# QUANTITATIVE ATOM-ATOM POTENTIALS FROM ROTATIONAL TUNNELING: Their Extraction and Their Use

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■ Abstract Rotational tunneling of small molecular groups has been the subject of considerable theoretical and experimental activity for several decades. Much of this activity has been driven by the promise of exploiting the extreme sensitivity of quantum tunneling to interatomic potentials, but until recently, there was no straightforward means by which quantitative information about these potentials could be extracted. This review explains how a quantitative method, suitable for general application, was developed. It then goes on to show how this has been used to understand tunneling systems for which no previous satisfactory explanation had been found. The application of the methodology, and its results, to other disciplines is discussed.

## INTRODUCTION

Although the continuing increase in the performance of modern computers has been accompanied by improvements in spectroscopic and diffraction techniques, particularly at central facilities, this would have been of little use if the software for analyzing the data in terms of a microscopic model had not undergone a similar revolution. This review shows how these technological, experimental, and computational advances have been brought together in the analysis of the very weak interactions between atoms that are probed via quantum dynamics. High-resolution spectrometers and diffractometers at central facilities provide precise dynamical and structural data that reveal the timescale and geometry of the quantum dynamics of molecular groups. These data can now be analyzed and understood using a range of computational methods, including force field and quantum chemistry techniques.

The sensitivity of quantum tunneling to the potential energy surface gives rise to a uniquely sensitive probe of the interatomic interactions that are at the origin of the energy landscape. In particular, molecular groups that tunnel measure intermolecular and weak intramolecular interactions (comparable to the thermal energy kT at room temperature) in molecular systems with remarkable accuracy. It is these weak interactions that determine why subtle conformational changes occur in biological systems (1) and soft materials and generally make structure prediction a difficult task (2). Furthermore, the weak interactions are normally difficult to quantify because of the large number of degrees of freedom that are excited in the classical processes where the interactions are dominant. Analyzing classical dynamics entails modeling highly convoluted trajectories involving the motion of many atoms. On the other hand, vibrational data measured at low temperature can be analyzed directly in terms of normal modes (3), but they only provide information about the bottom of the potential-energy wells. Tunneling has the advantage that it persists at low temperatures where the complications of thermal motion are quenched, yet because of their quantum nature, tunneling particles continue to explore potential energy surfaces right up to the barrier maximum. Potentials can be measured, almost without perturbation, in an ideal static environment and then justifiably modeled in the approximation of a static crystalline environment. This approach (molecular mechanics) is simple and gives direct access to the interatomic potentials, whereas the analogous classical approach (molecular dynamics), for simulating large systems at high temperature, depends in a complex way on the potentials.

Broadly speaking, there are two approaches to modeling the atom-atom potentials that govern the structure and dynamics of molecular systems: rapid empirical parametric methods, and slow electronic wave-function methods (4). They are embraced, respectively, in force field and quantum chemistry methods. Accordingly, the former are used for simulating large systems (>100 atoms) and long timescales (>1 ns), and the latter are applied to small systems when high accuracy is required. A conservation rule exists between calculation time and precision; force field methods are rapid and wave-function methods are precise. One of the principal topics of this review is how different aspects of these two approaches can be combined to provide a method that is appropriate for the weak potential energies probed by tunneling measurements. It is important that scientists who use modeling methods to study the subtle and slow processes of biological and other complex systems can judge the consequences of the approximations that they are obliged to accept. Tunneling data offer a means by which future parameterizations and functional forms, aimed specifically at weaker interactions, can be tested.

In this review, we discuss the most recent achievements in extracting these weak interactions from rotational tunneling spectroscopy. The measurements to be presented concern  $CH_3$  or  $NH_3$  groups, but in the general case we refer to methyl groups ( $CH_3$ ) because there are far more measurements of this group (5). In the context of this article, it is therefore fortunate that  $CH_3$  and  $NH_3$  are ubiquitous in physics, chemistry, materials science, and biology, as is the interest in weak interatomic interactions. The groundwork for rotational tunneling was reviewed

many years ago (6), but the theory and experiment outlined therein still forms a valid basis. We invoke a minimum of theoretical ideas in order to define the framework for the numerical work. Spectroscopic and crystallographic experimental work is presented because modeling atom-atom potentials establishes the quantitative link between molecular dynamics and structure. Once a reliable method has been established for modeling weak interactions, insight into more complex theoretical models and novel experimental results can be sought. This review concludes with an analysis of coupled rotational dynamics.

#### THEORY

Tunneling is a purely quantum phenomenon that is related to the description of particles by delocalized wavefunctions. A particle of energy *E* is reflected by a potential energy barrier of amplitude *V* if V > E. In the same conditions, a wavefunction traverses the barrier. For a plane wave of energy *E*, incident on a barrier with a width *a* and height *V*, the probability of transmission *T* is given by (7)

$$T \approx \frac{E}{V} \exp\left(-2\frac{a}{\hbar}\sqrt{2m(V-E)}\right).$$
 1.

There are two important points to note in this equation. (*a*) The probability depends exponentially on the mass of the particle and is consequently most important for light particles such as protons. In this review we are concerned entirely with protons and deuterons, where these terms refer to chemically bound hydrogen and deuterium, respectively. (*b*) The probability decreases exponentially with the height and width of the barrier. This is the origin of the practical sensitivity of tunneling in the context of characterizing potential energy surfaces (PESs).

For a small ensemble of tunneling protons (<4), *a* can be as large as  $\sim 2$  Å. Tunneling is a large-amplitude motion that probes the whole profile of a potential energy barrier, in contrast to molecular vibrations that only probe within a small radius (<0.1 Å) of the minima of a PES.

When the tunneling motion connects indistinguishable molecular configurations, the potential energy minima corresponding to each configuration are equivalent and the tunnel effect is coherent; tunneling persists at zero Kelvin, that is in the absence of external (lattice) excitations. The spectroscopic signature is the splitting,  $\Delta$ , of vibrational energy levels. Notable examples are the inversion of ammonia (8) and rotational tunneling of molecular groups (CH<sub>3</sub>, NH<sub>3</sub>, CH<sub>4</sub>, NH<sub>4</sub><sup>+</sup>). Otherwise, molecular configurations are inequivalent, either because particles are transferred to new, unoccupied sites, for example in hydrogen bonds (9), or because the reorienting particles are inequivalent, for example in the rotor CH<sub>2</sub>D (10). Potential energy minima are no longer degenerate, the tunnel effect is dissipative, or incoherent, with a rate proportional to  $\Delta^2$ , and it allows a tunneling particle to escape from a metastable well. In this review, we are concerned mainly with the coherent tunneling of methyl groups. The simplest model of rotation is one-dimensional: A single rotational coordinate,  $\phi$ , describes the orientation of a symmetric triangle of protons, and the axis of rotation passes through the central carbon atom, usually along a covalent bond. The Hamiltonian for the single particle motion (SPM) is

$$H = \frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} + \sum_{n \ge 1} \frac{V_{3n}}{2} (1 + \cos(3n(\phi + \alpha_{3n}))) = \frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} + \sum_n b_n e^{i3n\phi}, \quad 2.$$

