# The Methyl Rotational Potentials of Various Isotopic Methyl Iodides and Their Coupling to Phonons

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The rotational potentials of methyl groups in protonated and deuterated methyl iodide were determined from the observed tunnel splittings and the librational energies. The potential becomes stronger in the deuterated matrix by about 10 %. For pure $CD_3I$ the isotope effect on the librational modes shows a considerable further increase. No rotor-rotor coupling is found. The coupling to low-frequency phonons can explain the unusual increase of the tunnel splitting with temperature observed for T < 15 K.

## 1. Introduction

The methyl halides are the simplest molecules containing $CH_3$ groups and thus among the most simple molecules of all. They represent a symmetric prolate top, with the small momentum of inertia being equal to that of the $CH_3$ group. Methyl iodide has only one solid phase: Pnma with Z=4 molecules at c-sites /2/. The molecules are arranged in the a-c-plane as chains along the c-direction with alternating orientation of the molecules.

Various reasons make the methyl iodide interesting from the point of view of methyl group rotation: i) because of the molecular symmetry there is no intra-molecular hindering potential. The methyl rotation is identical with the overall rotation of the whole molecule around its small axis of inertia. The rotational potential fully originates from the interaction with neighbouring molecules. ii) The temperature behaviour of the tunnelling modes, i.e. their coupling to to phonons /3,4/, might be especially simple because the libration of the methyl group is an external mode. In force models available for molecular crystals /5,6/ it can be found out by symmetry analysis with what phonons at all the methyl rotation can interact. Thus not the full density of states /4/ but individual phonon branches might be of importance. This could stimulate new theoretical efforts. iii) The lattice dynamics of molecular crystals consisting of polar molecules is an actually very active field /6/. Due to the simplicity of the molecules and the structure of the methyl halides $CH_3I$ might be a candidate for a model system in this field.

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[1] This work is a part of a more comprehensive study of the methyl halides /1/

While methyl iodide is already intensively investigated with the Raman and FIR technique /7,8/ there is only one incoherent neutron scattering experiment known to us /9/ which was mainly concentrating on multiphonon scattering and not on the methyl group rotation. It is the scope of the present experiment, covering the energy range from 0.4 µeV to 60 meV and temperatures from 4K to 100K for various isotopic species, to determine the rotational potential of the methyl groups, the effect of isotopic substitution on this potential and the coupling of the quantum rotor to phonons.

## 2. Experiments and Results

The high-resolution experiments were performed at the backscattering spectro-meter IN10 at the ILL, Grenoble, using the best obtainable energy resolution $\delta E_{el}$ = 0.4 µeV. The energy range $2 < E \; [meV] < 60$ was investigated with the thermal time-of-flight spectrometer SV22 at the FRJ2 in Jülich using various combinations of incoming neutron energy and energy resolution.

The high-resolution spectrum of $CH_3I$ shows a tunnelling peak of resolution width at an energy transfer $\hbar\omega_t$ = 2.44 µeV (fig 1). With temperature this peak behaves quite unusually (fig. 2): Its frequency increases up to a temperature $T \sim 20$ K. Thereafter it decreases as usually observed. The broadening, described by a Lorentzian, follows in the whole temperature range very well an Arrhenius be-haviour with an activation energy $E_a^\Gamma$ = 14 meV. Tunnelling spectra were also recorded for 2 % and 50 % $CH_3I$ in $CD_3I$. A linear decrease with concentration is found yielding for infinitely low concentration $\hbar\omega_t$ = 2.02 µeV.

The prominent feature of the spectra in the meV region is a strong doublet line. Fig. 3 shows spectra of $CH_3I$, $CH_3I$ in $CD_3I$ and $CD_3I$. With increasing temperature
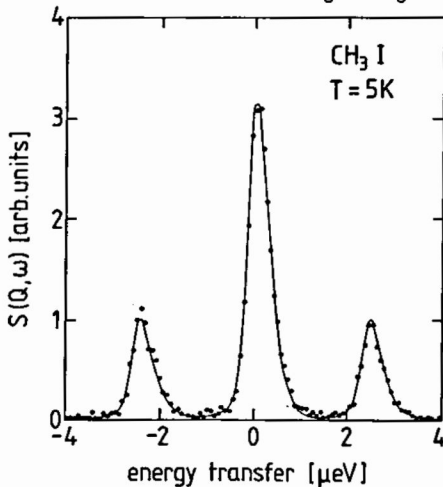


Fig. 1 Tunnelling spectrum of $CH_3I$.
Energy resolution $\delta E$=0.4 µeV.
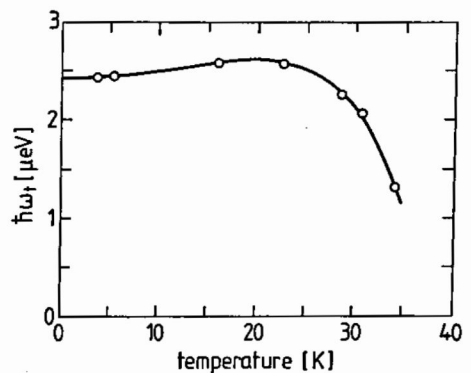Momentum transfer Q=1.88 $\AA^{-1}$.

