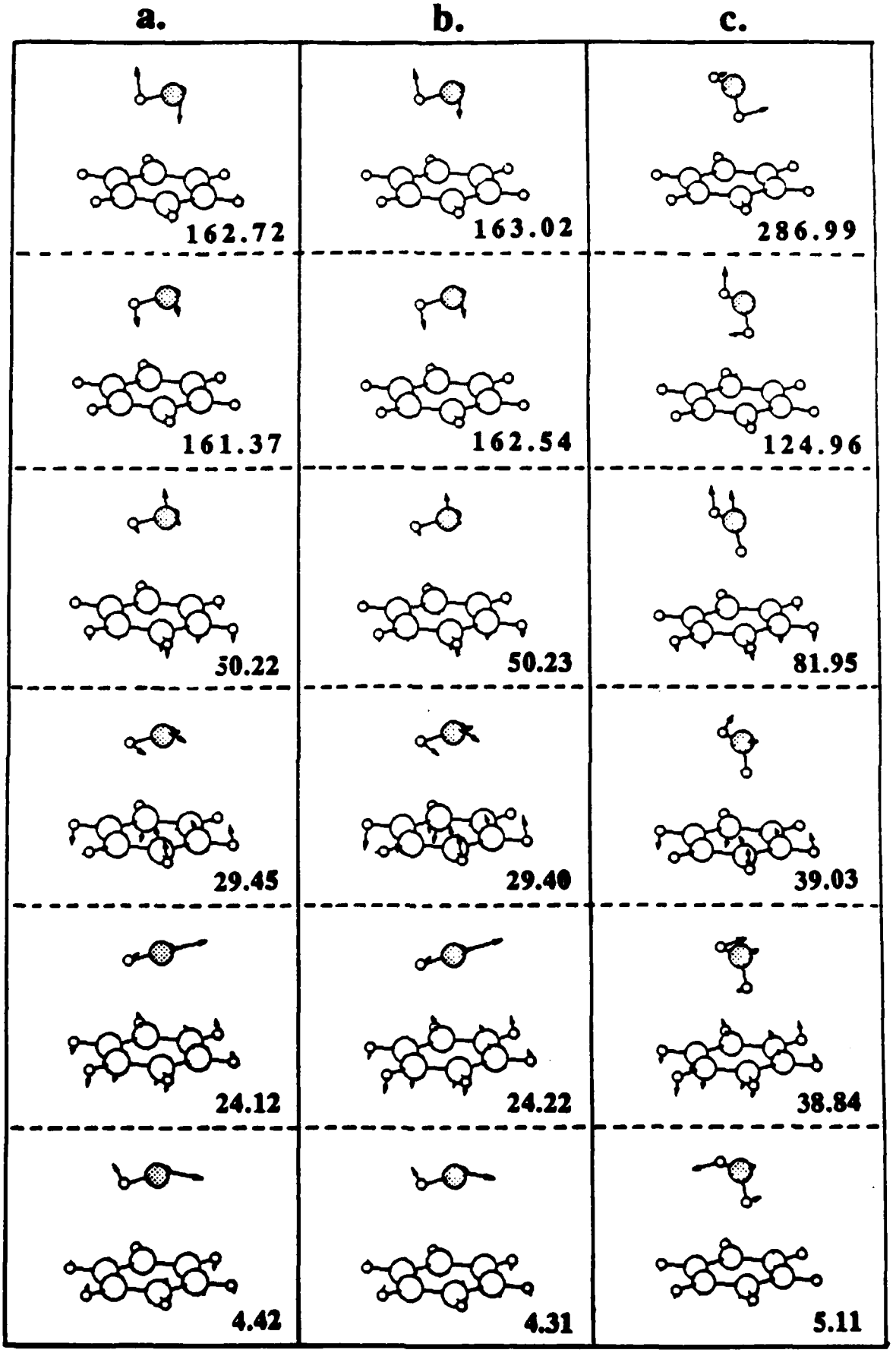
a.
b.
c.
162.72
163.02
286.99
161.37
162.54
124.96
50.22
50.23
81.95
29.45
29.40
39.03
24.12
24.22
38.84
4.42
4.31
5.11

Figure 4