where  $l = 3mr^2$  is the moment of inertia for three protons of mass *m* and radius of rotation *r*. The potential energy is expressed as a Fourier series, typically limited to  $n \le 2$ , in which case experimental data are required to determine three parameters,  $V_3$ ,  $V_6$ , and the relative phase,  $\alpha = \alpha_6 - \alpha_3$ . *H* can be expressed in matrix form, typically using a basis set of free rotor wavefunctions. Diagonalization then leads to a set a of tunneling and vibrational (librational) energy levels and wavefunctions. The  $\cos 3\phi$  form of the rotational potential is shown in the upper part of Figure 1 (see color insert), along with schematic energy levels for a CH<sub>3</sub> rotor. Each librational level is split into a singlet and a doublet, with symmetry species A and E, respectively. The exponential decay of the tunnel splitting and the approximately linear increase in libration frequency as a function of barrier height are shown in the lower part of Figure 1 (see color insert). The strength of the rotational potential at which the free rotor description (on the *left* of the figure) becomes tunneling is arbitrarily taken to be at about 2 meV (~20 K).

Because methyl group rotation connects indistinguishable molecular configurations, the total rotor wavefunction—the product of a spatial and a nuclear spin part—must be symmetric. The total wavefunction has A symmetry, which imposes the following correlation between spatial (*s*) and nuclear spin (*n*) terms:  $A_S A_n$ ,  $E_S^a E_n^b$ ,  $E_S^b E_n^a$ . The allowed combinations are called the spin symmetry species. They have important consequences for tunneling spectroscopy because a transition between A and E rotational states entails a "matching" change in the nuclear spin state.

When the rotational potential of a methyl group depends on the orientation of a neighboring rotor, a coupling potential exists. A network of coupled rotors may extend from a pair to a large cluster. In all cases we consider a set of one-dimensional rotors and pairwise coupling potentials *Vp* according to the following Hamiltonian:

$$H = -\sum_{i} \frac{\hbar^2}{2I_i} \frac{\partial^2}{\partial \varphi_i^2} + V(\varphi_1, \dots, \varphi_n), \qquad 3.$$

$$V(\varphi_1, \dots, \varphi_n) = \sum_{i=1}^n V_i^S(\varphi_i) + \sum_{i,j=1, i < j}^n V_{i,j}^p(\varphi_i, \varphi_j), \qquad 4$$

$$V_{i,j}^{p}(\varphi_i,\varphi_j) = \sum_k \sum_l b_{k,l,i,j} e^{i3k\varphi_i} e^{i3l\varphi_j}.$$
 5.

 $V^{S}$  is referred to as the static potential. It is independent of the orientation of neighboring rotors and is related to  $V^{spm}$  as follows:

$$V_i^{SPM}(\varphi_i) = V_i^S(\varphi_i) + \sum_{j \neq i} V_{i,j}^p(\varphi_i, \varphi_{j,SPM}).$$
6.

Resolving the coupled Hamiltonian is tractable by matrix diagonalization for two or three coupled rotors, the matrix dimensions being  $n^2$  or  $n^3$ , where *n* is the number of basis functions, typically 20 (11, 12). For larger clusters of coupled rotors, more sophisticated methods are required. One method based on Gaussian pocket states, rather than free rotor wavefunctions, allows up to five rotors to be handled (13). However, the method favored in this work is based on an eigenstateby-eigenstate search using the variational principle (14), which can be applied to systems of very high dimension, as are typically encountered, for example, in quantum chemistry methods (15). A one-dimensional mean-field solution of *H* can also be obtained that describes the effective potential due to delocalization of neighboring methyl groups (16).

A second type of coupled dynamics has been elaborated for a number of rotational tunneling systems, namely rotation/translation coupling (17). Rotation of the CH<sub>3</sub>/NH<sub>3</sub> group is accompanied by a small-amplitude displacement of the rotor center of mass, effectively the rotation axis (and the C/N atom) precesses during the rotation. The Hamiltonian to be resolved then contains kinetic terms for the center of mass and the rotor, and the potential term is three-dimensional, two additional coordinates being required to describe the amplitude ( $r_c$ ) and the precession ( $\alpha_c$ ) of the center of mass (18).

$$H = \frac{P_c^2}{2M} + \frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} + V(r_c, \alpha_c, \phi).$$
 7.

The Hamiltonian is solved in terms of products of two-dimensional oscillator functions and one-dimensional rotator functions.

The above Hamiltonians refer to dynamics with a very limited number of degrees of freedom: They are only valid at liquid helium temperatures when the lattice motion is quenched. As the temperature is increased, fluctuations in the rotational potential become important, and the coherence of the tunneling is lost. There is a gradual crossover to apparently classical rotational diffusion, and it is unusual to distinguish rotational tunneling above about 50 K.

## EXPERIMENTAL TECHNIQUES FOR ROTATIONAL TUNNELING SPECTROSCOPY

Tunnel splittings greater than about 0.5  $\mu$ eV, that is, methyl groups with rotational potentials of amplitude lower than 50 meV (500 K), are best measured with inelastic neutron scattering (INS) techniques. This lower limit corresponds to the resolution of the backscattering technique (19). Larger tunnel splittings  $(>20 \ \mu eV)$  are measured using variations on the time-of-flight technique or even triple-axis methods (19). The main advantage of neutron scattering for the present work is its ability to measure the tunnel splitting directly. This is because the neutron possesses nuclear spin 1/2, which is able to change the nuclear spin-state of the rotor. Furthermore, because the neutron interacts directly with the nuclei rather than the electrons, spectral intensities can be calculated from the Hamiltonian (20), and in principle, the whole spectral profile can be analyzed.

Neutrons also have the advantage that the scattering cross section of a hydrogen nucleus is about an order of magnitude greater than most other nuclei, so that tunneling peaks are characterized by their high intensity. Thus, measurements are rapid compared with many other neutron scattering experiments, and in many cases a good spectrum can be collected in under an hour.

 $\gamma$ -Picoline was one of the first examples of rotational tunneling measured with neutrons (21) (see Figure 2; see color insert). In fact, the spectrum is almost that of a free rotor, and it was originally interpreted in terms of a weak  $cos6\phi$ rotational potential. As an illustration of the improvement in instrumentation, the resolution (FWHM) of the original triple-axis measurement was about 100  $\mu$ eV (as in Figure 2*a*; see color insert). This is to be compared with a number of timeof-flight measurements with resolution as good as ~10  $\mu$ eV (22) (Figure 2*b*; see color insert), and the most recent spectrum of this compound that was measured with a resolution of 2  $\mu$ eV (23) (Figure 2*c*; see color insert). The increase in resolution has revealed that the free-rotor peak is split into a number of lines, and as is shown, spectra of this complexity can only be interpreted with the help of modern computational methods.