Fig. 2 Temperature dependence of
the tunnel splitting in $CH_3I$.
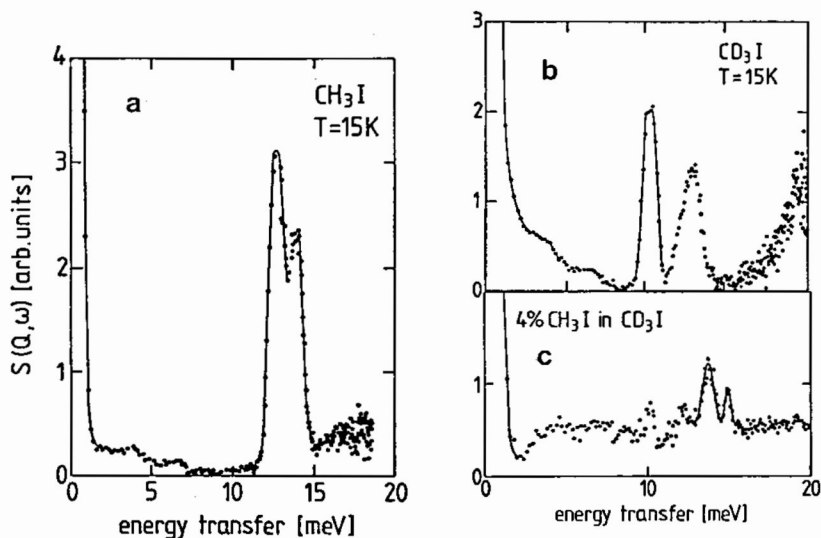The solid line is a fit with
the model described in the text.

Fig. 3 Spectra of a) $CH_3I$, b) $CD_3I$ and c) $CH_3I$ in $CD_3I$ (the spectrum of $CD_3I$ is subtracted to show only the transition energies of the protonated molecules) in the meV region. The low-energy peak of each doublet represents the libration of the methyl groups. See the text.

all transition energies shift to lower values and the line intensities diminish. The lines at 13.27 meV in $CH_3I$, 13.8 meV in $CH_3I$ diluted in $CD_3I$ and 10.6 meV in $CD_3I$ are faster damped with temperature than each second strong peak.

3. Discussion

As a consequence of the structure /1/ all methyl groups in solid methyl iodide are equivalent. The relative intensities of the tunnelling and elastic lines (fig. 1) are in agreement with the theoretically predicted values. No effect of coupling, suggestable from the head-to-head arrangement of the molecules and as found in lithium acetate /10/, is seen in the tunnelling spectrum. We first also believed that the doublet line in the meV region is a consequence of coupling. However, because of the different temperature dependences of the two lines and because of the different isotope effects (see below), they must be of different origin.

Since no effects of rotor-rotor coupling could be found we describe the methyl rotational energies by a single particle rotational potential:

$$V(\varphi) = \frac{V_3}{2} \cos 3\varphi + \frac{V_6}{2} \cos 6\varphi \quad . \tag{1}$$

From the eigenvalues $\hbar\omega_t = 2.44$ µeV and $E_{01} = 13.27$ meV we obtain

$$VS = V_3 + V_6 = 24.9 \text{ meV}, \qquad \delta = \frac{V_3}{VS} = 0.92 \quad . \tag{2}$$

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A second solution with $V_3$, $V_6 < 0$ can be excluded from the measured isotope effect (see below). Thus, in agreement with the general experience /10/, the deviation from a purely threefold cosine potential is small. The potential also describes rather well the second excited librational state found at 24.2 meV (calculated energy 24.6 meV). The second strong peak at 14.54 meV is assigned to a libration $R_x$, $R_y$ of the molecule perpendicular to its symmetry axis.

