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Rotational Tunneling and Neutron Spectroscopy: A Compilation

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1. Rotational Tunneling

Rotational tunneling describes the phenomenon of the librational states of a molecule whose rotating atoms are indistinguishable, e.g., all protons, being multiplets. The splitting between the substates is called tunnel splitting.

In a Gedanken experiment one can prepare a molecule with a well-defined orientation. This is equivalent to having fixed labeled protons of the molecule (numbers 1 to N) on labeled sites (position of the numbers in the N-tuple characterizing the molecular orientation). In case of methyl groups ($N = 3$) one of the three possible pocket states may be

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written as |123⟩. This pocket state is not an equilibrium state. It develops according to the laws of quantum mechanics: it oscillates between equivalent orientations |123⟩ → |231⟩ → |312⟩ → etc. The oscillation frequency is called the *tunnel frequency* and depends on the overlap of the pocket states which is mainly determined by the strength of the rotational potential. Since such transitions from one pocket state (orientation) to another are equivalent to permutations of the rotor atoms, the name of "permutational tunneling" is proposed for the phenomenon.[1]

The size of a tunnel splitting is determined by the inertial properties of the molecule and the rotational potential. Large tunnel splittings are found for light molecules in weak potentials. The molecule with the largest rotational constant $B = \hbar^2/(2I)$, where I is the momentum of inertia, is hydrogen H_2. The rotors with the next largest rotational constants are the ammonium ion NH_4^+, ammonia NH_3, and the hydrocarbons CH_4 and $-CH_3$. The rotational constants are generally taken as material independent and calculated on the basis of average structural molecular parameters. This assumption might not be completely right but is certainly close to reality. The rotational constants are $B(CH_3) = B(CH_4) = 0.655$ meV, $B(NH_3) = B(NH_4^+) = 0.782$ meV and for comparison $B(H_2) = 7.3$ meV. For one-dimensional rotation B refers to rotation about the symmetry axis.

The mentioned molecules, ions, or radicals are present in a large number of interesting compounds and thus open a huge field for spectroscopy. Except for their deuterated analogues with half the respective rotational constants no heavier systems have been studied so far with neutrons.

1.1. Neutron Scattering from Tunneling Molecules

The phenomenon of rotational tunneling became accessible to neutron spectroscopy with the development of high-resolution neutron spectrometers in the 1970s. Three axes and time of flight spectrometers using cold neutrons reached an energy resolution of about 10 μeV while the backscattering technique, newly developed at that time, gave a resolution of about 0.1 μeV. The first publications on rotational tunneling using inelastic neutron scattering (INS) techniques appeared around 1975.[2,3] After an initial period, mainly devoted to establishing the basic features of neutron tunneling spectroscopy,[4] the field was reviewed in the monograph *Single particle rotations in molecular crystals* by W. Press in 1981.[5] In this first review neutron scattering functions of one- and three-dimensional rotors are presented. In the latter case the influence of site symmetry on the ground-state multiplicity and the transition matrix elements is shown. The few examples of rotational tunneling that were known at the time are described. The effects of temperature, pressure, isotopic replacement (H−D), and change of environment are discussed within the single particle model. The evolution of a typical tunneling spectrum with temperature is shown in Figure 1. Further development of neutron scattering[6,7] and data analysis[8] techniques allowed a wider range of applications.

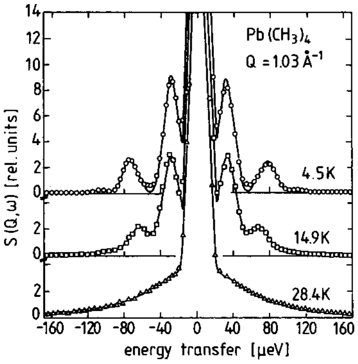

Figure 1. Temperature evolution of the tunneling spectrum of tetramethyllead.[248] The two tunneling transitions at low temperature belong to two crystallographically inequivalent methyl groups. At high temperature classical jump reorientation leads to quasielastic scattering.

The field developed quickly, both experimentally and theoretically. This progress is documented in proceedings of a sequence of biennial workshops of the field, the first one published in 1987,[9] the next ones recently.[10,11] These proceedings give a general overview of the application to more complex materials, new physical phenomena, and the connection of rotational potentials with the fundamental intermolecular interactions, and presents newly developed theoretical models.

Besides these proceedings, a number of short reviews have appeared. They concentrate on various special aspects or possible applications of rotational tunneling. One paper shows, for some special materials, how different experimental techniques (Raman, INS, NMR, IR) reveal different aspects of tunneling.[12] Others show the influence of disorder,[13,14] the evolution of the bond between the the hydrogen atoms in the hydrogen molecule when bound to different metal carbonyl complexes,[15] the application to adsorbed molecules[16] or matrix isolated guest molecules.[17] One article focuses on fundamental physical aspects.[18] A recent work summarizes the actually used theoretical models and relates them to published literature.[19,20] A very comprehensive review on potential calculations for tetrahedrons in surroundings of any symmetry appeared recently.[21] The subject is discussed under the broader aspect of the quantum character of many motions at low temperature,[22] including chemical dynamics,[23] hydrogen transfer,[24,25] and vibration−rotation tunneling spectroscopy of molecules and dimers.[26] This wide field is comprehensively reviewed in ref 27. The tunneling phenomenon in glasses and crystalline model systems is reviewed in ref 28. Many mathematical ideas outlined there are of similar importance for tunneling molecules.

What is missing so far and what could be helpful to newcomers in the field and experts is a critical compilation of results on all investigated materials. A first attempt in this direction is represented by an ILL Internal Report from 1987.[29] However the publication is not widely available and it lacks, after 10 years, most of the references. An easily accessible update version of this *Tunnelling Atlas* should describe the state of the art to scientists first entering the field, explaining the systems investigated so far and the specific questions asked. It could also offer a catalogue of materials suited for new research. It is intended in this work to present the most complete bibliography of papers on rotational tunneling studied by inelastic neutron scattering techniques.

1.2. Rotational Tunneling Studied by Other Methods

Rotational tunneling is accessible by various spectroscopic methods, as it influences a number of crystal properties. Qualitative and quantitative theories on the interaction of the various probes with a tunneling system have been developed.

One of the original techniques to detect tunnel splittings of librational levels of *gaseous* molecules was microwave spectroscopy.[30] It was soon realized that in the solid state, rotational tunneling influences the proton relaxation in nuclear magnetic resonance NMR-T_1[31−36] and this technique is widely used later on.[37,38] But only in the late 1960s were the features characteristic of quantum rotation observed and correctly explained.[34,39−41] The further methods actually used are NMR line-shape analysis,[42−45] the observation of motional narrowing of second moment,[43] NMR resonance techniques,[46−48] deuteron-NMR,[49−52] field cycling, zero-field NMR,[53] specific heat,[54,55] the observation of vibration−rotation combination lines in optical spectroscopy using the hole-burning technique,[56−61] and infrared spectroscopy.[62−64] Among these techniques, spectroscopic and resonance experiments have the advantage of yielding directly transition energies. Such methods are complementary and in certain respects advantageous to neutron scattering. For example, NMR covers the range of stronger potentials and has a high sensitivity for low concentration impurities. For slow tunneling reorientation, hole-burning techniques enable the most direct measurement of spin conversion.[65] No method yields such direct, model independent insight into the system as INS, however. Since the neutron interacts weakly with atoms, the results can be calculated in the first Born approximation and, as mentioned above, intensities can be interpreted quantitatively. This allows, for example, structural information to be extracted as site multiplicities, which are not that easily accessible by other methods. The extensive literature on tunneling studies using methods different from inelastic neutron spectroscopy is included in the references only insofar as the work is related to materials studied by neutrons and their obvious fundamental importance.

2. Rotational Tunneling: Basic Properties

The topic presented here contains two subproblems. The first consists of finding the eigenstates of a quantum rotor in a rotational potential of a certain symmetry. This problem is a rather old one and there exist a number of good specialized textbooks (see, for example, ref 66). The second problem deals with the interaction of a neutron with such tunneling molecules. This includes a calculation of the scattered intensities. A calculation of the transition matrix elements requires a knowledge of the correctly symmetrized nuclear spin wave functions of the molecule since the relevant interaction potential between neutron and molecule, the Fermi pseudopotential, is spin dependent.

2.1. Rotational Energy Levels

The quantized rotational energy levels of a molecule, which has a rotational constant B, are normally calculated under the assumption that the environment can be represented by a potential $V(\omega)$. This mean field approach is called the Single Particle Model. The rotor levels are then given by the solutions E_i of the stationary Schrödinger equation

$$H\Phi_i = E_i\Phi_i \tag{1}$$

with the Hamiltonian

$$H = B\nabla^2 + V(\omega) \tag{2}$$

H and the spatial wave function Φ_i depend on all angular variables ω. ∇ is the gradient operator. One recognizes that for a given dimensionality and symmetry only the the ratio $V(\omega)/B$ determines the eigenvalues if these are taken in units of the rotational constant also. It is because eq 1 only contains space variables that the knowledge of the molecular wave function in space is sufficient to calculate the rotor levels. The respective mathematics were first developed for the cases of highly symmetric molecules in a high symmetry environment. Calculations go back into the 1950s.[67] The qualitative effects of varying the molecular and site symmetry were established and corresponding phenomenological rotational potentials parameterized. However, for some well-known materials potentials could be derived from fundamental interactions. The most general and most comprehensive textbooks are the volumes *Molecular Spectra and Molecular Structure* of Herzberg.[68] A more specialized monograph *Molecular Rotation and Inversion* was published by Lister, MacDonald, and Owen.[66] This valuable book presents, following a clear general discussion of the topic, the quantum mechanical tools required for doing the necessary calculations in a very clear way. A selection of further useful reviews is given by refs 69−71.

Depending on the dimensionality of the problem the underlying mathematics shows different levels of complexity. The simplest case is represented by the one-dimensional 3-fold rotor.[5,72] Here the rotational potential can be described by a Fourier expansion into a series of trigonometric functions

$$V(\varphi) = \sum_{i=1}^{\infty} \frac{V_{3i}}{2}(1 - \cos(3i\varphi + \alpha_i)) \tag{3}$$

This series is usually truncated after the second term, yielding

$$V(\varphi) = \left\{\frac{V_3}{2}(1 - \cos 3\varphi) + \frac{V_6}{2}(1 - \cos(6\varphi + \alpha))\right\} \tag{4}$$

In a few cases potentials of higher symmetry are used.[73,74]

A treatment of three-dimensional potentials involves the use of the appropriate symmetry-adapted functions and the tools of group theory to determine the nonzero expansion coefficients. Accordingly the literature on potentials of three-dimensional rotors is much more extensive. More complex models are more conveniently tested for the mathematically simpler case of one-dimensional rotors.

Theories going beyond the single particle approach include various forms of coupling (sections 3.5 and 3.6) and had to extend existing or to develop new mathematical formalisms.[75−78] The theoretical results are typically not as complete as in the case of the single particle model.

2.2. Tunneling Transition Matrix Elements for Neutrons

An essential advantage of neutron spectroscopy over other methods is the ability to calculate quantitatively the intensities of all spectral features. The weak interaction of the neutron with matter allows the scattering process to be treated in the first Born approximation. A neutron with spin **i** interacts with, say, a proton labeled γ carrying the spin $\mathbf{s}_\gamma$ via the Fermi pseudopotential W_γ. The molecule may consist of Γ protons. Then the interaction of the neutron with the whole molecule is

$$W = \sum_{\gamma=1}^{\Gamma} W_\gamma \tag{5}$$

and

$$W_\gamma = a_{\mathrm{coh}} + \left(\frac{2a_{\mathrm{inc}}}{\sqrt{I(I+1)}}\right)\mathbf{s}_\gamma\cdot\mathbf{i}\cdot\delta(\mathbf{r}-\mathbf{r}_\gamma) \tag{6}$$

Here I is the total spin of the molecule in its state, where $\mathbf{r}_\gamma$ and $\mathbf{s}_\gamma$ are the position and the spin operators of the γth proton, a_{coh} and a_{inc} are the coherent and the incoherent neutron scattering cross sections of the proton. Since the protons of the molecule are linked by the wave function they scatter coherently with the spin-dependent part of the cross section a_{inc}.[79]

The intensities of transitions between molecular levels α and α' are determined by the transition matrix elements

$$A_{\alpha\mu\alpha'\mu'} = \langle \mu'\Psi_{\alpha'}|W|\mu\Psi_\alpha\rangle \tag{7}$$

Since the proton spin does not interact with the space coordinates the total wave function $|\Psi_\alpha\rangle$ of the molecule is the product of the spatial, Φ, and spin, χ, wave functions: $|\Psi_\alpha\rangle = |\Phi_\alpha\rangle\,|\chi_\alpha\rangle$. $|\mu\rangle$ is the spin operator of the neutron. In the case of plane triangles of protons (NH_3, CH_3) and tetrahedra (NH_4^+, CH_4) a rotation corresponds to an even permutation of protons. Thus, independent of whether we have fermions (H) or bosons (D) in the molecule, the double application of the Pauli principle requires the total wave function to be symmetric. Now subsequent rotational levels are connected with characteristic symmetries of the spatial wave functions. To make the total wave function symmetric, the spin functions have to show the same symmetry as the spatial wave functions. This leads to the separation into spin symmetry species.[80,81] All protons of a molecule are correlated through the spin functions. For δ -localized protons, the space wave functions contribute a sum of phase factors in the above expression which are weighted by some constants determined by the spin wave functions. Detailed calculations of transition matrix elements can be found in the literature.[5,82−86] The Q-dependent intensities are called inelastic and elastic incoherent structure factors. While the tunnel splittings change very significantly with potential strength, the transition matrix elements are only weakly affected by the potential. This was shown, for example, for tetrahedral molecules.[87] On the basis of this knowledge, transition matrix elements are generally calculated for δ -localised protons.