Nuclear magnetic resonance (NMR) tunneling spectroscopy depends on nuclear dipolar or quadrupolar interactions and enables smaller tunnel splittings to be measured (<0.5  $\mu$ eV), the lower limit being ~0.2 neV (24). The smaller tunnel splittings correspond to more strongly hindered methyl groups (V > 50 meV), which are less interesting in the context of this work on weak interactions because the potentials become dominated by an ever-stronger intramolecular term.

Optical techniques can also be used to investigate rotational tunneling in electronically excited states (25, 26). Photons cannot induce transitions between tunneling states of different symmetry, and it is the difference between the tunnel splitting in the ground electronic state and that in the excited electronic state that is observed: ||A-A'| - |E-E'||, where the prime indicates the excited state. The difference in tunnel splittings arises from the difference in rotational potentials in the ground and excited states, which, in turn, is due to the change in molecular structure caused by electronic excitation. In principle, a sensitive tunneling measurement is a probe of minor, optically induced molecular reorganization. The resolution of optical techniques is comparable with INS, and simple optically active systems where the ground state can be characterized by INS are desirable.

 $\gamma$ -Picoline is a complicated example, as is discussed, where complementary neutron and optical measurements have been made (27).

#### What Is Measured and Determining the Rotational Potential

A simple tunneling spectrum of the methyl group in aspirin (acetyl salicylic acid) (28), measured with INS, is illustrated in Figure 3*a*; (see color insert). The central elastic peak arises from neutrons scattered without energy change, and the two symmetrically placed inelastic features arise from neutrons scattered by upward or downward transitions between the tunnel-split librational ground-state. When there is more than one crystallographically distinct methyl group in the crystal, as in dimethyl pyrazine (29), a tunnel peak feature arises for each of these, assuming that they fall within the range of the instrument and can be resolved (Figure 3*b*; see color insert). In this case, if a single crystal is available (most tunneling measurements are performed on powders) and the crystal structure is known, it is possible to vary the intensity of the tunnel peaks by reorienting the crystal so as to enhance or diminish the scattering from crystallographically distinct methyl groups.

Normally, for true one-dimensional rotational tunneling systems INS spectroscopy provides only two data: the tunnel splitting of the librational groundstate, and the splitting between the average of the ground-state and the first excited state levels. On the basis of these two observations, it is usually only possible to determine the predominant term in the Fourier expansion ( $V_3$  or  $V_6$ ) in Equation 1.

Deuteration of the methyl group reduces the libration frequency by about a factor of root-two, and the tunnel frequency by a factor of about 20 according to Equation 1. For aspirin, the CD<sub>3</sub> tunnel splitting of 11.2 neV was measured using quadrupole NMR techniques (30). Additional data from deuterated analogues enable the rotational potential to be determined more completely  $(V_3, V_6, \alpha)$  within the approximation that deuteration only changes the moment of inertia of the rotor (28). However, the smaller zero-point motion of deuterium compared with hydrogen can compromise this approximation. First, when methyl-methyl coupling potentials are important, CH<sub>3</sub> groups probe relatively delocalized neighbors whereas CD<sub>3</sub> groups probe more localized neighbors. Consequently, the rotational potential may be expected to be stronger for CD<sub>3</sub> rotors. Second, samples containing  $CD_3$  groups are typically fully deuterated, which leads to a compression of the unit cell compared with the fully protonated sample. Such compression also tends to increase the amplitude of the  $CD_3$  rotational potential. Deuteration can also alter the temperature of phase transitions with the rather serious consequence that at a given temperature, the protonated and deuterated structures are not the same (31).

Deuteration-induced compression is typically equivalent to an applied hydrostatic pressure of  $\sim 1$  kbar, which may shift the tunnel frequency by about 10%, although this amounts to a small change in the rotational potential. A number of hydrostatic pressure experiments in the pressure range up to 5 kbar have been performed (32), and their analyses by the methods to be described below should allow the gradients of atom-atom potentials to be probed, provided the corresponding crystallographic information is available.

Although few examples of nearly free quantum rotors are known, they present a more favorable case for determining weak rotational potentials, because it is usually possible to measure all transitions between at least the first four levels (Figure 2*a*). Because rotational and vibrational levels for free rotors are not so clearly separated energetically, the effect of deuteration is close to a root-two reduction in the energy of the measurable transitions, which enables the spectra of the deuterated analogues to be measured by INS (33).

## Measuring Crystal Structures for Understanding Rotational Potentials

Many rotational potentials have been characterized within the SPM approximation, the amplitude and phase parameters of the potential function being adjusted within the limits of the available data. However, it is difficult to exploit this type of information because it tells us little about the origin of these potentials, either on an atom-by-atom basis or in terms of intra- and intermolecular interactions. Ideally, the rotational potential should be calculated from the crystal structure, and in this way, proposed atom-atom potentials can be tested by their ability to reproduce the measured tunneling spectra, within a given rotational model, such as the SPM.

When making a quantitative determination of a rotational potential that depends on interatomic separations, it is clearly important that all spectroscopic and crystallographic data be measured at the same temperature. In this way, lattice compression effects are removed from the analysis, and more important, the effect of phase transitions that can modify the crystal structure in a more pronounced way.

Since proton/deuterium positions are required, neutron diffraction is the technique of choice as the coherent scattering cross section of H/D, which gives rise to Bragg peaks, is comparable with that of other atoms, such as carbon, oxygen, and nitrogen. The minimum information required from the diffraction measurement is the unit cell dimensions and the atomic positions, and within these limits, powder diffraction is an appropriate and rapid technique. The inconvenience of neutron powder diffraction is that fully deuterated samples are required, otherwise the diffraction pattern is dominated by the background of incoherent, single-particle scattering from hydrogen. Typically, then, the tunneling measurements are performed on protonated samples and the diffraction measurements on deuterated samples, and rotational potentials are to be calculated in the approximation that the two structures are the same (see above). Single crystal neutron measurements can be performed on protonated samples, although these typically take a couple of weeks.

## DETERMINATION OF THE ROTATIONAL POTENTIAL IN THE SPM APPROXIMATION: Modeling Weak Interactions

The main advance in the field of rotational tunneling has been the exploitation of the wealth of existing tunneling measurements to obtain new and quantitative information on weak interatomic potentials. In order to have a large number of systems characterized for numerical work, our experimental program has included as many new diffraction measurements as tunneling measurements. Prior to our involvement in modeling weak interactions, only six crystal structures of tunneling systems were known at reasonably low temperature and they were used to calculate rotational barriers from atom-atom potentials (34–39). The systems were generally studied separately by several authors. Now nearly 30 systems have been characterized, corresponding to about 50 independent tunneling measurements (see Appendix).

Quantum molecular dynamics at low temperature ( $\sim 4$  K) are modeled numerically using the molecular mechanics method. Energy calculations, based on a given description of interatomic interactions, are used to map out the potential energy surface (PES), and (*c*) the quantum dynamics are obtained by resolving the appropriate Hamiltonian containing the PES. Such a calculation depends on three contributions: (*a*) the crystal structure, which defines all interatomic distances; (*b*) the potential energy calculation; and the rotational model used for displacing atoms along trajectories and thereby mapping out the PES.