Beside the temperature dependence, the isotope effect is useful to identify the character of the modes related with the observed transition energies. Generally the absolute strength of the potentials changes not or very little by deuteration,and the eigenvalues of the deuterated compound are obtained by simply scaling the masses. For librational modes the effect is roughly of the order $\sqrt{2}$. In $CH_3I$ we expect exactly 1.35 by scaling the potential (2). However, in $CD_3I$ we find only a shift by a factor 1.25 to 10.6 meV. The mode at 10.6 meV was identified as libration via its temperature dependence. This means that the rotational potential must have considerably increased by deuteration. Keeping fixed the shape of the potential (2), characterized by $\delta$, we find VS = 29.5 meV or an increase by 25 %, probably caused by a relaxation of the $CD_3I$ molecule into a new equilibrium orientation in the a-c-plane. Because of this strong isotope effect,earlier Raman and FIR lines were wrongly assigned /6/. The $R_x$, $R_y$ libration has little decreased to 13.1 meV as expected.

An independent determination of this large isotope effect was achieved by using $CH_3I$ as a probe in the matrix of $CD_3I$. Now two independent transition energies, $\hbar\omega_t$ = 2.02 µeV and $E_{01}$=13.8 meV are available to determine the rotational potential. The shape is found to be unchanged,while the strength has increased by 10 % to VS = 27.5 meV compared to pure $CH_3I$. It is reasonable that the potential is weaker than for pure $CD_3I$ since the properties of both, the surrounding and the 'Auf'-molecule, enter in the interaction (e.g. octopole-octopole interaction in methane).

The tunnel splitting in methyl iodide shows a very unusual increase with temperature before it decreases in the well-known way /11/. A similar behaviour wasrecently found in some other materials also, e.g. /12/ and /13/. The large isotope effect has already shown that the molecular orientation in methyl iodide is sensitive to shallow changes of the interaction. Thus we expect that it also might be influenced by the temperature and change the rotational potential. Such a temperature behaviour can be described in a model which couples the quantum rotor to low-energy phonons via an interaction Hamiltonian

$$H^c_{int} = g^c \sqrt{2m\tilde{\omega}/\hbar} \, x \cos3\varphi \tag{3}$$

not considered so far /3,4/. Here $g^c$ is the coupling constant, x the oscillator coordinate and $\varphi$ the rotational angle. The Hamiltonian of the whole system is

$$H = H_{rot} + H_{osc} + H^c_{int} \tag{4}$$

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with
$$H_{rot} = \frac{L_\varphi^2}{2\theta} + V_3 \cos 3\varphi ,$$

$$H_{osc} = \frac{p^2}{2m} + \frac{m}{2} \tilde{\omega}^2 x^2 .$$

Using the formalism developed in ref. 14 the tunnelling frequency correspon-
ding to the excitation of n and n + 1 oscillator levels is found to change as

$$\hbar \omega_t(n+1) / \hbar \omega_t(n) = 1 + A^C, \quad \text{with } A^C > 0$$

for moderate coupling $g^C$. If the decrease of the tunnelling frequency at higher
temperatures is taken into account phenomenologically, we get the following
expression for the temperature dependence of the tunnelling frequency

$$\hbar \omega_t(T) = \hbar \omega_t(o) \left\{ \frac{1-\exp(-E^C/k_B T)}{1-(1+A^C)\exp(-E^C/k_B T)} - A^S \exp(-E^S/k_B T) \right\} . \tag{5}$$

The solid curve in fig. 2 is a fit using this formula with parameters $A^C = 0.22$,
$A^S = 49.06$, $E^C = 2.15$ meV and $E^S = 12.94$ meV. While $E^S$ is close to $E_{01}$ as usu-
ally found, $E^C$ represents the phonon energy. Indeed the density of states shows
increased intensity in this energy range (fig. 3). The coupling parameter derived
from these values is $g^C = 2.9$ meV, the strength of the rotational potential
$V_3 = 18.2$ meV.

## 4. Conclusions

Rotational tunnelling and librations of methyl iodide could be well explained
as a single particle rotation. No methyl rotor-rotor coupling, suggested from
the structure, can be observed: the two transitions around 14 meV belong to
two different molecular rotations (around and perpendicular to the symmetry
axis) and are not a consequence of coupling. With deuteration the rotational
potential of the methyl group increases by 25 %, probably due to a change of
the equilibrium orientation. This large isotope effect beside the simple mass
effect is unambiguously confirmed by using $CH_3I$ as a probe in $CD_3I$. The very
unusual increase of the tunnel splitting with temperature for T < 15 K could
be explained by a coupling to low-frequency phonons via an interaction Hamiltonian
$H_{int}^C \sim x \cos 3\varphi$ not considered so far.
It would be very useful for a more thorough interpretation of our data to in-
vestigate the lattice dynamics of methyl iodide.

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