For the models including coupling tunneling, matrix elements are not or not accurately calculated.

In a time-dependent description the evolution of the wave-packages characterizes the tunneling process.[88,89]

3. Information To Be Extracted from Tunneling Spectra Measured with Neutrons

In the following sections, ideas and formulae are presented for one-dimensional 3-fold rotors for reasons of simplicity. The corresponding more complex results for three-dimensional tetrahedral rotors can be found in the cited literature.

3.1. Structural Information

The low temperature scattering function of a single CH_3 group in a 3-fold rotational potential and averaged over all orientations of the methyl group is[5]

$$S(Q,\omega) = (^5/_3 + {}^4/_3 j_0(Qd))\delta(\omega) + (^2/_3 - {}^2/_3 j_0(Qd))\{\delta(\omega+\omega_t) + \delta(\omega - \omega t)\} \tag{8}$$

and contains just one elastic and two inelastic lines, the latter at energy loss and energy gain $\pm\hbar\omega_t$. The spherical Bessel function j_0 appears as a result of orientational averaging. Equation 8 is derived for δ-localized protons at the corners of an equilateral triangle of edge length d. The prefactors depend on the momentum transfer Q and are called the incoherent structure factors. They reflect the geometry of the rotor via the proton-proton distance d. The generalization to extended wave functions is discussed below.

Many materials contain crystallographically inequivalent rotors. A tunneling spectrum of such a sample often shows a number of transitions. In the single particle model, found to be widely applicable, the respective scattering function is a superposition of single particle spectra weighted with the occurrence probabilities p_ν of the respective species

$$S(Q,\omega) = \sum_{\nu=1}^{N} p_\nu S_\nu(Q,\omega) \tag{9}$$

Thus the number of tunneling lines—if resolved—is equal to the number of inequivalent methyl groups and, since the structure factors are identical, the intensity ratios of the inelastic lines with respect to the elastic line are directly determined by their occurrence probabilities. Finally, these probabilities are characteristic of the space group of the molecular

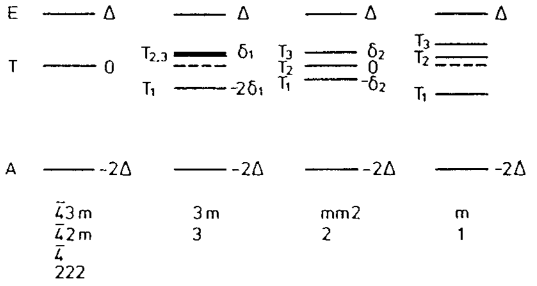

Figure 2. Ground-state tunnel splitting of a tetrahedral spherical top at sites of various symmetries (from ref 5).

crystal. If more than one methyl group is attached to a molecule, and in the case of three-dimensional rotors, where the tunneling sublevel structure is symmetry dependent, local site symmetries can be guessed. This latter aspect is similar to the situation in other spectroscopic methods (e.g., Raman). Single-crystal studies were performed to assign tunneling excitations to crystallographically identified methyl groups.[90]

A scattering function analogous of eq 8 is derived for a 3-fold one-dimensional rotor in a 6-fold potential.[84] (In this reference the matrix elements for the transitions 0 → 1 and 0 → 2 are interchanged.) For three-dimensional rotors the basic results are shown in the first monograph on the subject.[5] Due to the larger number of atoms and degrees of freedom, the tunneling groundstate contains five sublevels which, at high environmental symmetry, are partially degenerate. The qualitative changes of the ground state level scheme with site symmetry are shown in Figure 2.

3.2. Rotational Potentials

3.2.1. Tunnel Splittings and Rotational Potential

The splitting of the librational ground state is related to the strength and shape of the rotational potential. The overlap between pocket states decreases almost exponentially with the increase of the potential strength. A formula for three-dimensional rotors that is asymptotically correct for strong potentials of strength $|V|$ is given by the expression[91]

$$\hbar\omega_t = \beta \exp\left(-\alpha\sqrt{\frac{|V|}{B}}\right) \tag{10}$$

β is close to twice the rotational constant B and α is close to 1. Again, only the scaled potential appears. A very similar expression was derived in a WKB approximation for one-dimensional rotors, but contains an additional prefactor $|V|^{3/4}$.[67] According to this exponential variation with potential strength, the tunnel splitting changes much faster with changing V than any other molecular excitation. This makes tunneling spectroscopy uniquely sensitive for weak changes in molecular crystals.

In the case of methyl groups, the leading term in the rotational potential V is generally found to be the $\cos(3\varphi)$ term (cf. eq 3). For this reason there exist systematic dependences between the tunnel splitting and other characteristic quantities of the potential. Such relations are derived on the basis of results from a large number of different materials for the barrier height V_3 or the activation energy.[92] Similarly the classical correlation time and thus the position of the minimum in a NMR-T1 experiment at a given Larmor frequency changes systematically with the barrier height.[93] These correlations can then be used to estimate the tunnel splitting of an unknown material from the mentioned quantities.

In pure V_6 potentials, the librational ground state represents a quartet where the separation of the sublevels approaches a ratio 1:2:1 with increasing strength of V_6.

3.2.2. Structure Factors and Wave Functions

The rotational potential is directly related to the molecular wave functions via the Schrödinger equation eq 1. At temperatures where only the ground state is populated, the proton density is simply

$$\rho_0 = \Phi_0\Phi_0^* \tag{11}$$

At a higher temperature T, the density distribution becomes a thermal average over all populated levels with eigenenergies E_i

$$\rho(T) = \frac{\sum \exp\left(-\frac{E_i}{kT}\right)\rho_i}{\sum \exp\left(-\frac{E_i}{kT}\right)} \tag{12}$$

From the density distribution observed in a diffraction experiment, one can derive a mean-squared librational displacement $\langle u^2\rangle_{\text{lib}}$ which, according to eq 11, is determined by the rotational wave function. For reasons of feasibility the structure factors were calculated assuming δ-localized protons.[82] In a semiclassical treatment, the effect of the broadened proton distribution can be taken into account by extending eq 8 by a Debye–Waller factor[94]

$$S'(Q,\omega) = \exp(-\overline{\langle u^2\rangle}_{\text{lib}}Q^2)S(Q,\omega) \tag{13}$$

In the case of methyl groups $\overline{\langle u^2\rangle}_{\text{lib}} = {}^1/_3\langle u^2\rangle_{\text{lib}}$. The factor ${}^1/_3$ appears because the methyl libration has only one degree of freedom. For large amplitude librations the inelastic structure factor at large momentum transfer Q is strongly reduced compared to the result obtained for δ-localized protons (eq 8). This effect can be used to directly access the molecular wave function. There are two problems. At first, the librational part $\langle u^2\rangle_{\text{lib}}$ has to be separated from the translational part $\langle u^2\rangle_{\text{ph}}$ of the molecular motion due to acoustic phonons. Secondly, the rather large Q values ($Q > 1.5$ Å^{-1}) needed to determine the differences to δ-localized protons had been accessible only by the thermal backscattering instrument IN13 of ILL, which is no longer operational. For this reason, there exist only very few such experiments.

Structure factors different from those of the fundamental tunneling transition as shown in eq 8 determine the Q dependence of transitions to higher excited rotational states. An exact calculation of structure factors is possible for free rotors. Their expansion for small momentum transfer Q leads to a characteristic increase of the inelastic intensity with a power $Q^{2(|m-n|+1)}$ for a transition from the mth to the $(m + n)$-th rotor level.[95] These dependencies are also valid in the case of three-dimensional rotors in weak potentials of various symmetries.[96−99] The Q dependence can be exploited to identify transitions to higher excited rotational states.

3.2.3. Isotope Effects

Connected with the different types of protons in an investigated material, various types of isotope effects can be distinguished. At first there is the special methyl group under investigation. Its deuteration leads to the *internal* isotope effect. The rotational potential relevant to the calculated eigenvalues is the absolute potential scaled by the rotational constant of the rotor (cf. for example eq 10). Deuteration of a protonated molecule doubles the relevant scaled rotational potential. For a typical rotational potential of peak-to-peak amplitude VS = 40 meV, the tunnel splitting of the deuterated species is reduced by about a factor 20 compared to the protonated analogue. Compared to this dramatic change, the librational modes change in harmonic approximation just by $\sqrt{2}$.

If the molecule under investigation remains protonated but only its environment is deuterated, one speaks of the *external* isotope effect. The stronger localization of deuterons may slightly modify the interactions, such as the multipole moments, or the atomic positions might change a little. In most cases this external isotope effect is very weak and of the order of a few percent.

A way of increasing the rotational potential *continuously* consists of applying hydrostatic pressure. A typical pressure which doubles the rotational potentials is 12 kbar. This is about the maximal pressure actually attainable at He temperatures with standard devices.[100] Since deuteration of the rotor also increases (doubles) the scaled potential, it is in this respect equivalent to applying a high pressure to a sample.

Partial deuteration modifies the molecular symmetry. Except for almost free rotors, this symmetry reduction suppresses the tunneling effect completely in the one-dimensional case. Examples of such studies are cited in refs 101−108. Early publications only calculated the levels, but neglected to consider transition probabilities.[109]

In the case of three-dimensional rotors, symmetry reduction with different partial deuteration leads to a wider variety of isotope effects.[110,111] For different isotopomers in the same environment the sublevel structure of the librational states is changed characteristically.[5,68]

3.2.4. Calculating Potentials from Intermolecular Interactions

The rotational potentials are the result of intramolecular interactions between the atoms of the rotor, usually protons, and the atoms of its environment. These interactions are, for example, parametrized as atom−atom potentials and usually contain a repulsive and a van der Waals term. Typical forms are Born−Meyer or Lennard-Jones potentials. In addition a Coulomb interaction between charges is taken into account. In this model two atoms of type κ and λ with charges e_κ and e_λ separated by a distance r_{ij} are exposed to a potential

$$V\kappa\lambda(r_{ij}) = \alpha_{\kappa\lambda}\exp(\beta_{\kappa\lambda}r_{ij}) - \frac{\gamma_{\kappa\lambda}}{r_{ij}^6} + \frac{e_\kappa e_\lambda}{r_{ij}} \qquad (14)$$

A convincing description of the rotational potential is obtained when it can be derived from such phenomenological pair interactions parametrized by the factors $\alpha_{\kappa\lambda}$, $\beta_{\kappa\lambda}$, and $\gamma_{\kappa\lambda}$. In the framework of atom−atom potentials the pair potentials are just summed up. If the molecule of interest is rotated, the intermolecular distances become dependent on its rotational angle ω and the calculated molecular rotational potential is

$$V(\omega) = \sum_{i=1}^{\Gamma}\sum_{j=1}^{N} V_{\kappa\lambda}(r_{ij}(\omega)) \qquad (15)$$

where the first sum runs over the protons of the molecule and the second over all neighboring atoms within a chosen distance. If the calculated rotational potential does not agree with the experimentally determined one, the existing pair potential parameters can be refined on the basis of the new information, the tunnel splitting. Since the existing parameters are already optimized to describe certain experimental results, this modification has to be performed under the restriction that the quality of the description of these other quantities, such as the crystal structure or the phonon spectra, are maintained. To perform these calculations the intermolecular distances, i.e., the low-temperature crystal structures, have to be accurately known. There are only a few, but in recent times, an increasing number of attempts to exploit tunneling spectra in this way.[60,95,112−119] This approach toward an improvement of intermolecular interaction potentials might be extended beyond single-particle rotation and include cases of more complex tunneling processes as rotation−translation−coupling[26] (section 3.6).

With the availability of commercial molecular simulation program packages as, for example, CERIUS[2], such calculations, including eventually an equilibration of the crystal structure, become feasible for a wider community. A good recent example which includes structural and spectroscopic data, the latter ranging from microelectronvoltd to almost 1 eV, is presented in ref 60.

A more experimental route toward a determination of the part of the pair potentials most relevant for the tunnel splitting consists of determining its dependence on changes of external pressure δp. Pressure usually reduces intermolecular distances r. In the simplest case of an isotropic solid the relative change $\delta r/r$ can be described by a isothermal compressibility κ by

$$\frac{\delta r}{r} = -\ \frac{1}{3}\kappa\ \delta p \qquad (16)$$

Thus, the rotational potential increases with increasing pressure and the overlap of the wave function and the related tunnel splitting decreases. Combining the above equation with the theory of rotational tunneling yields[120]

$$\delta\hbar\omega_t = Cn^* \frac{\delta r}{r} \tag{17}$$

Here n^* is the power connected to the r dependence of that part of the atom–atom potential which mainly determines the tunnel splitting. This is found to be the repulsive interaction. Changes in $\delta\hbar\omega_t$ by up to a factor of 3 are observed when applying pressures up to 5 kbars. Examples are presented in refs 100 and 121–125.

3.3. Coupling to Phonons: The Temperature Dependence

One of the most fascinating aspects of rotational tunneling is its temperature dependence. By coupling to lattice phonons the low-temperature coherent quantum rotation (tunneling) transforms into classical stochastic jump reorientation (hopping). Thus, with increasing temperature the ground-state tunneling transition shifts toward the elastic line and broadens. At the same time a quasielastic line emerges from the elastic line which shows the same intensity as the tunneling peaks. The broadening of tunneling lines is due to fluctuations of A and E states with respect to each other at finite temperature while the new quasielastic line is due to fluctuations of E_a and E_b excited tunneling states which in average are degenerate. All nonelastic intensity merges until the spectrum looks quasielastic (classical). But even there, quantum effects may be observable.[126,127] In the case of methyl groups, the problem contains one rotational degree of freedom only and is one of the most clearly defined phenomena of the Bohr correspondence principle.