If the object of the work is to test the second contribution, then the crystal structure must be reliable and the rotational model must be appropriate. In addition, it is desirable that the rotational model be simple so that the different contributions to the potential energy calculation can be easily deciphered. The SPM model appears to fulfill these criteria: It is simple, and a wealth of tunneling data has been satisfactorily interpreted within this approximation. The numerical modeling work should confirm the validity of the SPM model. Finally, a large database should be available in order to avoid coincidental agreement between experiment and calculation.

## Calculating the Rotational Potential in the SPM Approximation

To calculate the rotational potential in the SPM approximation, a computer model of the crystal is constructed from the known crystal structure using periodic boundary conditions. A single methyl group is then rotated, typically by  $10^{\circ}$  steps over at least  $120^{\circ}$ , and the potential energy of the crystal is recalculated at each step. Although the smallest crystal model is a single-unit cell, it is often necessary to double the unit cell in one or even two directions so that the effect of the rotation of image methyl groups does not affect the calculation via coupling potentials.

Measured methyl groups never have geometrical  $C_3$  symmetry, and simple rotation will not generate the symmetric rotational potential. Physically, the methyl group must deform during rotation so that rotational configurations connected by an average rotation angle of 120° are identical. A deforming, rotating methyl group is beyond the scope of the SPM model, in which the rotor must be symmetrized before rotation. The rigid-rotor approximation is expected (and is shown) to be valid because the energy associated with molecular deformation is much greater than the typical amplitude of the rotational potential.

A further difficulty arises because standard crystallographic methods, in particular modeling nuclear delocalization with ellipsoids, produce C–H bonds that are too short. Neutron diffraction is better than X rays at locating H/D positions, but C–H bond lengths from powder measurements may vary by 0.05 Å ( $\approx$ 5%). Where the methyl group geometry is poorly measured, average values are taken from neutron, single-crystal, diffraction data.

Conceptually, the potential energy calculated at each step can be broken down into intra- and intermolecular contributions, which correspond to regions of high and low electron density, respectively.

$$V(\phi) = V_{Inter}(\phi) + V_{Intra}(\phi)$$
8.

The intermolecular part is typically divided into van der Waals (VDW) and Coulomb contributions, where the latter depend on the partial charges attributed to each atom.

$$V_{Inter}(\phi) = V_{VDW}(\phi) + V_{Coulomb}(\phi)$$
9.

The relative importance of the three components of the rotational potential varies from one system to another, and it is clear that if one component dominates strongly, then errors in the other two parts will not be apparent. For a general procedure, however, we need to know in advance that all three components will be evaluated with acceptable precision. Dimethyl pyrazine (DMP) provides a useful example of the typical contributions for organic molecules (29) and was among the first systems to be analyzed using the standard procedure (described in detail below). The dimethyl pyrazine molecule is illustrated in Figure 3b. In the gasphase, the lowest energy conformation is with one C-H vector of each methyl group in the plane of the aromatic ring, and pointing toward the N-atom. In the crystal, however, the intermolecular forces cause one of the CH<sub>3</sub> groups to be rotated by  $60^{\circ}$ . The question of why the two methyl groups adopt different orientations is tackled by calculating the potential energy of the crystal as a function of the orientations of the two methyl groups. The VDW, Coulomb, and internal energy surfaces are shown in Figure 4 (see color insert). Coulomb and internal surfaces show the gas-phase orientation for the two methyl groups, whereas the VDW surface shows the orientation found in the crystal. When these three surfaces are added, the total PES is found with the position of the minima agreeing perfectly with the measured crystal structure. The barrier to reorientation is smaller than the sum of the three amplitudes, the relative phases between the components are important, and the calculated tunnel frequencies are consistent with the measured values (Figure 3*b*).

The concept is simple, but the critical point is how these energies are determined. Until recently, only a few calculations of this type had been made and some rather ad hoc approximations were made that are justified on a case-by-case basis. For example, electrostatic interactions have been ignored (35), taken from literature (34), or calculated from quantum chemistry methods (37). In all cases, point partial charges were used, and these were assumed to be the same for all methyl protons, and invariant under rotation. In order to improve agreement between observed and calculated tunnel splittings, VDW parameters were adjusted (39). These early efforts highlighted the difficulties, but because of the paucity of accurate lowtemperature crystal-structure data and accessible quantum chemistry calculations, there was no incentive to establish a general method.

#### Towards a Standard Calculation Using Force Field Methods

Essentially, this method was established by evaluating the consequences of different approximations in the potential energy calculation for a large number of tunneling systems (40).

The simplest approach uses force field methods. These are based on a parameterization of a set of functional forms, describing bonded and nonbonded interactions, which has been optimized to give best agreement with bulk, structural, and spectroscopic properties of a large number of related molecules. A number of force fields are available, and the choice depends on the similarity of the molecule under study with those used in the parameterization. For simplicity, we will restrict our discussion to the universal force field (UFF) (41), which has the virtue of being able to accommodate most atom-types.

Only three terms in the force field are required in the SPM model. (*a*) A torsional force constant dominates the intramolecular term. Interactions between atoms within the same molecule but separated by more than three bonds are treated as VDW and Coulomb interactions. (*b*) The VDW interaction can be modeled using a variety of functional forms, but the popular default is the computationally efficient Lennard-Jones 12-6:

$$E_{LJ12-6} = D_0 \left\{ \left[ \frac{R_0}{R_{ij}} \right]^{12} - 2 \left[ \frac{R_0}{R_{ij}} \right]^6 \right\},$$
 10.

where  $R_{ij}$  is the distance between atoms *i* and *j*,  $D_0$  is the bond strength, and  $R_0$  is the bond length. (*c*) The Coulomb energy is modeled as

$$V = \frac{Q_i Q_j}{4\pi \varepsilon_0 R_{ii}},$$
 11.

where  $Q_i$  and  $Q_j$  are partial charges that are localized on the atoms *i* and *j*. Ewald summations for these long-range interactions must be used.

Some force fields, such as Compass (42), include partial atomic charges within the parameterization, but because these are not contained within the UFF, they were calculated by the QEQ method (43). This is an empirical method that is based on the relative positions of atoms and ionization potentials.

This method has been applied to nearly 30 crystals starting from the measured crystal structure. Figure 5 (see color insert) shows the comparison between observed and calculated tunnel splittings using this simple force field method. Any points falling on the leading diagonal of this plot would correspond to perfect agreement, but it can be seen that the majority of points fall below this line, some by several orders of magnitude.