A quantitative theory applicable to a wide range of temperatures and strengths of coupling and for a general phonon spectrum is ambitious. Many different attempts have been made to describe the shift and broadening of the tunneling levels with increasing temperature. All theories assume that a coupling to phonons is responsible for the effects. Coherent mixtures of the lowest librational states were considered to represent the relevant effect.[128,129] The influence of coupling the rotor to an internal molecular vibration was elaborated.[130] The model of a tunneling rotor experiencing stochastic torques with increasing temperature was developed.[131,132] All these theories did not produce a quasielastic component. The ultimately accepted model is based on a linear coupling of the rotor to individual phonons[133–135] or a Debye spectrum of phonons.[134,136] The possibility of lifting degeneracies of states by coupling is controversely discussed.[137,138]

Some basic features can be qualitatively understood using a simple model Hamiltonian consisting of a pure rotational, a pure phonon, and a coupling or interaction term

$$H = H^{\mathrm{Rot}} + H^{\mathrm{Phon}} + H^{\mathrm{Int}} \tag{18}$$

with

$$\begin{aligned} H^{\mathrm{Rot}} &= -B\frac{\partial^2}{\partial\varphi^2} + V_3\cos(3\varphi) \\ H^{\mathrm{Phon}} &= \sum_{i=1}^{2}\left(\frac{p_i^{\,2}}{2m_i} + \frac{m_i}{2}\omega_i^{\,2}x_i^{\,2}\right) \\ H^{\mathrm{Int}} &= \sqrt{\frac{2m_1\omega_1}{\hbar}}g^{\mathrm{c}}x_1\cos(3\varphi) + \sqrt{\frac{2m_2\omega_2}{\hbar}}g^{\mathrm{s}}x_2\sin(3\varphi) \end{aligned} \tag{19}$$

Here the rotor term is a special form of eq 2. The phonon spectrum is represented by two harmonic oscillators (dispersionless Einstein modes) of mass m_i, space coordinate x_i, momentum p_i and frequency ω_i. The interaction Hamiltonian H^{Int} couples the translation x_1, usually related with the low energy mode, symmetrically to the rotational angle φ by a cosine term. The coupling strength is represented by the parameter g^c of dimension millielectronvolts. It is called the *breathing* term because it modulates the strength of the rotational potential. For analogous reasons the second term related to mode 2, usually the high-energy mode, is called the *shaking* term, since it modulates the orientation of the rotational potential in the crystal lattice. The coupling strength in this case is g^s. The two terms cause shifts of the tunnel splitting in opposite directions. The breathing term increases the tunnel splitting, the shaking term reduces it[136]

$$\Delta\hbar\omega_t(T) = \hbar\omega_0\left[S1\,\exp\left(-\frac{E_{S1}}{kT}\right) - S_2\exp\left(-\frac{E_{S2}}{kT}\right)\right] \tag{20}$$

Since the activation energies obey $E_{S1} < E_{S2}$ the reduction of the tunnel splitting dominates at high temperature as observed. Increasing temperature simultaneously causes a broadening of the tunneling line

$$\Gamma_t(T) = \Gamma_0\exp\left(-\frac{E_\Gamma}{kT}\right) \tag{21}$$

Shift and broadening of the tunneling line are not related in a simple manner, as is the case for a damped harmonic oscillator. There are cases with large shifts and almost no broadening, and vice versa, as well as intermediate cases. The meaning of energies E_{Si} and E_Γ follows from a more rigorous treatment discussed next.

The most advanced theory treats the problem using second-order perturbation theory.[139] It includes the complete phonon spectrum of a molecular solid. This theory explains the line broadening by resonant coupling to phonons of energy E_{01}, the first librational energy of an isolated rotor in a potential, thus yielding $E_\Gamma = E_{01}$ in eq 21, in agreement with many experiments, while $E_{S2} \leq E_{01}$ (eq 20) due to a coupling to *all* phonons with energies below E_{01}. Equations 20 and 21 describe all observations to methyl groups.

Mostly the shift toward larger tunnel splittings (first term of eq 20) is not observed and the tunnel splitting decreases continuously with temperature while the transition broadens by Γ_t.

Equation 21 offers the possibility of relating the librational energy $E_{01} \approx E_\Gamma$ of a given rotor to its tunnel frequency in the case of systems containing inequivalent rotors. Only such an unambiguous assignment of two rotational excitations of the same rotor allows the derivation of the shape of a rotational potential by determining a next higher Fourier components. Another possibility is based on studies of the Q-vector dependence of tunneling and librational modes in a single crystal.[90] This method also allows the excitation to be attributed to a crystallographically identified rotor.

The aforementioned theories yield reliable results only for weak coupling and temperatures, where the shift and broadening of the tunneling line is small compared to the tunnel splitting itself. Advanced path integral methods were developed which do not have this shortcoming.[140] An appropriately modeled harmonic oscillator system was invented[141,142] that does not contain all the details of a real system, but allows an analytical treatment of the problem with answers valid for any strength of coupling the rotor to phonons. The results confirm the equations derived by second-order perturbation theory.[139] Refined models were developed that explain such details as the different broadening of the inelastic and quasielastic lines.[143−145] Numerical solutions of the time dependent Schrödinger equation[146−148] confirm the analytical results. The same problem, coupling a quantum degree of freedom to a classical one, is also treated for a general two level system.[149]

Recently, using the mathematical formalism developed for describing translational tunneling, a new description of damping a tunneling rotor via librational transitions was obtained.[150,151]

Finally, a gauge potential theory different from concepts of classical solid-state physics was proposed.[152−155] The gauge potential contains *a priori* the reduced symmetry of the combined rotor-phonon system, which in the perturbational access to the problem is introduced *a posteriori*. By requiring a quantum theory consistent with relativity,[156,157] this theory comes to the conclusion that such fundamental concepts as the rotational quantization are no longer valid and the Pauli principle loses its straightforward interpretation.[156−162] The early states of this theory are reviewed in ref 18.

3.4. Coupling to Phonons: Spin Conversion

The spectroscopy of tunneling systems also gives direct access to the phenomenon of spin conversion. The time evolution of a quenched tunneling rotor system into thermal equilibrium is slowed down since the transition from an excited to the ground tunnel state involves a spin flip. In systems with magnetic or paramagnetic constituents this process is fast, but it is very slow (days) in other molecular crystals. In such systems this evolution can be studied in real time by INS. Global results can be obtained using a neutron transmission method which exploits the fact that, for sufficiently long neutron wavelengths where the molecule is "seen" as an entity, the total cross section of a molecule depends on the total spin I in the respective state.[163] The spin is maximum in the ground state. Thus, transmission of the sample decreases after a jump to low temperature with approaching thermal equilibrium. The most comprehensive data in this field were obtained by this technique.[164,165] However, in systems with complex tunnel spectra (three-dimensional rotors, inequivalent molecules) detailed results can only be obtained if the population of every individual level is obtained from the spectroscopic observation of the intensities of transitions starting from this level. See for example ref 110.

After the transition into the ground state the protons within one molecule scatter coherently. This leads to new elastic intensity which can be observed in a neutron diffraction experiment. Its broad angular distribution is determined by the form factor of the molecule, which is identical to the elastic incoherent structure factor (EISF) of the molecule in a quasielastic scattering experiment. By this route the evolution of the elastic "background" with time offers a way of studying spin conversion.[166]

For methyl rotors, theories were developed explaining the spin conversion of the protonated species on the basis of intramolecular dipole−dipole interaction[167,168] and of deuterated molecules on the basis of the intramolecular quadrupole−quadrupole interaction[50,51,169−171] and involving spin diffusion.[40,172,173] With decreasing temperature the spin conversion rate follows different T dependences due to different processes involved in the conversion process. At zero temperature the direct emission of a phonon of energy $\hbar\omega_t$ yields a constant conversion rate. It increases at low temperatures linearly with T. Thereafter two-phonon scattering (Raman process) leads to an increase of the conversion rate proportional to T^7. At the highest temperature ($T \geq 10$ K), the one-phonon scattering and simultaneous excitation of the rotor into its excited torsional state (libron−phonon process) yields an Arrhenius dependence of the conversion rate.[168] Coupling via a shaking term cannot lead to complete conversion.[167] Experiments have revealed regimes with the proposed different T dependences.[59,85,174,175]

For methane a similar theory was established back in the 1970s.[176,177]

To produce thermal nonequilibrium at the beginning of the experiment, temperatures significantly lower than the tunnel splitting under study must be achieved. This limits the number of materials accessible to INS techniques. NMR methods allow a dynamic inversion of the population of tunnel levels and thus a study of conversion at any temperature and for small tunnel splittings.[178]

In addition to neutron scattering, optical holeburning spectroscopy represents, in certain cases,[59,179] a very sensitive method to study spin conversion.

3.5. Directly Coupled Molecules

Direct coupling of rotors leads—in a few cases—to new features not described by the single particle model. For example, methane is contained in a rare gas matrix as a statistically distributed substitutional defect. Effects of coupling appear with increasing concentration, when the presence of dimers[180−185] and larger clusters exceeds that of isolated molecules.[186] In other cases the crystal may contain dimers[187] or higher multimers as structural units. The problem of two and three coupled tunnel rotors was treated long before neutron scattering investigations entered the field.[188−190] In the case of one-dimensional 3-fold rotors, the general phenomena are derived using a model Hamiltonian consisting of two single-particle Hamiltonians analogous of eq 8 and a coupling potential W of strength W_3 which depends only on the relative orientation of the two tops

$$H(\varphi_1,\varphi_2) = -B\frac{\partial^2}{\partial\varphi_1^{\,2}} + V_3\cos(3\varphi_1) - B\frac{\partial^2}{\partial\varphi_2^{\,2}} + V_3\cos(3\varphi_2) + W_3\cos(3(\varphi_1-\varphi_2)) \quad (22)$$

As a result of coupling, the tunneling sublevels of a librational state get labeled with two quantum numbers and contain twice the number of sublevels as the uncoupled system. This new complexity leads to three tunnel bands instead of one. Depending on the sign of W_3 the coupling can apparently reduce or enhance the single particle potential. The validity of various theoretical approaches is studied.[191,192] Again, the respective transition matrix elements of the neutron scattering function can be calculated[193] which enables quantitative understanding of the spectra.

According to the outlined procedure, the theory of coupled methyl groups has been extended to three units[194] and larger clusters.[195] Only recently has a sufficiently efficient and exact algorithm been developed which has allowed the number of coupled rotors to be extended to 10 units.[76,196] The deviation of results of molecular field approximation from exact solutions[197] is studied and an analytically solvable harmonic oscillator model is developed.[198] These calculations show that the effects of coupling which appeared for dimers are continuously diminishing with increasing the number of coupled rotors. Already for four coupled methyl groups, the calculated tunnel spectrum looks almost like a single particle spectrum. The tunnel splitting, however, is rescaled to smaller values due to the intermolecular interaction. Thus one might be misled when extracting potential parameters according to the Single Particle Model from data ressembling single particle spectra.

The temperature dependence of the rotational tunneling spectrum of coupled pairs is discussed in ref 199. The main effect here due to coupling is that the first excited librational level is split into a doublet. Both energies enter into the equations which determine the shift and broadening.

A generalization to the case of coupled inequivalent rotors would follow the formalisms applied in molecular spectroscopy, e.g., see ref 200.

For the special symmetry of four methyl groups attached to a central metal(IV) ion, in the case of tetramethyltin, the topology of coupled tunneling rotation differs from that of a linear chain. All rotors are equivalent and interact with each other.[201,202]

There exists a different approach to the problem of many coupled tunneling rotors. In analogy to phonons—the excitations of atoms coupled by springs in a crystal—a rotationally coupled infinite chain of rotors will develop quantized rotational excitations. A possible Hamiltonian of such a linear chain of quantum rotors is[75]

$$H = \sum_j \left(-B_j\frac{\partial^2}{\partial\varphi_j^{\,2}} + \frac{V_3}{2}(1-\cos(3\varphi_j)) + \frac{V_C}{2}(1-\cos(3(\varphi_{j+1}-\varphi_j))) \right) \quad (23)$$

Here V_3 is a local single-particle potential identical for all rotors and V_C is the interaction potential between neighboring rotors which, again, depends on the relative orientation of the neighbors. This quantum-mechanical Hamiltonian with an infinite number of degrees of freedom and anharmonic potentials cannot be diagonalized either analytically or numerically. Thus the interaction potential is expanded harmonically for small angular differences $\varphi_{j+1} - \varphi_j$. This step violates the symmetry of the problem. However, after this linearization the Hamiltonian is equivalent to that of the sine-Gordon potential, a problem which has been intensively studied. The excitations of the quantum sine-Gordon equation are in-phase and out-of-phase tunneling transitions and quantized traveling states of the breather mode. The rotational excitations of various compounds have been interpreted with this model[203−205] and found to be consistent with theoretical expectations. Unfortunately structure factors are not yet derived for the different transitions. Further evolution of the theory was able to describe spectra of partially deuterated samples as excitations of a breather in a box.[75] Despite these results we are left with the problem that the results of the sine-Gordon model contradict the solution of the nonlinearized problem for four and more coupled groups.[76,196,198]