## Improving the Potential Energy Calculation with Quantum Chemistry Methods

The agreement shown in Figure 5 is very poor, the rotational barrier being systematically overestimated, often by orders of magnitude. The effect of the various approximations on the force field/SPM calculation as described above was investigated in the case of acetic acid (44). Figure 6a (see color insert) shows the above calculation based on the crystal structure measured at 278 K. Although the rotational potential appears to be good, the agreement arises from a fortuitous cancellation of errors. Applying the same calculation to the 2 K crystal structure leads to the overestimated rotational potential and therefore an underestimated tunnel frequency (Figure 6b; see color insert), as indicated in the correlation plot (Figure 5). The total potential is dominated by the VDW term, which dramatically increases with unit cell compression, which suggests that the problem lies with the repulsive part of the potential. A more physically reasonable and less computationally efficient form of the VDW interaction is the Buckingham potential,  $E = a \cdot exp(b/r) + cr^{-6}$ , which has a softer repulsive term than the LJ 12–6 form. When expressed in the exponential-6 form, the connection with the LJ parameters,  $R_0$  and  $D_0$ , can be carried over.

$$E_{\exp^{-6}} = D_0 \left( \left\{ \left( \frac{6}{\gamma - 6} \right) \exp\left[ \gamma \left( 1 - \frac{R_0}{R_{ij}} \right) \right] \right\} - \left[ \left( \frac{\gamma}{\gamma - 6} \right) \left( \frac{R_0}{R_{ij}} \right)^6 \right] \right),$$
12.

where  $\gamma$  is a scaling factor (typically 12). The VDW term recalculated with the exponential-6 form and UFF parameters is shown in Figure 6*c*; its amplitude has been reduced by more than a factor of three.

The second contribution, which changes markedly between Figure 6*b* and *c*, is the intramolecular term. In the force field calculation, a potential of  $C_6$  symmetry is imposed by the local  $C_2$  symmetry of the acetate oxygen atoms. The torsion force constant cannot be sensitive to small molecular deformations, but quantum chemistry calculations, in which the total intramolecular potential is given as a function of molecular geometry, show that a deformation of only a few degrees is required to produce a  $C_3$ -dominated potential. A series of ab initio calculations (basis functions 6-31G<sup>\*\*</sup>, MP2 correction for electron correlation effects) on the set of rotational configurations gives the molecular energy variation shown by the torsion curve in Figure 6c.

The final contribution to the rotational potential is the Coulomb term, which arises from changes in the electrostatic potential during the rotation of the methyl group. It depends crucially on the partial charges assigned to atoms. The series of ab initio calculations, used to obtain the intramolecular potential, can also be used to obtain partial charges as a function of methyl group orientation, either simply by analyzing the population of electron orbitals (Mulliken analysis) or, more accurately, by deriving charges that reproduce the electrostatic potential around the molecule (ESP charges) (4). The second type of charges have been used to obtain the Coulomb potential in Figure 6c; it is much weaker than in Figure 6a and b.

The accuracy with which partial charges must be calculated has been addressed in a study of rotational tunneling in the ionic systems  $Co(CH_3COO)_2$  and  $Ni(CH_3COO)_2$  (45). These systems give greater insight than acetic acid because the Coulomb term dominates the rotational potential, being typically three times stronger than the VDW term. Four Coulomb rotational potentials were determined using (*a*) average, rotation-independent QEQ charges, (*b*) average, rotation-independent ESP charges, (*c*) rotation-dependent QEQ charges, and (*d*) rotation-dependent ESP charges.

The results are assembled in Table 1. QEQ is unreliable, giving better results for rotation-independent charges, whereas, logically, the ab initio method gives better tunnel splittings and libration frequencies for ESP charges, recalculated for each orientation of the methyl group. Clearly, where Coulomb interactions are negligibly small, more approximate methods would suffice, but we are trying to define the approach that will work in the general case.

The result of these three corrections for acetic acid is a rotational potential, calculated from the 2 K crystal structure that reproduces the tunnel splitting

		2		
Method	Nickel acetate tetrahydrate		Cobalt acetate tetrahydrate	
	Tunnel splitting/µeV	Libration freq./ meV	Tunnel splitting/µeV	Libration freq./ meV
QEQ	0.3	17.5	0.6	16.4
ESP	0.3	18.1	0.4	17.1
$QEQ(\phi)$	< 0.001	24.9	0.03	22.2
$\text{ESP}(\phi)$	1.2	16.8	2.0	16.0
Experiment	1.4	15.0	1.2	15.0

**TABLE 1** Comparison of calculated and measured methyl group dynamics in nickel and cobalt acetate tetrahydrate<sup>a</sup>

<sup>a</sup>QEQ, an empirical method based on the relative positions of atoms and ionization potentials; ESP, electrostatic potential. See text for more information on each calculational method. From Reference 45.

Method	Correlation	RMS difference of log( $\Delta$ )
FF (LJ 12-6, QEQ)	0.376	2.486
FF (exp-6, QEQ)	0.546	1.828
MOPAC AM1 (exp-6)	0.786	0.866
AB (exp-6)	0.896	0.872

**TABLE 2** Comparison of different force field (FF) and hybrid methods for calculating tunnel splittings<sup>a</sup>

<sup>a</sup>For perfect agreement, the correlation would be unity and the root mean square (RMS) difference of log( $\Delta$ ) would be zero. QEQ, an empirical method based on the relative positions of atoms and ionization potentials; MOPAC, molecular orbital package; AB, ab initio; exp, exponential.

measured at 2 K. Are the results as good when applied to a large number of systems?

### The Hybrid Method for a Standard Calculation

Applying the above method, which invokes Buckingham potentials and ab initio methods  $(6-31G^{**}$  basis functions, MP2 corrections, ESP geometry-dependent charges), to a large number of systems gives the correlation curve shown in Figure 7 (see color insert). The overall agreement between observed and calculated tunnel splittings is good. The majority of points fall between the *dashed diagonal lines* that define a factor of 3 between observation and calculation, which translates to a level of agreement of ~90% for the rotational barrier. Clearly, this method offers a reasonable compromise between speed and accuracy, but it does show some systematic errors, particularly for hydrogen-bonded systems (see next section).

Semi-empirical methods can be used, instead of ab initio methods, and allow some precision to be traded for a reduction in computation time. A correlation, as in Figure 5, has been calculated using the AM1 Hamiltonian in MOPAC (46, 47). A charge scale-factor of 1.3 has been applied, because the charges are underestimated when compared with ab initio charges (48), in order to optimize the correlation.

The results of different potential energy calculations are summarized in Table 2, which quantifies the gain in precision over (*a*) the default UFF method by using (*b*) Buckingham instead of LJ 12-6 potentials, (*c*) MOPAC to obtain intramolecular potentials and partial charges, and (*d*) ab initio methods instead of MOPAC.

## USING OUR KNOWLEDGE OF WEAK INTERACTIONS WITHIN THE SPM MODEL: Probing the Static Properties of Hydrogen Bonds

The success of the hybrid model depends on separating interactions into inter- and intramolecular terms and using quantum chemistry methods, where possible, to define charges for the former and torsions for the latter. The cumulative effect of

Method	Tunneling ( $\mu eV$ )	Librations (meV)	Orientation (degrees)
Paracetamol			
Measured	3.10	13.8	75.8
Ab initio	0.998	18.4	88.6
DFT	5.42	13.1	75.0
Acetanilide			
Measured	0.30	18.0	54.7
Ab initio	1.15	14.5	46.5
DFT	0.850	16.3	53.6

**TABLE 3** Comparison of the hybrid (ab initio) and density functional theory (DFT) methods for calculating methyl group dynamics and orientation in hydrogen bond networked systems<sup>a</sup>

<sup>a</sup>From Reference 49

intermolecular interactions is still treated by pairwise summations. The validity of the separation, approximately according to regions of low and high electron density, and therefore the success of the hybrid method are compromised by the existence of intermolecular hydrogen bonds. Although the hybrid method still works for certain samples, like acetic acid and *n*-methyl urea, for three samples containing the peptide group (–CONH–), acetanilide, paracetamol, and acetamide, the results are poor (see Table 3 and Figure 7). An accurate calculation of the rotational potential should also reproduce the equilibrium orientation of the methyl group to within a few degrees, but an error of about  $10^{\circ}$  is obtained. For methyl groups bonded to peptide groups, the ab initio–determined, intramolecular potential is weak with an equilibrium orientation of zero degrees, that is, a C–H bond aligned with the C–O bond. The methyl group orientation in the solid state is therefore a sensitive probe of the description of the intermolecular interactions in these peptide systems.

The correct treatment of the effect of intermolecular hydrogen bonds on neighboring methyl groups requires the electron density to be calculated in the intermolecular regions. Two approaches have been pursued (49). The first uses semi-empirical methods, as these can be applied to small clusters of molecules containing up to 200 atoms, in contrast to ab initio methods, which are limited to tens of atoms. Calculations show that the presence of hydrogen bonds causes a modification of the electron density, which is quantified, primarily, as a 10% change in the partial charges of the donor-oxygen and hydrogen atoms. Applying this correction to the standard hybrid calculation shows the correct trends, but quantitatively, the results do not constitute a significant improvement. The second approach uses density functional theory (DFT) methods (15), which have an accuracy comparable to ab initio methods, but for the same computational cost they can be applied to a periodic system instead of an isolated molecule. Computational requirements depend on the size of the periodic cell; for paracetamol, the unit cell is 700 Å<sup>3</sup> and the calculations were performed on a workstation using CASTEP

[available in the Cerius 2 software package (see www.msi.com)], whereas for acetanilide and acetamide, the unit cells are  $\sim$ 1400 Å<sup>3</sup> and a T3E parallel-processor machine was used. As noted earlier, the calculation cell must be big enough to ensure convergence, and this is the case for one unit cell of these systems. For paracetamol and acetanilide, the results are excellent (see Table 3), almost perfect agreement being obtained for the equilibrium orientation of the methyl groups. For acetamide, poor results were obtained and further DFT calculations are ongoing. In conclusion, numerical modeling has rendered the methyl group a quantitative probe of its molecular environment, and in the case of peptide systems, the methyl group is a probe of the static properties of intermolecular hydrogen bonds.

# USING OUR KNOWLEDGE OF WEAK INTERACTIONS BEYOND THE SPM MODEL

#### **Rotor-Rotor Coupling**

When there are more tunnel peaks in an inelastic spectrum than crystallographically distinct methyl groups, this is a clear, experimental indication that the SPM model is no longer appropriate. From a numerical viewpoint, coupling potentials can be calculated rapidly with the hybrid method. When the amplitude of the strongest coupling potential is comparable to the static potential (Equation 4), coupled dynamics are expected to be experimentally observable. All systems are tested numerically for coupling potentials. They always exist but are generally small and the SPM model is widely applicable, as shown in Figure 7. An analysis of coupled dynamics has, however, been essential in several cases: lithium acetate and  $\gamma$ -picoline, where highly structured tunnel spectra have been interpreted in terms of various models of coupled methyl groups, methyl acetate, and durene.

In the case of durene, the NMR tunneling data were originally interpreted in terms of intramolecular coupling of pairs of energetically equivalent methyl groups on neighboring carbon atoms on the benzene ring (51), and recent, high-resolution vibrational spectroscopy also revealed structure in the band of methyl-librational excitations (52). Figure 8 shows the pairwise coupling potentials in durene. Although the strongest (intramolecular) potential is significant ( $\sim$ 50 meV), the static rotational potentials are high for the two inequivalent methyl groups ( $\sim$ 130 meV), and coupling effects are not expected in the tunneling spectrum. The SPM potentials are significantly different ( $\sim$ 80 meV and  $\sim$ 110 meV), and it is combinations of the corresponding tunnel splittings that because of dipolar coupling potentials, and they have been determined as a function of the size of a cluster of coupled methyl groups, that is, as a function of an increasing number of ever-weaker coupling potentials (see Figure 8). The librational band shows two structured peaks at 20.5 meV and 23.5 meV, respectively (Figure 9*e*; see color insert). The peaks



**Figure 8** The six strongest coupling potentials between different pairs of methyl groups in durene. (From Reference 52, Figure 7.)

are not due to in-phase and out-of-phase librations of equivalent rotors but correspond to the different methyl groups. The structure arises from coupling that has been analyzed for eight methyl groups by solving Schroedinger's equation and by harmonic, normal mode analysis (Figures 9b and a, respectively; see color insert). Although the former method shows the effect of anharmonicity, a 1-meV shift to lower energy, the normal mode analysis can be extended to much bigger systems, 16,000 methyl groups (Figure 9c; see color insert). Applying the anharmonicity correction (Figure 9d; see color insert) gives a spectral profile that compares favorably with the measurement. Perfect agreement is not expected because vibrational modes involving out-of-plane motion of the methyl groups occur in the same spectral region.

In the case of  $\gamma$ -picoline, a multiplet of tunneling peaks is observed for one crystallographically unique methyl group (Figure 2). The spectral structure has been interpreted in terms of soliton-type excitations along infinite chains of coupled methyl groups (22). Within this model, single particle and coupling potentials were adjusted to achieve agreement with the observed energies, and values of 3.6 and 5.5 meV, respectively, were obtained. Numerical modeling, however, reveals that the coupling potential between neighboring methyl groups along the chain is only 2.5 meV, which is not sufficient for the proposed dynamics. Furthermore, the coupling potential between coaxial pairs of rotors, and thus between chains, is stronger (4.3 meV). Accordingly, a model of four coupled methyl groups was developed that reproduces spectral frequencies and intensities (53) (Figure 2*c*), the latter as a function of the populations of rotational levels that can be controlled by quenching from different temperatures to 2 K, due to slow nuclear spin conversion at this temperature (54, 55).

Lithium acetate is the second sample that has been regarded as a prime example of a coupled pair of methyl groups (11, 12). In the low-temperature crystal structure, acetate groups are coaxial with methyl groups face-to-face, and they are surrounded by molecules of water of hydration (56). There is, however, only one crystallographically unique methyl group. In the tunneling spectrum, three strong peaks are observed and the model of coupled pairs was elaborated, with values of 4 meV for the amplitude of the SPM potential and 10 meV for the coupling potential, obtained from the spectroscopic data (11, 12). Numerical modeling, however, reveals values of 7.2 and 3.9 meV, respectively (18); that is, the model of coupled pairs is not consistent with known interatomic interactions and the measured crystal structure. Indeed, the water molecules make the strongest contribution to the rotational potential of the methyl group. The solution to this problem is the subject of the next section.