By taking into account a dynamical coupling between just two rotors in the form of the mixed derivative term in the following Hamiltonian

$$H = -B\frac{\partial^2}{\partial\varphi_1^{\,2}} - B\frac{\partial^2}{\partial\varphi_2^{\,2}} - B\frac{\partial^2}{\partial\varphi_1\partial\varphi_2} + V_3(\cos(3\varphi_1) + \cos(3\varphi_2)) \quad (24)$$

some of the spectra described by the sine-Gordon model have found another possible interpretation.[206]

3.6. Coupling to Their Own Center of Mass Rotation: Tumbling Tunnel Rotors

A strange observation in the diffraction patterrns of $Ni(ND_3)_6I_2$[207] has initiated the development of a model of coupled rotation which might assume general importance. Very surprisingly the deuteron density of the ND_3 is represented by a square, characteristic of the environmental symmetry of the ammonia in this material. This was finally interpreted as a correlated reverse rotation of the offcentered whole molecule, rotation angle α, and the ammonia, rotation angle φ, measured with respect to the vector $\vec{R}$ connecting the center of symmetry with the molecular center of mass (com), such, that the ammonia rotates by $\Delta\varphi = 2\pi$ when the center of mass has moved by $\Delta\alpha = -{}^3/_4(2\pi)$ only. Thus at any time

$$\alpha = -{}^3/_4\varphi \tag{25}$$

holds. This motion can be visualized as an evolution of the ammonia triangle on the square of the surrounding potential surface in such a way that subsequent corners of the triangle (rotor) and the square (environment) successively coincide. If the com motion is restricted to a circle the respective potential surface is

$$V(\varphi,\alpha) = A_1 \cos(3\varphi + 4\alpha) + A_2 \cos(4\alpha) \tag{26}$$

It contains the 3-fold symmetry of the rotor and the 4-fold symmetry of the environment. A_1 represents the potential strength for a pure ammonia rotation at any fixed off-center position α. Both, A_1 and A_2, determine the barrier height of the com rotation. The Hamiltonian of this coupled rotation is

$$H = -B_{\mathrm{NH}_3}\frac{\partial^2}{\partial\varphi^2} - B_{\mathrm{com}}\left(\frac{\partial}{\partial\alpha} - \frac{\partial}{\partial\varphi}\right)^2 + V(\varphi,\alpha) \tag{27}$$

The eccentricity $R = |\vec{R}|$ of the center of mass rotation is related to the potential parameters and the geometry of ammonia ($\rho = d((\sqrt{7})/4)$, d = proton–proton distance) by

$$R = \rho\sqrt[3]{\frac{4A_2}{A_1}}$$

$$B_{\mathrm{com}} = \frac{\hbar^2}{2m_{\mathrm{ges}}R^2} \tag{28}$$

Depending on the values of the potential parameters this model covers the situation of the centered free single particle rotor ($A_1 \ll 1$ and $A_2/A_1 \ll 1$) up to the case of a localized off-center hindered rotor (finite A_1 and $A_2/A_1 < 1$) with the interesting intermediate regime of rotation–translation–coupling. Here the complex two-dimensional potential surface involves a tunneling ground state with an increased number of sublevels compared to the single particle model with a 3-fold potential. Thus this model offers a possibility to explain complex tunneling patterns.[77,78] In determining transition matrix elements, spin wave functions have to be included in addition to the product free rotor basis wave functions. These complex calculations have recently been done (P. Schiebel, et al. *Phys. Rev. B*, submitted). Thus intensities can be used to distinguish between different models.

The first spectroscopic proof of the combined coherent counterclockwise tunneling rotation of a one-dimensional 3-fold rotor and its center of mass is given for NH_3 adsorbed on a MgO[100] surface.[95] A second example, a Hofmann clathrate, is shown in ref 209, together with a simple mathematical recipe for determining the eigenvalues of eq 27 based on product free rotor wave functions. The method also yields the eigenfunctions which can be derived from a quantum mechanically correctly averaged temperature dependent proton density. Calculated proton density distributions agree well with the fourfold pattern observed experimentally.[210]

The model might be adapted to other environmental symmetries also. In the case of lithium acetate and γ-picoline, it offers a convincing alternative interpretation (P. Schiebel et al., to be published).

3.7. Influence of External Fields

A series of papers has considered the influence of static magnetic fields on the tunneling level schemes.[72,211–213] These papers represent the theoretical basis of level crossing NMR. The idea of a molecular motor is based on interaction with a rotating magnetic field.[162]

3.8. Systematic Studies and New Materials

Systematic studies of series of compounds differing only in a few well-defined properties have been found to be very useful. Such investigations were performed for acetates, methylbenzenes, the halomesitylenes, hexaammines and metal hexaammines, alkanes,[214,215] ketones,[216,217] tetramethyl metal compounds, organometallic methyl–tin materials,[218] ammonium hexahalometalates, ammonium in alkali halides, methane in rare gas matrices and hydrogen-substituted metal carbonyls.[15,219] The relevant references are found in the corresponding tables (see section 5).

Well-defined characteristic changes of the environment can also be obtained by structural phase transitions. If they happen at low temperatures ($T \leq 20$ K)[220,221] they modify the rotational tunneling spectrum. A famous model example is methane.[222] Such materials offer a unique possibility of testing interaction potentials: the spectrum of the new phase must follow purely from the structural changes.

It was shown in the case of some technically interesting materials, such as inclusion compounds and catalytically useful surfaces, that tunneling molecules can be used as probes to study the local potentials of adsorption sites.[223] Thus rotational tunneling seems to have developed from an exotic phenomenon to a useful spectroscopic method.

3.9. Some Special Remarks on Three-Dimensional Rotors

The extraction of rotational potentials from the eigenvalues (transition energies) is much more difficult in the case of three-dimensional rotors (NH_4^+ and methanes) because the potential has to be expanded into three-dimensional symmetry adapted functions (usually cubic rotator functions or Wigner *D* functions). Different site symmetries require different expansions of the rotational potential. The high symmetry problem of a tetrahedron in a tetrahedral field was solved decades ago.[224–226] The theory of neutron scattering from tunneling three-dimensional rotors was developed for this case.[82,227,228] The accuracy of numerical results was improved using more sophisticated wave functions.[91,120] The formalism was adapted to lower symmetries[5,229−231] and molecules of different shape.[232] The correlation between rotational potentials and pair interaction potentials was developed independently for methane in various surroundings[233−235] and ammonium compounds, e.g., see refs 113 and 236−239. D. Smith has derived expressions for the rotational potentials at many symmetries in terms of Wigner *D* functions and has calculated the potential parameters from atom−atom potentials for various materials.[21,240] Because of the much larger parameter space, the problem of describing the wave functions correctly and the much more complex mathematics required, no general expressions or tables of transition energies as a function of potential parameters can be presented, as in the case of one-dimensional rotors. For more detailed information the reader is referred to ref 21.

4. Translational Tunneling

Translational tunneling describes the quantum mechanical transition of a particle, in our case protons, from one well of a (possibly asymmetric) double minimum potential to the other. Despite the basic physical process is common to both, rotational and translational tunneling, there are some important differences. First, the crystallographic situation is not the same after a transition from one potential minimum to the other and the environment might relax toward a new equilibrium. Thus the calculation of tunneling rates is based on somewhat different techniques.[27,28,241] Secondly there are no symmetry restrictions to the wave function due to the Pauli principle for a single atom, which would lead to selection rules for transitions. Both differences make translational tunneling very sensitive to phonon interaction. The low-temperature properties of glasses and various crystalline model systems as for example KCl doped with Li can only be explained by tunneling states. Recent developments and progress in this field is reviewed in ref 28, including a table of the tunneling energies (10 to 100 μeV). Another famous specific example of this type of quantum motion are protons in the hydrogen bond.[242] Protons trapped near impurities at sites of 2-fold symmetry in hydrogen−metal systems represent another type of interesting material.[243−246] Usually the presence of the particle creates the asymmetry in a double minimum potential (self-trapping).[247] For the simple model of a symmetric potential an analytical solution of the problem is outlined in ref 66. Since the physics of translational tunneling is closely related to rotational tunneling, some impressing examples are included in this review.

5. Technical Information

The materials studied are presented in 17 tables showing in the first two columns the name and the chemical formula and in the last one the related references. Unpublished results show in this column the source of information (name of the involved researcher).

5.1. One-Dimensional 3-fold Rotors

The rotational potential is usually represented by the first two terms of a Fourier expansion into trigonometric functions of the angle φ (eq 3). The parameters are quantified on the basis of the expression eq 4. Except for two experimental examples, toluene and nitromethane, which fit a general value for α to the data, and in cases where $V(\varphi)$ is determined by calculations from atom−atom potentials and Fourier analyzed according to eq 3, the phase angles $\alpha = 0$ or $\alpha = \pi$ are used. The first case ($\alpha = 0$) describes potentials with broad barriers and shallow minima while the second one ($\alpha = \pi$) gives potentials with broad minima and narrow barriers. Even in these two cases the two coefficients of the potential can only be derived if a second characteristic energy is also observed. This is usually either the energy difference to the first excited librational state or the activation energy for rotational jumps. Using two energies one can obtain the potential parameters V_3 and V_6 for fixed α. Often three other parameters are used to define the potential: $VS = |V_3| + |V_6|$, $\delta = |V_3|/VS$, and $k = 0(1)$ for $\alpha = 0(\pi)$. The eigenvalues of a one-dimensional, 3-fold rotor were calculated for a wide range of potential parameters by R. F. Gloden[248] using a method of expansion in continued fractions. Nowadays it is straightforward to do the diagonalization of the Hamiltonian matrix directly using a standard computer program. Despite this possibility it is useful to have tabulated eigenvalues. The parts of a−f of Figure 3 show the calculated eigenvalues for general potentials of shape (3) in an energy range resolvable by INS. They allow the reader to interpret his data within the single particle model. The parametrization uses the independent variables V_3, VS, and k. While the ground-state tunnel splitting $\hbar\omega_t$ as the distance between the two lowest eigenstates is clearly defined, the librational energies E_{0n} are the distances between the averaged energies of the lowest two and a following pairs of levels. For example

$$E_{01} = \frac{E_3 + E_2}{2} - \frac{E_1 + E_0}{2}$$

and so on. This is a useful approximation for large barriers where the doublet structure of librational levels is not resolved in the scattering experiment. For very low barriers or potentials with dominating 6-fold term, which are rare, this simplification is misleading, however. In such cases all eigenvalues indeed must be calculated. The activation energy E_a is taken here as the distance to the barrier top from the ground state.

The 10 tables on one-dimensional rotors treat monosubstituted methanes (Table 1), alkanes, halogenated alkanes, alkenes and alkines (Table 2), ketones (Table 3), ethers and thioethers (Table 4), acids (Table 5), salts of acids, mainly acetates (Table 6), benzene derivatives (Table 7), heteroaromates (Table 8), organometallic compounds (Table 9), and ammonia compounds with a strong weight on hexaammine halides (Table 10).

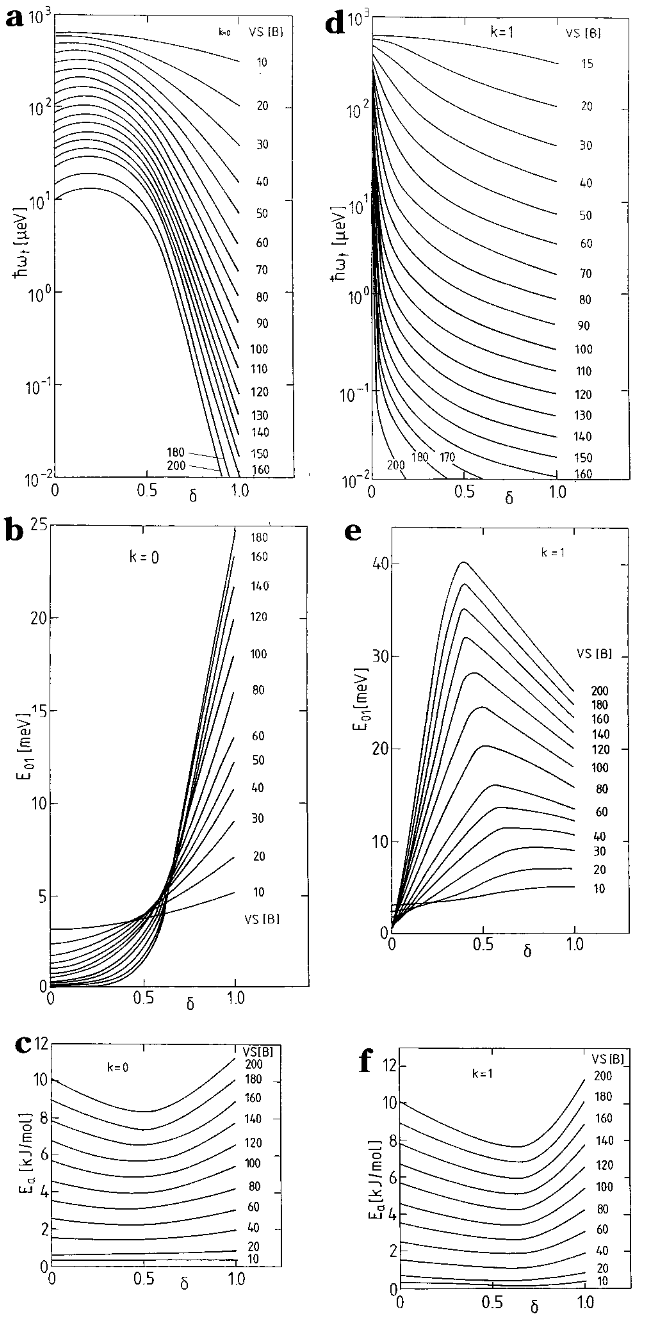

Figure 3. Transition energies obtained from the eigenvalues of the CH_3 rotor in a potential of general shape of eq 4. V_3 and V_6 are taken ≥ 0. $VS = V_3 + V_6$ is a measure of the potential strength, $\delta = V_3/VS$ determines the shape of the potential: (a) $k = 0$ ($\alpha = 0°$); ground state tunnel splitting; (b) $k = 0$; distance between the two lowest tunneling doublets. $E_{01} = (E_2 + E_3 - E_0 - E_1)/2$. E_i are eigenenergies of the methyl rotor; (c) $k = 0$; the activation energy is taken as the barrier height measured from the librational ground state; (d) as a but $k = 1$ ($\alpha = 180°$); (e) as b but $k = 1$; (f) as c but $k = 1$.

If values of V_3 and V_6 are given in Tables 1−10, then the ground-state tunnel splitting $\hbar\omega_t$ and the first excited libration E_{01} have been used to derive the rotational potential. If V_6 is not given, a pure $\cos(3\varphi)$ potential is assumed and derived from the ground-state tunnel splitting alone. In cases where no potential was derived it is easy to estimate the strength of a purely 3-fold cosine potential from Figure 3 or, for very small tunnel splittings not contained in this figure, from an expression analogous to eq 10 for the asymptotic behavior. If more than one set of potential parameters was able to describe the data we have only given those closer to $\cos(3\varphi)$ because experience has shown that the potentials are usually dominated by the $\cos(3\varphi)$ term. For pure 3-fold potentials a systematic relation is expected between the size of a tunnel splitting and the temperature $T_{\min}$ where the inverse spin lattice relaxation time T_1^{-1} in an NMR-T_1 curve shows its classical minimum. The data have to be transformed to identical experimental conditions, that is, equal Larmor frequency. This correlation was indeed found.[93] We thus show in the column 8 the value $T_{\min}$ with the experimental Larmor frequency in brackets. Finally, we note the technique used to measure the tunnel splitting. The abbreviations have the following meanings: (I)NS, (Inelastic) neutron scattering; NMR-T_1, nuclear magnetic resonance; spin lattice relaxation; FC, field cycling NMR; LC, level crossing NMR; lf, low field NMR; D-NMR, Deuteron NMR; LS, NMR line-shape analysis; HC, heat capacity; OS, optical spectroscopy; IR, infrared spectroscopy; MW, microwave spectroscopy; VR, viscoelastic relaxation; AR, anelastic relaxation; ENDOR, electron nuclear double resonance; TH, theoretical paper, and list the references of the relevant publications. These references should lead the interested reader to literature section.

In the few cases where coupling between methyl groups has an effect on the tunnel spectrum, the interpretation of spectra is done on the basis of the combined single particle and interaction potential contained in eq 22. In such cases we show W_3 instead of V_6 in column 6.

5.2. Three-Dimensional Tetrahedral Rotors

The tables on three-dimensional rotors list the studied material according to the following order: ammonium hexahalo metallates (Table 11), pure and mixed ammonium halides and others (Table 12), methane in its various phases (Table 13), methane in rare gas and other matrices (Table 14), methane on surfaces, silane, and germane (Table 15). Tunneling of molecular hydrogen is included only in as far as hydrogen exists in special environments (Table 16).

Because of the higher multiplicity of the ground state, the tunneling spectra from tetrahedral molecules show at least two transitions per molecule. This is in the case when molecular and site symmetry are identical and tetrahedral. This number can increase to up to nine if the site symmetry of the molecule, given in column 3 if available, is successively reduced (Figure 2 and ref 5). If, in addition, inequivalent rotors are present in the sample the situation quickly becomes rather complex. Thus we do not show all observed tunneling lines but give mostly only the value of the highest tunnel frequency and the number of lines (in brackets). The other information is presented the same way as for one-dimensional rotors. The potentials reproduced in column 6 only explain the observed ground state tunnel splitting. For the simplest case, a tetrahedron in a tetrahedral field, the reduction of the tunnel

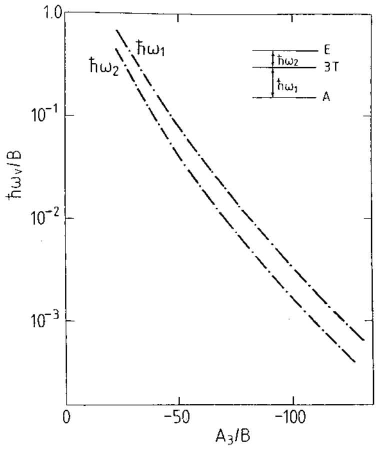

Figure 4. Ground-state tunnel splitting of a tetrahedral spherical top (methane) in a purely tetrahedral potentials $V(\omega) = A_3H_{11}^{(3)}(\omega)$. ($\omega$ = Eulerian angles; $H_{11}^{(3)}(\omega)$ = cubic rotator function.) (From ref 119.)

splittings with increasing potential strength is shown in Figure 4.

To avoid the problem of complex mathematics, estimates on the basis of one-dimensional models are helpful. This analogy is justified by the fundamental property of a wave function to decay exponentially into a potential wall. Thus the tunnel splittings decrease almost exponentially with increasing potential strength in any dimension. The recipe is the following: Determine the average tunnel splitting of the 3d system, scale it down by a factor 2, which is the ratio of the respective fundamental free rotor transition energies 1*B*/2*B* and eventually rescale to the same rotational constant *B*. With this value refer to Figure 3, $\delta = 1$. The peak-to-peak height VS gives a rather good estimate of the strength of the 3d potential.

5.3. Others

A final table (Table 17) is devoted to topics related to the scientific neighborhood of rotational tunneling. It contains some arbitrarily selected theoretical calculations of simple molecular complexes, and translational tunneling in metal hydrates and hydrogen bonded systems. The references in this table offer only a few examples of work thematically related to rotational tunneling.

Table 1. CH_3 Rotors, Monosubstituted Methanes

compound name	compound formula	crystal structure	ν_t (μeV)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
methyl fluoride	CH_3F	$P2_1/c$	23.1	1	26.6	0			INS	250
methyl fluoride in Ar	CH_3F/Ar		340	≪1					INS	Prager
			(148)						TH	251
methyl chloride	CH_3Cl		0.1						INS	252
methyl bromide	CH_3Br	*Pnma*	0.9	1	50.7	0.6	0		INS	252
					50.3	0.5	0	48 (30)	NMR	253
methyl iodide	CH_3I	*Pnma*	2.44	1	41.0	1.9	0		INS	252
										254
					41.8	1.5	0			253
									INS	124
	CD_3I		>0.01						D-NMR	49
nitromethane	CH_3NO_2	$P2_12_12_1$	35.1	1	25.2	15.4	α = 30°		INS	255
									INS	101
									INS	94
										256
										257
										112
									INS	258
										104
										117
									NS	164
	CD_3NO_2	$P2_12_12_1$	1.7	1					INS	101
	CHD_2NO_2, CH_2DNO_2									103
methyl iodide on grafoil	CH_3I/C		40.0		23.6				INS	16
			20.0							
methanol in hydroquinone	CD_3OH		>2 MHz		<50				NMR	259
			~0.04		40					51

Table 2. CH_3 Rotors, Aliphates: Alkanes and Halogenated Alkanes, Alkenes, and Alkynes

compound name	compound formula	crystal structure	ν_t (kHz)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
iodoethane	CH_3CD_2I		18.3						NMR	260
									NMR	261
hexane	$CH_3(CH_2)_4CH_3$		298						LF	214
										215
									NMR	262
heptane	$CH_3(CH_2)_5CH_3$		298/146						LF	214
										215
									OS	263

Table 2 (Continued)

compound name	compound formula	crystal structure	ν_t (kHz)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
octane	$CH_3(CH_2)_6CH_3$		300						LF	214 215
nonane	$CH_3(CH_2)_7CH_3$		299/134						LF	214 215
decane	$CH_3(CH_2)_8CH_3$		301						LF	214 215
undecane	$CH_3(CH_2)_9CH_3$		342/44						LF	214 215
dodecane	$CH_3(CH_2)_{10}CH_3$		301						LF	214 215
tridecane	$CH_3(CH_2)_{11}CH_3$		343						LF	214 215
tetradecane	$CH_3(CH_2)_{12}CH_3$		303						LF	214 215
pentadecane	$CH_3(CH_2)_{13}CH_3$		344						LF	214 215
hexadecane	$CH_3(CH_2)_{14}CH_3$		299						LF	214 215
heptadecane	$CH_3(CH_2)_{15}CH_3$		338						LF	214 215
octadecane	$CH_3(CH_2)_{16}CH_3$		301						LF	214 215
2-chloropropane	$CH_3(CHCl)CH_3$		290/50						LF	214 215
dimethylacetylene	$CH_3C{\equiv}CCH_3$		1.74 μeV	1	27.9	2.26	1		INS	3 264
2,4-hexadiyne	$CH_3C{\equiv}CC{\equiv}CCH_3$		1.06 μeV	1					INS	265
									INS	266
2-methyl-2-butene	$CH_3CH{=}C(CH_3)_2$		0.89 μeV	1/3	52.6			49/77 (21)	INS FC	267
polymethylmethacrylate (PMMA)			1						VR	268 269

Table 3. CH_3 Rotors, Aliphates: Ketones

compound name	compound formula	crystal structure	ν_t (μeV)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
acetone	CH_3COCH_3		0.4						MW	188
									FC, LC	270
2,3-butanedione (=diacetyl)	$CH_3COCOCH_3$	monoclinic $P2_1/n$	74 kHz	~1	159			131 (24)	LF-NMR	271
					129	30	1	128 (21)	LF-NMR	272
2-butanone	$CH_3(CH_2)COCH_3$		0.81/495 kHz	1/2, 1/2				50/114	LF	273 274
2-pentanone	$CH_3(CH_2)_2COCH_3$		6.3/1.76/1.31						INS	275
3-pentanone	$CH_3(CH_2)CO(CH_2)CH_3$		0.015						NMR	216 276
2-hexanone	$CH_3(CH_2)_3COCH_3$		5.8/5.0/2.3/ 1.5/152 kHz	../1/2				29/145	LF	216 276
									LF	277
3-hexanone	$CH_3(CH_2)CO(CH_2)_2CH_3$		210 kHz	1/2	142			142 (21)	NMR	216
									NMR	276
									LF	278
2-heptanone	$CH_3(CH_2)_4COCH_3$		63 kHz	1/2				31/149	LF	216 276
									LF	277
3-heptanone	$CH_3(CH_2)CO(CH_2)_3CH_3$		272 kHz					115	LF	216 276
4-heptanone	$CH_3(CH_2)_2CO(CH_2)_2CH_3$		491 kHz	1	129			132 (21)	LF	216 276
			495 kHz	1					NMR	278
2-octanone	$CH_3(CH_2)_5COCH_3$		110 kHz	1/2				30/151	LF	216 276
									LF	277
3-octanone	$CH_3(CH_2)CO(CH_2)_4CH_3$		338 kHz					112	LF	216 276
2-nonanone	$CH_3(CH_2)_6COCH_3$		90 kHz	1/2				28/143	LF	216 276
									LF	277
3-nonanone	$CH_3(CH_2)CO(CH_2)_5CH_3$		200 kHz						LF	216 276
5-nonanone	$CH_3(CH_2)_3CO(CH_2)_3CH_3$		386 kHz/ 150 kHz/ 36 kHz						LF	214

Table 3 (Continued)

compound name	compound formula	crystal structure	ν_t (μeV)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
2-decanone	$CH_3(CH_2)_7COCH_3$		293 kHz		1/2				LF	277
2-undecanone	$CH_3(CH_2)_8COCH_3$		353 kHz	1/2					LF	277
2-dodecanone	$CH_3(CH_2)_9COCH_3$		343 kHz	1/2					LF	277
2-tridecanone	$CH_3(CH_2)_{10}COCH_3$		361 kHz	1/2					LF	277
acetylacetone	$CH_3COCH_2COCH_3$		42/4.0	1/2, 1/2	19.6/38.1			11/42 (21)	INS, NMR	276
									INS	279
					coupling				NMR	213
									NMR	262
	$CH_3COCD_2COCH_3$		34.4/3.4	1/2, 1/2	20.85/39.3			13/51 (21)	INS, NMR	279
acetonylacetone	$CH_3CO(CH_2)_2COCH_3$		97 MHz	1	62			54 (21)	NMR	18
									NMR	271
2-hexadecanone	$CH_3(CH_2)_{13}COCH_3$		343 kHz	1/2					LF	277
2-nonadecanone	$CH_3(CH_2)_{16}COCH_3$		350 kHz	1/2					LF	277
methyl ethyl ketone	$CH_3COC_2H_5$		469 kHz						LF	280
trans-4-phenyl-3-buten-2-one	$C_6H_5(CH)_2COCH_3$		0.74	1	54.5			51 (21)	NMR	281
acetophenone	$C_6H_5COCH_3$	$P2_1/n$	0.00598	1	113.7			97 (25)	NMR	281

Table 4. CH_3 Rotors, Aliphates: Ethers and Thioethers

compound name	compound formula	crystal structure	ν_t (kHz)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
dimethyl ether radical	CH_3OCH_3									282
			(44−391)	Coupled	Pairs				TH	283
dimethyl sulfide	CH_3SCH_3		752/95						LF	181
									LF	284
			(93−749)	Coupled	Pairs				TH	283
									LF	285
										286
										287
										262
methyl phenyl sulfide (thioanisole)	$C_6H_5SCH_3$		557	1	127.2			114 (21)	LF-NMR	274
octyl ether	$CH_3(CH_2)_7O(CH_2)_7CH_3$		260/107						LF	Clough
octyl sulfide	$CH_3(CH_2)_7S(CH_2)_7CH_3$		222/149						LF	Clough
dimethyl ether	CH_3OCH_3		390/45						LF	214
										181
dipropyl ether	$CH_3(CH_2)_2O(CH_2)_2CH_3$		330/110						LF	181
dipropyl sulfide	$CH_3(CH_2)_2S(CH_2)_2CH_3$		140/85/60						LF	Clough

Table 5. CH_3 Rotors, Aliphates: Acids

compound name	compound formula	crystal structure	ν_t (μeV)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
acetic acid	CH_3COOH		3.3		40			46 (30)	NMR	288
			1.52						INS	Johnson
propionic acid	CH_3CH_2COOH		216 kHz						LF	Clough
										260
						coupling			LC-NMR	287
4-tolyacetic acid	$CH_3C_6H_4CH_2COOH$		1.17						NS	Clough
acetylsalicylic acid (aspirin)	$C_8O_4H_5CH_3$		1.22		55.8[a]	10.3[a]			INS	60
	$C_8O_4H_5CD_3$		2700 kHz		44			57.6 (72)	D-NMR	289
									D-NMR	290
methyl malonic acid	$HOOCCH(CH_3)COOH$		75 kHz						LF	291
										292
										293
										260
										262
dimethyl malonic acid	$HOOCC(CH_3)_2COOH$		337 kHz	1	206			135 (21)	LF	278
tiglic acid	$CH_3CH{=}C(CH_3)COOH$		10.8	1/2	44.5			23 (21)	INS,LC-NMR	267
			0.47	1/2	88.9			52 (21)		
3-toluic acid	$CH_3C_6H_4COOH$		15.0						NS	Clough
4-toluic acid	$CH_3C_6H_4COOH$		13.0						NS	Clough

[a] General phase factors used.