#### Translation/Rotation Coupling

In lithium acetate, it transpires that the major cause of the structure in the tunnel spectrum is the departure of the methyl dynamics from uniaxial rotation (18). As the methyl group rotates, the minimum energy path maps out a trajectory of the center of mass that encircles the would-be axis of rotation in the SPM model, that is, the crystallographically-defined, average rotation axis. Diagnosing this kind of dynamics is relatively straightforward; either the position of the center of mass of the rotor is minimized for each orientation ( $\phi$ ) of the rotor, or a molecular dynamics trajectory at relatively low temperature is determined, both revealing a tendency for non-uniaxial rotation. Molecular dynamics simulations also reveal the nature of the coupled movement: The carbon atom describes an ellipse of average radius 0.1 Å, whereas the methyl group rotates by 120° in the opposite sense. The center-of-mass rotation has a frequency three times greater than that of the rotor.

A quantitative determination of the multi-dimensional quantum dynamics requires the PES for the important degrees of freedom to be mapped out using the hybrid method. For lithium acetate, two coordinates  $(r, \alpha)$  define the centerof-mass motion and  $\phi$  the rotation of the methyl group. The calculated PES is fitted with the analytical form corresponding to a two-dimensional harmonic oscillator coupled to a one-dimensional rotor. Solving Schroedinger's equation for this potential term (Equation 7) gives the energy levels and eigenfunctions that allow a full determination of the spectral profile. Excellent agreement is obtained with spectroscopic measurements. Indeed, a new weak peak was predicted and observed at 500  $\mu$ eV. The calculated eigenfunctions can also be used to predict the nuclear density that is measured in a diffraction experiment. Indeed, the clearest confirmation of the dynamical model for lithium acetate comes from a single crystal diffraction experiment at 15 K because the rotation/precession motion gives rise to a square of nuclear density rather than a triangle! Figure 10 (see color insert) shows the excellent agreement between calculated and measured nuclear densities, the latter being extracted by maximum entropy methods (57).

One consequence of the motion of the center of mass is the increased moment of inertia *I*, or the reduced rotational constant, which leads to rotational excitations being observed at lower energy than expected from the SPM model and a given PES. This is the case of  $\gamma$ -picoline, calculated rotational potentials being too weak to give uniaxial-rotation excitations at ~500  $\mu$ eV. As in the case of lithium acetate, clear evidence of rotation/precession is obtained from single crystal diffraction measurements, a characteristic square being observed in Fourier difference maps (58). So although the multiplets of peaks in Figure 2 are mainly due to methyl-methyl coupling, their positions are a consequence of rotation/precession dynamics.

In fact, the first proposal for rotation/precession motion was made almost 10 years ago to account for the square form of the Fourier maps of nuclear density for the  $NH_3$  groups in metal hexammines (59). Shortly after the hexammine work appeared, a similar model was proposed to account for unexpected splittings of the vibrational modes of  $NH_3$  groups in the Hoffman clathrate, which undergo essentially free rotation (60). This model was also used to account for the apparent reduction in the rotational constant of the  $NH_3$  group. A classical MD simulation of the Hoffman clathrate reveals that this type of motion arises when a threefold rotor is constrained to occupy a site of fourfold, or near fourfold, symmetry (61). The square trajectory allows the hydrogen atoms to reduce their interaction with the environment by moving toward the corners during the rotation.

#### PERSPECTIVES

Over the past 30 years, nearly 1000 tunneling measurements have been accumulated (5). Until recently, fewer than 10 of the corresponding low-temperature (T < 77 K) structures were known, and currently the number is on the order of 30.

By applying a range of numerical methods for calculating SPM rotational potentials to these 30 systems, the sensitivity of the tunneling measurement has been used to calibrate the different computational approximations. A hybrid method, combining force field and ab initio techniques, has been shown to give an accurate description of the inter- and weak intramolecular interactions that hinder torsional motion. At the same time, the SPM model is shown to be generally valid. The methyl group is therefore a simple and sensitive probe of weak interactions. Although the range of applicability of quantum chemistry techniques will continue to increase, force field methods will always have a role in studying the biggest (biological) systems, and the need to parametrize force constants will remain. When it is the weak interactions that dominate the physical/chemical/biological behavior to be simulated (protein folding, general structure prediction), we propose that the force fields to be used should be simply tested against tunneling data within the SPM model. All of the necessary structural, spectroscopic, and computational information is contained in this article and the tunneling atlas (5).

Remaining in the field of quantum tunneling, our modeling with interatomic interactions has enabled insight to be gained into a number of anomalous systems where the SPM model is no longer appropriate. In the cases of durene,  $\gamma$ -picoline, and lithium acetate, alternative descriptions of spectroscopic data have been elaborated that have the advantage of being consistent with crystallographic and spectroscopic data and established descriptions of interatomic interactions.

Many of the tunneling measurements concern three-dimensional (tetrahedral) rotors like  $NH_4^+$  (62) and  $CH_4$  (63), and we have started to extend the methyl-rotor work to these systems. The ammonium compounds are challenging in that they are ionic and they often contain difficult atoms, from a computational point of view, like halogens and transition metals. However, although it would be useful to have a simple, microscopic probe of these atoms, the ammonium ion dynamics are not necessarily simple; there is no covalent bonding to a heavy molecule, and observations of non-uniaxial rotation have been reported. Methane is in itself an interesting quantum object, and from the point of view of probing interactions in the solid state, it can be loaded onto surfaces (64) and injected into cavities (65). The challenge, as before, is to render these probes quantitative.

This article has been concerned with rotational tunneling measurements, but in the tunneling atlas, a small number of measurements of coherent (66, 67) and incoherent (68) translational tunneling are reported. Tunneling proton dynamics in metal hydrides (66) is of practical importance in fuel cell applications, whereas tunneling along hydrogen bonds (67, 68) is of fundamental importance in the proton transfer reactions that are ubiquitous in physical and life sciences. In this latter case, proton tunneling mediates a chemical reaction (69), and proton displacements are smaller ( $\sim 0.5$  Å) than in rotational problems, but the potential barriers can be very strong ( $\sim 0.5$  eV) and soft molecular vibrations participate in the tunneling dynamics; a one-dimensional dynamical model is not sufficient (70). It is an ongoing challenge for experimentalists and computational chemists to elucidate and quantify the role of molecular vibrations in proton transfer. In this article, an evolution in computational techniques has been exposed, from pure force field (parametric) methods through hybrid methods to pure quantum chemistry (wavefunction) methods. A periodic DFT approach has been used successfully to simulate rotational dynamics in the presence of hydrogen bonds in peptide systems, that is by treating inter- and intramolecular interactions with electronic wavefunctions. These methods are currently being applied to the whole set of methyl tunneling systems with encouraging results (71,72). The advantage of a computationally efficient, periodic quantum chemistry method is that the crystal structure can easily be optimized and compared with the measured equilibrium structure, prior to determination of a rotational potential. In this way, potential energy calculations are required to reproduce both solid state structure and dynamics. Crystal structure optimization is difficult with a hybrid calculation, and experimental structures have always been used. Energy minimizations with force fields are unreliable and again experimental structures have been retained.