Table 6. CH_3 Rotors, Aliphates: Salts of Acids and Other Derivatives

compound name	compound formula	crystal structure	ν_t (μeV)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
lithium acetate dihydrate	$(CH_3COO)_2Li\cdot 2H_2O$		250	1	coupled	dimers			NMR	294
									INS	295
									INS	187
									INS	296
									INS	297
									INS	298
									INS	106
									NMR	173
									INS	100
									TH	283
									INS	164
	$(CH_3COO)_2Li$ in $(CH_2DCOO)_2Li\cdot 2H_2O$		166	1					INS	205
manganese acetate tetrahydrate	$(CH_3COO)_2Mn\cdot 4H_2O$	$P2_1/c$	137.0	1/3	7.4			4.5 (24.5)	INS	299
			50.0	1/3	11.6					164
			1.2	1/3	31.7					
lead acetate trihydrate	$(CH_3COO)_2Pb\cdot 3H_2O$		45.0		50	7.9	1	10 (21.7)	INS	300
ammonium acetate	CH_3COONH_4		16.2		17.1			19 (21.7)	INS	300
									INS	295
									INS	301
									NS	164
					24.2	2.0	1	20 (30)	NMR-T1	Kuhnen
			80 kHz						NMR	286
potassium acetate	CH_3COOK		0.23		64	2.1	1		NMR	92
sodium acetate trihydrate	$CH_3COONa\cdot 3H_2O$		5.7	<1	22.6			28 (21)	INS	300
									INS	121
									INS	301
			5.6		38	5.2	0	46 (30)	NMR	92
										173
									NS	164
					33	1.3	1	29 (30)	NMR-T1	Vermathen
sodium acetate	CH_3COONa		1.5 at $T =$ 46 K					37 (30)	NMR	Montjoie
	CD_3COONa		>0.01						D-NMR	49
zinc acetate dihydrate	$(CH_3COO)_2Zn\cdot 2D_2O$		5.33	<1	23.0	10% V_3		28 (21)	INS	300
	$(CH_3COO)_2Zn\cdot 2H_2O$		4.95	<1	23.2			28 (21)	INS	301
									NS	164
					38.7	2.0	0	30 (30)	NMR-T1	Vermathen
magnesium acetate tetrahydrate	$(CH_3COO)_2Mg\cdot 4H_2O$		1.80			10% V_3		50 (21)	INS	300
					43.9	1.3	1	50 (30)	NMR-T1	Vermathen
nickel acetate tetrahydrate	$(CH_3COO)_2Ni\cdot 4H_2O$		1.40			10% V_3			INS	300
									NS	164
copper acetate monohydrate	$(CH_3COO)_2Cu\cdot H_2O$		0.3			13% V_3		60		300
										302
										303
cadmium acetate	$(CH_3COO)Cd$		41.0						FC	304
									NS	164
	$(CD_3COO)Co$		610 kHz						D-NMR	49
zinc acetyl acetate	$Zn_3COOZnCH_3CO$		0.51						FC	Clough
methyl acetate	CH_3COOCH_3	$P2_1/n$	1.33	1/2	48.4			45 (21)	NS	305
			84 kHz	1/2	156.6			120 (21)	LF	
scandium acetate	$Sc(CH_3COO)_3$		7/9	1/3, 1/3	38.8	7.3	0		INS	306
	$Sc(CD_3COO)_3$		≥0.01						D-NMR	306
mercuric acetate	CH_3COOHg		7 kHz						FC	Clough
cobalt acetate dihydrate	$(CH_3COO)_2Co\cdot 2H_2O$		30.0/4.9/1.1						NS	Heidemann
									NS	164
lithium lactate (free radical)	$CH_3CH(OH)COOLi$		90.0						NMR	291
									NS	164
	$(Ni(OCH_3)(acac)(CH_3OH))_4$		~68						HC	307
acetyl fluoride	CH_3COF		0.35		63				NMR	288
acetyl chloride	CH_3COCl		0.128/0.09/0.08		78				NMR	288
acetyl bromide	CH_3COBr		0.12		72				NMR	288
methyl isocyanate	CH_3NCO		0.62		56			46 (30)	NMR-T1	253
methyl urea	$CH_3NHCONH_2$		0.35						FC	Clough
acetamide	CH_3CONH_2			1				28 (11.4)	NMR	308
	CH_3CONH_2	$R3c$	32	1	21				INS	105
										118
										309
	CD_3COND_2, CD_3CONH_2	$R3c$	1.18	1	21.7				INS	105
paracetamol	$CH_3CONH_2C_6H_4OH$	$P2_1/a$	3.1	1					INS	Prager
methylmalonamide	$CH_3COCH_2CONH_2$		455 kHz					129 (20)	LF	280
oxo-centered triangulochromium carboxylate	$(Cr_3O(OOCH_3)_6\cdot H_2O)_3)^+Cl^-\cdot 5H_2O$		75/48.5/37						INS	174
	$(Cr_3\ O(OOCH_3)_6\cdot (H_2\ O)_3)^+ClO_4{}^-\cdot 5H_2O$		37/29						INS	174

Table 7. CH_3 Rotors, Benzene Derivatives

compound name	compound formula	crystal structure	ν_t (μeV)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
toluene	$C_6H_5CH_3$	$P2_1/c$	28.5	1/2	14.8	−1.2	α = 35°	17 (30)	INS	102
			26.0	1/2	19.3	−9.6	α = 17.2°			
										256
										123
										104
										310
									NMR-T1	311
	$C_6D_5CH_3$		25.8/24.7						INS	102
	$C_6D_5CD_3$		1.1						INS	102
									NMR	312
toluene(1:1) *p*-*tert*-butylcalix-[4]arene			160/200/360/630						INS	313
									INS	314
									INS	223
2-fluorotoluene	$C_6H_4FCH_3$		5.8	1	32.1	5.1	1	29 (30.0)	INS	315
2-bromotoluene	$C_6H_4BrCH_3$		0.038						NMR	Langen
3-fluorotoluene	$C_6H_4FCH_3$		13.8	1	29.5	5.1	0	29 (30)	INS	315
									MW	316
4-fluorotoluene	$C_6H_4FCH_3$		17.6	1	21.8	7.1	1	22 (30)	INS	315
									MW	30
4-iodotoluene	$C_6H_4ICH_3$		108	1	14.8	4.5	0	10.2 (30)	INS	Langen
2,6-dichlorotoluene	$C_6H_3Cl_2CH_3$		1.56	1	45	1.3	0		INS	Langen
2,6-dichlorotoluene	$C_6H_3Cl_2CH_2D$		0.2					43 (30)	NMR	99
2,6-dibromotoluene	$C_6H_3Br_2CH_3$		4.0 at T = 43 K		27	1.3	1	29 (30)	NMR	Jahnke
o-xylene	$(CH_3)_2C_6H_4$		0.026	1/2	85	5.1	0	87 (30)	NMR,FC	315
			0.037	1/2	92	9.3	1	72 (30)		
p-xylene	$(CH_3)_2C_6H_4$	$P2_1/n$	0.97	1	50	0		55 (30)	INS/NMR	315
					53.8	1.1	0		NMR	253
									INS	116
p-xylene(1:2) *p*-*tert*-butylcalix-[4]arene			626	1					INS	223
										317
m-xylene	$(CH_3)_2C_6H_4$		25.6/14	1/2, 1/2	21.8	1.3	1	17 (30)	INS	315
tetramethylbenzene (durene)	$(CH_3)_4C_6H_2$		0.12						NMR	318
pentamethylbenzene	$(CH_3)_5C_6H$		6.3/0.67	1/5, 2/5				39 (25)	INS	319
									NMR	320
hexamethylbenzene	$(CH_3)_6C_6$		0.040/0.033		86.5/89.0				NMR	321
									FC	182
in C_6Cl_6	$(CD_3)_6C_6$		0.011		47				D-NMR	322
in glassy PDB	$(CD_3)_6C_6$		>0.01		<50				D-NMR	322
trichloromesitylene	$(CH_3)_3Cl_3C_6$	triclinic	4.3	1/3	31	8	α = 150°	40 (6.95)	INS	323
			9.2	1/3	34.5	7.5	α = 150°			
			13.1	1/3	41	7.5	α = 150°			
									NMR	324
									HC	55
tribromomesitylene										
pure	$(CH_3)_3Br_3C_6$	triclinic	14	1/3	25.41	4.11	α = 172°		INS	119
			25.2	1/3	10.01	3.61	α = 120°			
			48.9	1/3	15.0	4.8	α = 172°		NMR	55
										90
3.7% in Hexabromo benzene		monoclinic	102	1					INS	325
triiodomesitylene	$(CH_3)_3I_3C_6$	triclinic	14.4	1/3					INS	323
			26.7	1/3						
			87.4	1/3					HC	55
1,3-dichloro-2,4,6-trimethylbenzene	$(CH_3)_3HCl_2C_6$	monoclinic	451						INS	325
1,3-dibromo-2,4,6-trimethylbenzene	$(CH_3)_3HBr_2C_6$	monoclinic	390						INS	326
toluquinone			12 MHz						OS, NMR	327
4-methyl-2,6-di-*tert*-butylphenol (MDBP)									NMR-T1	328
			37.5		12.8			15.5 (21)	INS	329
									NMR	121
									INS	330
									FC-NMR	331
									NS	164
4-methyl-2,6-di-*tert*-butylphenol radical			26						ENDOR	332

Table 8. CH_3 Rotors, Heteroaromates

compound name	compound formula	crystal structure	ν_t (μeV)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
4-methylpyridine (γ -picoline)	$CH_3C_5NH_4$		520.0	1	7.3			2.2 (15)	INS	333
										334
									INS	335
									INS	206
					coupled	chains			INS	336
									NS	337
									NS	164
									OS	61
	$CH_2DC_5NH_4$		410						INS, HC	338
									INS	339
									INS	335
									INS	75
			388 ($T = 2$ K)		coupled	chains			INS	340
			436 ($T = 5$ K)						INS	203
	$CHD_2C_5NH_4$		337		coupled	chains			INS	340
4-methylpyridine *N*-oxide	$CH_3C_5NH_4O$								INS	341
									HC	55
4-methylpyridine zinc chloride	$Zn(4\text{-}CH_3C_5NH_4)_2Cl_2$	$P2_1/n$	146		5.2	16.8			INS	203
			14.3		9.9	32.1				
4-methylpyridine manganese chloride	$Mn(4\text{-}CH_3C_5NH_4)_2Cl_2$		7.1		32.6				INS	203
4-methylpyridine cobalt chloride	$Co(4\text{-}CH_3C_5NH_4)_2Cl_2$		19.5		24.6				INS	203
3-methylpyridine (β -picoline)	$CH_3C_5NH_4$		10.0	<1	24.2	7.2	0	23(15)	INS	342
									INS	343
3,5-dimethylpyridine (3,5-lutidine)	$(CH_3)_2C_5NH_4$		1.51					42(15)	INS	342
									INS	343
2,6-dimethyl pyridine (2,6-lutidine)	$(CH_3)_2C_5NH_4$		186/53/30/23/15/11.7					18 (15)	INS	204
									INS/NMR	342
									INS	343
									HC	55
2,5-dimethyl-1,3,4-thiadiazole	$(CH_3)_2C_2N_2S$		0.014	1	101			89 (21.0)	LF	344
									LF	345
1-methylimidazole	$(CH_3)C_3H_3N_2$		0.33					52 (30)	NMR	346
5-methylisoxazole	$(CH_3)C_3H_2NO$		0.039		83.5	6.4	1	87 (30)	NMR	346
3-methylpyrazole	$(CH_3)C_3N_2H_3$		2.7 ($T = 53$ K)		25.7	25.7	0		NMR	346
4-methylpyrazole	$(CH_3)C_3N_2H_3$								FC	347
			0.56 ($T = 48$ K)		45.6	5.1	0	39 (30)	NMR	346
3-methylfuran	$(CH_3)C_4OH_3$		0.55		53	4.1	1		FC	347
					61.6	9.0	1		NMR	346
2-methylfuran	$(CH_3)C_4OH_3$		0.09		69.4	4.1			FC	347
			0.19		66.8	0		65 (30)	NMR	346
3-methylthiophene	$(CH_3)C_4SH_3$		0.53		51.4	3.1	1		FC	347
									NMR-T1	253
2-methylthiophene	$(CH_3)C_4SH_3$		17.6 ($T = 53$ K)		25.7	17.8	0	19 (30)	NMR	346
2,5-dimethyl pyrazine	$(CH_3)_2C_4N_2H_2$		0.031						FC	182
tetramethylpyrazine	$(CH_3)_4C_4N_2$		0.11/0.08/0.06						FC	318
dimethyl-*s*-tetrazine	$C_2N_4(CH(D)_3)_2$									
in durene	$(CH_3)_4C_6H_2$		$h(\nu_0 - \nu_0^*) = 5$						OS	56
									OS	57
									OS	58
			$h(\nu_0 - \nu_0^*) = (3.5 - 5)$						OS	125
in *n*-octane	C_8H_{18}		$h(\nu_0 - \nu_0^*) = 154\ (87)$						OS	59
			$h\nu_0 = 508$		3.3					
in *n*-octane	C_8D_{18}		$h(\nu_0 - \nu_0^*) = 90(21)$		7.4				OS	108
in hexane	C_6H_{14}				14.4				OS	108
									OS	348

Table 9. CH_3 Rotors, Organometallic Compounds: Group IV and Others

compound name	compound formula	crystal structure	ν_t (μeV)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
tetramethyl lead	$Pb(CH_3)_4$	$Pa3$	74	1/4	14.9	13.8	0	11.5 (15)	INS	249
			30.7	3/4	13.4	1.3	1			
tetramethyl tin	$Sn(CH_3)_4$	$Pa3$	13.2	3/4	16.6	2.7	1	22 (15)	INS	349
			1.72	1/4	24.2	7.2	1			
									NS	164
	$[Sn(CH_3)_4]_x$ $[Sn(CD_3)_4]_{1-x}$	$Pa3$	1.72−13.8						INS	350
tetramethyl metal mixtures	$Sn_xPb_{1-x}(CH_3)_4$	$Pa3$	1.7−74						INS	351
									INS	352
tetramethylgermanium	$Ge(CH_3)_4$		0.47	3/4	39.5			59 (15)	INS	353

Table 9 (Continued)

compound name	compound formula	crystal structure	ν_t (μeV)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
tetramethylsilicon	$Si(CH_3)_4$		0.21/0.13							353
tetramethyltin/ germanium	$Sn_{1-x}Ge_x(CH_3)_4$		12						INS	Prager
tetramethyltin in argon	$Sn(CH_3)_4/Ar$		80						INS	354
			68							355
tetramethyllead in argon	$Pb(CH_3)_4/Ar$		190						INS	356
hexamethylditin	$Sn_2(CH_3)_6$		3−127 (T < 14 K) (8 lines)						INS	220
		$Pnm2_1$	13.7/54.3/77 (T > 14 K)							
trimethyltin fluoride	$(CH_3)_3SnF$	$Pnma$	0.3	1	58	0			INS	218
trimethyltin chloride	$(CH_3)_3SnCl$	$I2/c$	0.89	1/3					INS	218
			4.47	1/3						
			8.67	1/3						
trimethyltin bromide	$(CH_3)_3SnBr$		4.5/32.0	2/3 1/3	44.5, 27.5	11.1, 11.8			INS	218
trimethyllead chloride	$(CH_3)_3PbCl$	$C2$	1.72/3.35	1/3 1/3	48.5, 42.2	2.5, 3.7			INS	218
dimethyltin difluoride	$(CH_3)_2SnF_2$	$I4/mmm$	14.3	1	28.8	3.5	0		INS	218
									NS	164
dimethyltin dichloride	$(CH_3)_2SnCl_2$	$Imma$	49	1	26.6	$W_3 = 16.5$			INS	357
										358
									NMR-T_1	359
										360
						coupling				213
	$(CD_3)_2SnCl_2$		3.88						INS	358
	$(CH_3CD_3)SnCl_2$		57						INS	358
dimethyltin dibromide	$(CH_3)_2SnBr_2$		6.8/11.0	1/4 1/4	53.0, 30.1	3.4, 0.0	0		INS	218
methyltin tribromide	CH_3SnBr_3		0.75	1/2	56	2.9			INS	218
bis(trimethyltin)sulfate dihydrate	$[(CH_3)_3Sn]_2SO_4\cdot 2D_2O$	$Pbcn$	1.1/11.36	2/3 1/3	52.3/32.6	3.3/6.2	1		INS	361
bis(trimethyltin)selenate dihydrate	$[(CH_3)_3Sn]_2SeO_4\cdot 2H_2O_4$	$Pbcn$	1.31	1/3	26.2	2.9	1		INS	362
			3.47	1/3	20.8	1.9				
			21.0	1/3	14.0	3.5				
tetramethyldistiban	$(Sb)_2(CH_3)_4$	$Pnma$	23	1/2				19 (15)	INS	Kuhnen
tetramethyldibismutan	$(Bi)_2(CH_3)_4$		3.35/13.8/ 16.7					17 (15)	INS	Kuhnen
trimethylbismutan	$Bi(CH_3)_3$		5.5	~1/3					INS	Kuhnen
tetramethylstibonium	$(Sb(CH_3)_4)PF_6$								NMR/INS	363
hexafluorophosphate			22/42/61							Burbach
tetramethylnickel dicyanate	$(Ni(CH_3)_4)(SCN)_2$		4						INS	Carlile

Table 10. Ammonium Compounds

compound name	compound formula	crystal structure	ν_t (μeV)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
nickel hexaamine										
hexafluorophosphate	$Ni(NH_3)_6(PF_6)_2$		540						INS	Kearley
									NS	166
iodide	$Ni(NH_3)_6I_2$		83/68/47						INS	364
										365
										366
									NS	164
									NS	166
perchlorate	$Ni(NH_3)_6(ClO_4)_2$		12						INS	Kearley
nitrate	$Ni(NH_3)_6(NO_3)_2$		5.56/18.94						INS	525
hexafluoroarsenate	$Ni(NH_3)_6(AsF_6)_2$		15						INS	Kearley
bromide	$Ni(NH)_3)_6Br_2$		8	<1					INS	367
									NS	164
chlorine	$Ni(NH_3)_6Cl_2$		0.1						INS	367
cobalt hexaamine										
hexafluorophosphate	$Co(NH_3)_6(PF_6)_2$		542						INS	368
										526
					11.1	$W_6 = -4.3$			INS	366
									NS	166
iodide	$Co(NH_3)_6I_2$		83/56/45						INS	Kearley
bromide	$Co(NH_3)_6Br_2$		83/68/47						INS	Kearley
perchlorate	$Co(NH_3)_6(ClO_4)_2$		20						INS	Kearley
trichlorine	$Co(NH_3)_6Cl_3$		4						NMR	369
			9						NMR	370
			5.6/4.5						INS	Prager
zinc amine iodide	$Zn(NH_3)_xI_2$		60/40						INS	Kearley
calcium hexaamine	$Ca(NH_3)_{5.9}$	$Fm3m$	670						INS	371
										372
										373
										374
										107

Table 10 (Continued)

compound name	compound formula	crystal structure	ν_t (μeV)	occurrence ratio	V_3 (meV)	V_6 (meV)	k	T_{min} (K) (ω_o (MHz))	technique	ref
	$Ca(ND_3)_{5.93}$	$Fm3m$	315						INS	371
										107
	$Yb(NH_3)_{\sim 6}$	$Fm3m$	≤100						INS	375
Hofmann clathrate	$Ni(NH_3)_2M(CN)_4$* $2C_6D_6$	tetragonal $P4/m$								
	M = Ni	tetragonal	700		$V_{12} = 16$				INS	74
									INS	376
			710						INS	377
										209
	M = Zn		710						INS	377
	M = Cu		698						INS	377
	M = Fe		681						INS	377
	M = Mn		703						INS	377
Hofmann clathrate	$Ni(NH_3)_2Ni(CN)_4$	unknown	86/142	2:1					INS	377
ammonia on magnesium oxide	NH_3/MgO	4 *mm*								
	0.2 monolayer		618		rotation–translation–coupling				INS	378
	0.5 monolayer		484						INS	378
										209
									INS	208
									INS	379
ammonia in argon	NH_3/Ar		745						INS	380
			648/740						INS	381
									INS	382
	NH_2D/Ar		555						INS	382
	NHD_2/Ar		437						INS	382
ammonia–argon	$NH_3–Ar$								FIR	383
										384
ammonia in nitrogen	NH_3/N_2	$Pa3$	638						INS	381
ammonia dimers	$(NH_3)_2$								TH	385
									TH	185
									TH	386
ammonia in cesium intercalated graphite	$(NH_3)_xCsC_{28}$		26/89/126						INS	387
									INS	388
ammonia in rubidium fullerite	$Rb_3C_{60}(NH_3)_x$		220						INS	221

Table 11. Ammonium Compounds: Hexahalo Compounds

compound name	compound formula	crystal structure	site symmetry	ν_t (μeV)	occurrence ratio	potential (meV)	T_{min} (K) (ω_o (MHz))	technique	ref
ammonium hexachloro-palladate	$(NH_4)_2PdCl_6$	$Fm3m$	$\bar{4}3m$	56 (2)	1			INS	389
								INS	97
								INS	122
								TH	390
								NS	164
platinate	$(NH_4)_2PtCl_6$	$Fm3m$	$\bar{4}3m$	34 (2)	1			INS	389
								LS	391
								LS	45
								TH	390
								NS	164
iridate	$(NH_4)_2IrCl_6$	$Fm3m$	$\bar{4}3m$	18.8 (2)	1			INS	389
								TH	390
								NS	164
osmate	$(NH_4)_2OsCl_6$	$Fm3m$	$\bar{4}3m$	11.6 (2)	1			INS	389
								NS	164
stannate	$(NH_4)_2SnCl_6$	$Fm3m$	$\bar{4}3m$	2.96 (2)	1			INS	392
								LS	45
								TH	393
								TH	394
								TH	390
	$(ND_4)_2SnCl_6$	$Fm3m$	$\bar{4}3m$	0.044 (2) (A–E)	1	61.1	60 (5.7)	D-NMR	395
									396
									397
									398
									399
								TH	283
	$(NH_{4-n}D_n)_2SnCl_6$ $n = 1,2,3$			(1/0.3/0.08)				TH	400
rhenate	$(NH_4)_2ReCl_6$	$Fm3m$	$\bar{4}3m$	8.4 (2)	1			INS	389
								TH	390
plumbate	$(NH_4)_2PbCl_6$	$Fm3m$	$\bar{4}3m$	0.14				NMR	401
								NMR	402
								LS	45
								TH	390

Table 11 (Continued)

compound name	compound formula	crystal structure	site symmetry	ν_t (μeV)	occurrence ratio	potential (meV)	T_{min} (K) (ω_o (MHz))	technique	ref
tellurate	$(NH_4)_2TeCl_6$	$Fm3m$	$\bar{4}3m$	0.11				FC	303
								TH	390
ammonium hexabromo-									
platinate	$(NH_4)_2PtBr_6$		3	6 (4)				INS	403
stannate	$(ND_4)_2SnBr_6$							D-NMR	404
ammonium/potassium hexachlorostannate	$(NH4)_{2-2x}K_{2x}SnCl_6$		$\bar{4}$	3 (2)				INS	405
ammonium hexafluoro-									
phosphate	NH_4PF_6		2	5 (7)				INS	406
	NH_3DPF_6			~1.8				INS	407
antimonate	NH_4SbF_6			5 (>2)				INS	Kearley
germanate	$(NH_4)_2GeF_6$	$P3m1$	$3m$					LS	45
				0.03				NMR	408
				0.4				TH	113
silicate	$(NH_4)_2SiF_6$	$Fm3m$	$\bar{4}3m$	0.04				TH	113
		$P3m1$	$3m$	0.5				TH	113
	$(NH_3D)_2SiF_6$	$Fm3m$						TH	390
titanate	$(NH_4)_2TiF_6$	$P3m1$	$3m$	(0.09)				TH	113