Analysis of molecular vibrations in the solid state has historically been based on an isolated-molecule approach, leading to problems with low-energy vibrations that have significant intermolecular contributions. Although semi-empirical cluster calculations have been used to introduce intermolecular interactions (73), DFT provides a better description of these interactions, and another current application of DFT is therefore normal mode analysis in the solid state, starting from an optimized crystal structure. Comparison with experiment is always an essential step, and as in tunnel spectra, neutron measurements of molecular vibrations have the advantage, over traditional optical methods, that the full spectral profile can be calculated (3).

Periodic DFT methods have the technical advantage over the hybrid method of allowing simple geometry optimization in the solid state and subsequent vibrational calculations, but they are limited by the volume of the supercell that can be treated ( $<2000 \text{ Å}^3$ ). Hartree-Fock methods in the hybrid method, however, are limited by the size of molecules to be treated (practically 30–40 atoms). Once the set of ab intio molecule calculations has been performed, complex PESs, which require thousands of calculations to be performed, can be mapped out, as in the coupling calculations presented here. Such work would have been prohibitively time consuming with DFT methods. The general availability of new computational methods, most recently periodic DFT codes, does not make existing methods redundant; as before, the scientist has to choose the most appropriate method for the problem.

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## APPENDIX

**TABLE 4** Compilation of crystallographic information of samples studied in this work

Sample	No. measured splittings	Structure <sup>a</sup> (Reference)
Octane	2h	2 K, N, P (72)
Dimethyl acetylene	1h	2 K, N, P (74)
Toluene	2h, 1d	2 K, N, P (37)
p-Xylene	1h	2 K, N, P (38)
Durene	2h	2 K, N, P (52)
Pentanoic acid	1h	2 K, N, P (72)
Acetophenone	1h	154 K, X, C (75)
Diacetyl	1h	173 K, X, C (76)
Aspirin	1h, 1d	2 K, N, P (77)
Acetic acid	1h	2 K, N, P (44)
Methyl acetate	2h	150 K, X, C (78)
Nickel acetate	1h	2 K, N, P (45)
Cobalt acetate	1h	2 K, N, P (45)
Lithium acetate	1h	2 K, N, P (56)
γ-Picoline	1h	20 K, N, C (58)
Dimethyl pyrazine	2h	20 K, N, C (79)
Nitromethane	1h, 1d	2 K, N, P (80)
Acetonitrile/hydroquinone	1h, 1d	20 K, N, C (81)
Acetamide	1h, 1d	20 K, N, C (82)
Paracetamol	1h	20 K, N, C (83)
Acetanilide	1h	20 K, N, C (84)
n-Methyl urea	1h	100 K, N, C (85)
Dimethyl sulfide	2h	2 K, N, P (86)
Bromomethane	1h	77 K, X, C (87)
Iodomethane	1h	2 K, N, P (72)
Tribromomesitylene	3h, 1d	20 K, N, C (88)
Triiodomesitylene	3h, 1d	20 K, N, C cr (88)

<sup>a</sup>Temperature given in degrees kelvin (K). N or X, neutron or X-ray measurement; P or C, powder or single-crystal measurement.

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**Figure 1** (*upper*) A simple rotational potential (V/2) cos3 $\phi$  and the corresponding, tunnelsplit energy levels in the lowest two librational levels (n = 0,1). (*lower*) The measurable quantities, the tunnel splitting and libration frequency, are shown as a function of the amplitude of the rotational potential V, for CH<sub>3</sub> (*solid curves*) and CD<sub>3</sub> (*broken curves*) rotors.



**Figure 2** Rotational tunnelling spectra of g-picoline measured with increasing resolution (FWHM): (a) 100  $\mu$ eV and (b) 10  $\mu$ eV on the time-of-flight spectrometer IN5 at the Institute Laue-Langevin (ILL) and (c) 2  $\mu$ eV on the backscattering spectrometer IN10b at the ILL. The tunnel peak at 500  $\mu$ eV in (a), originally measured by triple axis techniques, is resolved into a triplet of peaks using higher resolution (b). Further improvement in resolution reveals structure in each of these three peaks; the blue curve is the result of a calculation based on an ensemble of four coupled methyl groups (see "rotor-rotor coupling" section). The broader peaks between 1 and 2  $\mu$ eV in (a) are transitions to higher rotational levels.



**Figure 3** (a) The simple tunnel spectrum of the crystallographically unique methyl group in aspirin, measured on the backscattering spectrometer IN16 at the ILL (resolution 0.3  $\mu$ eV (FWHM)). The tunnel splitting is 1.22 ueV (b) Two crystallographically distinct methyl groups in dimethyl pyrazine give two tunnel peaks (20  $\mu$ eV and 29  $\mu$ eV), measured on the backscattering spectrometer IN10b at the ILL. Note that the energy scales in the two figures are not the same.

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Figure 4 The total PES and its three contributions, as a function of the orientation of the two methyl groups, in dimethyl pyrazine. Both methyl groups with one C-H bond in the plane of the molecule pointing towards the nitrogen atom (60, 0) is the stable orientation for an isolated molecule. A dominant VDW term gives the stable orientation for the solid state (0, 0) as measured.



**Figure 5** A comparison (log-log plot) of measured tunnel splittings with those calculated from known crystal structures using the UFF. The solid diagonal indicates perfect agreement, the dashed diagonals indicate levels of disagreement from one to four orders of magnitude. The molecules are not indicated as there is nothing systematic in the disagreement. With LJ 12-6 potentials, the calculated tunnel splittings are very sensitive to the methyl group geometry.



**Figure 6** Rotational potentials for the methyl group in acetic acid, showing VDW, Coulomb and torsion contributions, calculated at 278K (a) and 2K (b) using the UFF and at 2K using the hybrid method (c).



**Figure 7** A comparison (log-log plot) of measured tunnel splittings with those calculated from known crystal structures using the hybrid-ab initio method. Halogenated systems are not included since they are too electron-rich for the ab initio methods. Lithium acetate and  $\gamma$ -picoline are also omitted as the SPM model is clearly inappropriate. The central diagonal line indicates perfect agreement, the outer diagonals indicate agreement within a factor of three.



**Figure 9** Measured (e) and calculated librational spectra for coupled methyl groups in durene. (a) and (b) are calculated for a 2x2x2 supercell containing 16 methyl groups using the harmonic approximation and an "exact" solution of Schroedinger's equation respectively. The difference between (a) and (b) is a result of the anharmonicity of the rotational potentials. (c) and (d) are calculated in the harmonic approximation for a 20x20x20 supercell, a correction for anharmonicity being applied in (d).

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Figure 10 Contour plots of calculated (left) and measured (right) nuclear density for the methyl group in lithium acetate dihydrate. In both cases, four peaks of strong intensity are found at the corners of the square, and weaker peaks are observed at the middle of the upper and lower sides.



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