Table 12. Ammonium Compounds, Others and BH_4

compound name	compound formula	crystal structure	site symmetry	ν_t (μeV)	occurrence ratio	potential (meV)	T_{min} (K) (ω_o (MHz))	technique	ref
ammonium bromine	NH_4Br	cubic		5.1 kHz	1	155	166 (30)	NMR	409
									410
				(9.6 kHz)				TH	393
ammonium iodide	NH_4I	tetragonal		71.5 kHz	1	136.6	128 (17)	NMR	409
									410
				(96 kHz)				TH	393
ammonium/ kalium halides									
iodide	$(NH_4)_{.023}K_{.977}I$	$Fm3m$	$\bar{4}3m$	530−1200 (4)	1			INS	411
									412
									413
bromide	$(NH_4)_{.005}K_{.995}Br$	$Fm3m$	$\bar{4}3m$	1200 (3)	1			INS	411
								INS/HC	414
ammonium-alkali mixed halides	$(NH_4)_cM_{1-c}X$ [M = K, RB; X = I, Br, Cl] $(NH_4)_{.045}\,K_{0.955}I$	$Fm3m$		600				INS	415
									416
	$(NH_4)_{.032}K_{.968}Br$	$Fm3m$		515				TH	417
								INS	415
								HC	55
									416
	$(NH_4)_{.031}K_{.969}Cl$	$Fm3m$		480				INS	415
	$(NH_4)_{.03}Rb_{.97}I$	$Fm3m$		570/1250				INS	418
	$(NH_4)_{.03}Rb_{.97}Br$	$Fm3m$		470				INS	418
	$(NH_4)_{.03}Rb_{.97}Cl$	$Fm3m$		410				INS	418
ammonium perchlorate	NH_4ClO_4	$Pnma$	m	11.3 (5)	1			INS	419
								LS	45
								INS	420
								INS	421
				120−360(?)				IR	422
				(8.3/8.4/10.2)				TH	423
								NS	164
	ND_4ClO_4			0.088(A−E)	1	31.1	32 (6.6)	NMR-LS	391
									424
				0.079(A−E)				D-NMR	425
	ND_3HClO_4, NH_3DClO_4							TH	231
	NH_3DClO_4			~3		39		INS	407
ammonium tetrachloro-									
zincate	$(NH_4)_2ZnCl_4$			0.21 (4)				NMR	426
									427
palladate	$(NH_4)_2PdCl_4$			0.1 (3)				FC	Vandemaele
platinate	$(NH_4)_2PtCl_4$			0.1 (3)				FC	Vandemaele
ammonium tetraphenyl borate	$NH_4B(C_6H_5)_4$					small		OS,IR	428
									429
									430
									431
						62		IR,OS	432
ammonium tetrafluoroborate	NH_4BF_4 NH_3DBF_4	$Pnma$						IR,OS	433

Table 12 (Continued)

compound name	compound formula	crystal structure	site symmetry	ν_t (μeV)	occurrence ratio	potential (meV)	T_{min} (K) (ω_o (MHz))	technique	ref
ammonium perrhenate	NH_4ReO_4			0.013				NMR	408
								NS	164
ammonium sulfate	$(NH_4)_2SO_4$							LS	45
	$(NH_3D)_2SO_4$				1/2, 1/2	196/140		IR	434
ammonium cobalt sulfate (Tutton salt)	$(NH_4)_2Co(H_2O)_6(SO_4)_2$, $(NH_3D)Co(H_2O)_6(SO_4)_2$	$P2_1/a$		$1/\nu_t = 0.2$ h, 0.08 h				IR IR	65 435
ammonium nitrate	NH_4NO_3	orthorhombic (phase V)		$1/\nu_t = 1$ h		110			436
ammonium alkali metal sulfates	$(NH_4)_xK_ySO_4$							OS	437
	$(NH_4)_xRb_ySO_4$							OS	438
ammonium persulfate	$NH_4S_2O_7$			1.1				INS, LC-NMR	439
								INS	
sodium tetrahydroborate	$NaBH_4$			0.009				MW,TH	440
									441
poly(ammonium styrene sulfonate)								OS	438

Table 13. Methane, Silane, and Germane

compound name	compound formula	crystal structure	site symmetry	ν_t (μeV)	occurrence ratio	potential (meV)	T_{min} (K) (ω_o (MHz))	technique	ref
light methane									
phase II	CH_4 (II)	$Fm3c$	$\bar{4}2m$	142	3/4	23.9		INS	2
			432	1090	1/4				
								NMR	48
								TH	233
								TH	442
								TH	443
								INS	444
								INS	97
								INS	445
								INS	14
								INS	446
								INS	186
								NS	175
								TH	447
								NS	165
phase III	CH_4 (III)			180 (8)	1/2:1/4:1/4			INS	222
								HC	54
heavy methane									
phase III	CD_4 (III)			8 (8)	1/2:1/4:1/4			INS	448
phase II	CD_4 (II)	$Fm3c$		4.3/2.2				IR	64
								IR	449
				(4/434)				TH	447
partially deuterated methanes	CH_3D (II)	$Fm3c$	$\bar{4}2m$	82 (4)	3/4			INS	450
				(52/760−892)				TH	400
	CH_3D (III)			130(6)				INS	451
	CH_2D_2 (III)			70(4)				INS	451
	CHD_3 (III)			15				INS	451
silane	SiH_4	tetragonal (phase II)		0.2				FC	452
								NMR	453
								IR	454
								IR	455
germane	GeH_4	tetragonal (phase IV)		0.05				IR	454
								IR	455

Table 14. Methane, Mixed Systems

compound name	compound formula	crystal structure	site symmetry	ν_t (μeV)	occurrence ratio	potential (meV)	T_{min} (K) (ω_o (MHz))	technique	ref
methane/rare gas mixtures									
Krypton	$(CH_4)_{0.73}Kr_{0.27}$							INS	456
	$(CH_4)_{>0.8}Kr_{<0.2}$	$Fm3c$	432	1090	1/4			INS	457
			$\bar{4}3m$	140	3/4				
	$(CH_4)_{0.01}Kr_{0.99}$	$Fm3m$	432	970	1			INS	275
								INS	458
								IR	459
								INS	460
								INS	461
								INS	186
								INS	175
	CH_3D			690/840					85

Table 14 (Continued)

compound name	compound formula	crystal structure	site symmetry	ν_t (μeV)	occurrence ratio	potential (meV)	T_{min} (K) (ω_o (MHz))	technique	ref
Argon	$(CH_4)_{0.01}Ar_{0.99}$	$Fm3m$	432	890	1			INS	458
								IR	459
				900	2/3			INS	462
								INS	186
									175
				600	1/3			INS	98
				750/920				INS	463
	$(CH_{4-n}D_n)_{0.01}/Ar_{0.99}$			460−910				INS	110
	CH_3D			650/760					85
	CHD_3			515					86
									464
Xenon	$(CH_4)_{0.016}Xe_{0.984}$	$Fm3m$	432	1130	1			INS	458
								IR	459
				~990				IR/TH	465
								INS	186
								INS	175
								INS	466
Neon	$(CH_4)_{0.02}Ne_{0.98}$			<1000				INS	467
methane/ deuteriomethane	$(CH_4)_{1-x}(CD_4)_x$ (II)			75/143	3/4				468
	$(CH_4)_{1-x}(CD_4)_x$ (III)			<160(12)					
				1077	1/4				
methane in nitrogen	CH_4 in N_2	*hcp*	$\bar{3}$					IR	62
				1010					469
				400−1010					
methane in argon/ nitrogen	CH_4 in Ar/N_2	*fcc*/*hcp*		<880				INS	469

Table 15. Methane on Surfaces

compound name	compound formula	crystal structure	site symmetry	ν_t (μeV)	occurrence ratio	potential (meV)	T_{min} (K) (ω_o (MHz))	technique	ref
methane on grafoil	CH_4/C		C_{3v}	112 (5)	1			INS	470
									471
								TH	472
								INS	96
								INS	473
				(92/112)				TH	400
								HC	55
								HC	474
	CH_3D/C			55 (5)				INS	475
									111
				(16)				TH	400
								HC	55
	$(CH_4)_xKr_{1-x}/C$			800 (≥ 2)				INS	476
									477
methane on magnesium oxide	$CH_4/MgO(100)$		C_{2v}	70−451(8)		2.6		INS	478
	monolayer			55−457 (8)				INS	479
	doublelayer			55−457 (8)				INS	479
				880−1080 (3)					
				(216)				TH	400
	$CH_3D/MgO(100)$			140				INS	Larese
				(54)				TH	400
methane in Cs intercalated	$C_{24}Cs(CH_4)$			<1					480
graphite									481
									482
	$C_{28}Cs(CD_4)$								483
methane in silica	CH_4/SiO_2			(50−1100)	1			INS	484
									471
methane in docecasil 3C				<1100					484
methane in silica gel 100				<1100					484
methane in MCM-41				<400					484

Table 16. Hydrogen

compound name	compound formula	crystal structure	site symmetry	ν_t (μeV)	occurrence ratio	potential (meV)	technique	ref
hydrogen in cesium	$C_{24}Cs(H_2)_x$			799	2 sites			485
intercalated graphite								486
hydrogen in rubidium	$C_{24}Rb(H_2)_x$			595/1170/1340	2 sites		INS	485
intercalated graphite								486

Table 16 (Continued)

compound name	compound formula	crystal structure	site symmetry	ν_t (μeV)	occurrence ratio	potential (meV)	technique	ref
hydrogen in argon	H_2/Ar			14500			INS	487
hydrogen in CoNaA zeolite				3800		55−60	INS	488
H_2 in $M(CO)_3(R_3)_2$ (η^2-H_2)	M = W, R = i-C_3H_7			90			INS	489
							INS	490
	M = W, R = C_6H_{11}			110		96	INS	491
							INS	489
							INS	490
	M = Mo, R = C_6H_{11}			350			INS	490
	M = Cr, R = C_6H_{11}			537			INS	492
							INS	490
H_2 in Mo(CO)(η^2-H_2)-(dppe-d_{20})$_2$·X	X = 4.5C_6D_6			1560			INS	490
	X = 2$C_6D_5CD_3$			2140			INS	490
other H_2 complexes	trans (Fe(ηH_2)						INS	493
	$(H)(H_2CH_2PPh_2)_2)BF_4$			260		100	INS	490
	$MH(\eta^2$-$H_2)PPh_3$ BPh_3						INS	494
	M = Fe			143		79	INS	490
	M = Ru			320		59	INS	490
	$IrClH_2(\eta^2$-$H_2)(P$-i-$Pr_3)_2$			2460		22	INS	495
							INS	490
	$[FeH(H_2)(dppe)]BF_4$			260			INS	490
	$[FeH(H_2)(PP_3)]^+$					91	INS	490
	$FeH(H_2)(PEtPh_2)_3$			793			INS	490
	$RuH_2(H_2)_2(PC_6H_{11})_2$			535		48	INS	490

Table 17. Translational Tunneling

compound name	compound formula	crystal structure	site symmetry	ν_t (μeV)	occurrence ratio	potential (meV)	technique	ref
hydrogen chlorine dimers	$(HCl)_2$			1920				63
								496
								497
hydrogen sulfide in potassium chlorine	H_2S/KCl			2000			INS	498
hydrogen sulfide−carbon dioxide vdW complex	H_2S-CO_2							499
hydrogen chlorine−diborane	HCl-B_2H_6							500
hydrogen chlorine in hydrochinone clathrate	HCl			4300			INS	501
hydrogen fluoride dimers	$(HF)_2$							502
				80				503
water dimers	$(H_2O)_2$							504
								505
								506
								507
hydroxyl in NaCl	OH^--NaCl							508
water−carbon monoxide	H_2O-CO							509
water−argon complex	H_2O-Ar							384
H_2O in argon		*fcc*		2850			INS	510
							INS	511
sulfur dioxide−argon	SO_2-Ar							512
acetylene−carbon dioxide dimers	$((C_2H_2)_2$, $(CO_2)_2$							513
	C_2H_2-CO_2							514
hydrogen in *meso*-tetrapheylporphine	2H in 4N			5 Hz				515
hydrogen in tantal	$TaO_{0.0006}D_{0.0025}$	*bcc*		65			AR	
hydrogen in yttrium	$YO_{0.002}H_{0.016}$	*hcp*					AR	
hydrogen in niobium	$Nb(CH)_{0.0002}$			162			INS	
	$Nb(OH)_{0.0002}$			226			INS	
hydrogen in niobium−titanium	$Nb_{1-x}Ti_xH_y$			200/400			INS	
hydrogen in niobium−zirconium	$Nb_{1-x}Zr_{0.0045}H_y$			4 levels				519
carboxylic acid dimers	$(CH_3COOH)_2$			(140−250) kHz			SQUID-NMR	520
benzoic acid dimers	$(HCOOH)_2$							242
								521
							NMR	24
							NMR	522
							NMR	523
							OS	61
tetrafluoroterephtalic acid	(X-COOH)$_2$							524

6. Outlook

Tunnelling spectroscopy using neutrons started in the 1970s as an exotic application of high-resolution neutron spectroscopy. Neutron scattering, compared to NMR, quickly proved to be a very direct and powerful method for studying molecular tunneling. Once a quantitative understanding of the scattering function in the mean-field single particle model (SPM) was established, the technique became ready for standard application.

As in vibrational spectroscopy, the originally simple SPM required a variety of extensions, mainly taking into account various types of interaction, from directly coupled methyl groups to rotation−translation−coupling. The development of specific models is needed for many new complex systems under study. Such systems are described by multidimensional potential surfaces. A broader spectroscopic access is required to characterize such potential surfaces.

One of the most promising future applications of tunneling spectroscopy is to combine it with computer modeling (molecular dynamics (MD)) and to extract better intermolecular pair potentials (IPP). In particular, the repulsive part of these potentials can be improved substantially. Remember that no other excitation than tunneling is so sensitive to small changes of the potential surface. Potential surfaces of excited molecular states can also be explored in special cases. Phenomenological transferable pair potentials still play the most important role in exploring reaction paths ahead of real chemical manufacturing or in characterizing the interaction between two molecules in biological systems.

The evolution of the dynamical behavior of a methyl group coupled to the thermal bath of phonons, revealed by the temperature dependence of the scattering function, can be considered as the model system par excellence describing the transition from quantum to classical mechanics. Such data offer a basis to test fundamental concepts of solid-state physics. For rotation−translation coupled systems increasing temperature leads to a transition from ordered to chaotic trajectories. This phenomenon will probably lead to future studies of the temperature dependence of rotational tunneling of appropriate systems.

Finally, tunneling is a fundamental process influencing dynamical properties of many different materials. For example, the low-temperature properties of glasses are widely determined by two level tunneling states. The similarity of the concepts applied in both fields, rotational and translational tunneling,[27] should enable significant mutual progress to be made.

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