HOMOGENEOUS IR LINE SHAPE OF MATRIX ISOLATED MOLECULES
IN THE DEBYE APPROXIMATION

Martin DUBS
Laboratory for Physical Chemistry, Swiss Federal Institute of Technology,
ETH-Zentrum, CH-8092 Zürich, Switzerland

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The homogeneous line shape of vibrational transitions of matrix isolated molecules is calculated in the Debye approximation for lattice vibrations. The interaction between matrix and molecule is assumed anharmonic and expressed in space time phonon correlation functions. Excluding local modes and libration of the molecule, analytical expressions for the temperature dependence of line width and line shift are derived which permit verification by experiment.

1. Introduction

Application of high resolution laser spectroscopy to molecules isolated in rare gas matrices made precise line shape measurements of vibrational transitions possible and stimulated the present theoretical study. Apart from irreversible changes of absorption profiles with temperature, which are attributed to lattice and molecule reorientation, clear evidence of reproducible and reversible temperature effects have been found [1]. These can be explained by anharmonic interactions between molecule and matrix, leading to vibrational modulation effects. Theories using correlation functions for the calculation of homogeneous line shapes have to our knowledge only been applied to diatomic molecules [2,3]. The extension to polyatomic molecules would be straightforward, but lack of detailed knowledge of interaction potentials makes theories difficult to verify experimentally. In this paper the complexity of the problem is reduced considerably by restriction to low temperatures and assuming a Debye phonon spectrum. In correspondence to the Debye theory of specific heat, expressions for temperature dependent matrix shifts and line widths are derived. Several other mechanisms influence line width (translational and librational modes of the molecule, local modes of the lattice), but in order to arrive at manageable expressions these mechanisms have been excluded in the present work. They are treated by other authors [2,4], using the same formalism. Contained in our equations is therefore only the contribution of bulk modes of the matrix to line width.

Inhomogeneous broadening, multiple site and concentration effects are not treated in the present paper. They depend to a large extent on experimental conditions during deposition of the matrix and require detailed knowledge of matrix structure and the condensation process.

2. The model

We examine a single molecule at a substitutional site in a perfect lattice of noble gas atoms, interacting weakly via intermolecular forces with nearest neighbours. The model Hamiltonian is written

\[ H = H_1 + H_2 + V, \]  

\[ H_1 = \frac{1}{2} \sum_{k=1}^{3n} (\omega_k^2 Q_k^2 - \hbar^2 \frac{d^2}{dQ_k^2}), \]
where $Q_k$ are normal coordinates including internal, translational and librational coordinates, related to cartesian displacement vectors as follows:

$$q_j = (m_j)^{-1/2} \sum_{k=1}^{3n} l_{jk} Q_k \quad (j = 1, ..., n),$$  

\[ (3) \]

$H_2$ is the hamiltonian of the lattice in the harmonic approximation, written in phonon creation and destruction operators (without molecule and associated local modes):

$$H_2 = \sum_{k,p} \hbar \omega_p (k) (a_{kp}^+ a_{kp} + \frac{1}{2}),$$  

\[ (4) \]

with the cartesian coordinates [5]:

$$u(l) = \frac{\hbar}{2NM} \sum_{k,p} \epsilon(k, p) [\omega_p(k)]^{-1/2} \exp[i k \cdot x(l)] (a_{kp}^+ + a_{kp}),$$  

\[ (5) \]

for the displacements $u(l)$ of the $l$th atom with mass $M$ and equilibrium coordinates $x(l)$. The origin of the coordinate system $x(0)$ is chosen at the center of the molecular site. For the present model we use a sphere with radius $k_D$ and the summation by an integration over this sphere. Coupling between molecule and lattice is provided by the anharmonic interaction potential $V$, expressed as a sum over pair potentials $V_{jl}(r)$ between atoms of the molecule and the lattice ($V$ may contain also anharmonic interactions between lattice atoms, which however can be neglected, as an estimate of phonon lifetime shows). It is expanded in a Taylor series of the displacements $u(l)$ and $q_j$ up to fourth order:

$$V = \sum_{l,m} V_{jl}^{(n)} d_{jl}^m / n!,$$  

\[ (6) \]

$$V_{jl}^{(n)} = \frac{\partial^n V_{jl}(r)}{\partial r^n} \bigg|_{r=|x(l)| - x(l)},$$  

\[ (6') \]

$$d_{jl} = [u(l) - u(0)] \cdot e_{jl} - q_j \cdot e_{jl},$$  

\[ (7) \]

$$e_{jl} = [x(l) - x(j)] / |x(l) - x(j)|,$$

with the assumption that the displacement of the center of the molecule is described by eq. (5). This is only true when neglecting local modes, but justified because we are interested in the influence of the pure phonon field. In the following calculations we limit ourselves to a single, nondegenerate, isolated transition $\nu_k = 0 \rightarrow \nu_k = 1$, with frequency much higher than maximum phonon energy, so that the influence of vibrational relaxation on line width can be neglected [6].

3. Calculation of line shape

As a starting point we express the line shape as the Fourier transform of the dipole moment correlation function [7]:

$$I_0(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp[i \omega t \langle [e \cdot \mu(t), e \cdot \mu(0)] \rangle],$$  

\[ (8) \]

where the bracket denotes averaging over phonon and molecular states in thermodynamic equilibrium, $e$ the polarization vector of the incident wave and $\mu(t)$ the dipole moment operator in the Heisenberg representation. The theory for calculation of the correlation function is presented in ref. [8] for Raman scattering and summarized in ref. [2] for Raman scattering and IR absorption. Therefore we can give the result of expressing the line shape by correlation functions of the potential. In this derivation [2] the correlation function has been evaluated using Liouville operator formalism and Kubo's cumulant expansion method [9]. The line shape of a single transition up to second order in the potential $V$ can be written as:

$$I_{ij}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp[i (\omega + \omega_f)t$$

$$+ i\hbar^{-1}(\langle \hat{J}(V) \rangle \hat{H} - \langle \hat{J}(V) \hat{H} \rangle )]$$

$$\times \exp\left[ -\hbar^{-2} \int_{0}^{t} dt(t - t') \right]$$

$$\times \left[ \sum_{l \neq f} e^{-i\omega_{lf}t} \langle j(V(l)) | f' \rangle \langle f'| V(l') | f \rangle$$

$$+ \sum_{l \neq f} e^{i\omega_{lf}t} \langle f(V(l')) | f' \rangle \langle f'| V(l) | f \rangle$$

$$+ \langle \hat{J}(\Delta V(l)) | \hat{H} \rangle \langle \hat{J}(\Delta V(l)) \rangle \right].$$
\[ I_0 = \frac{1}{2} I_0'(\rho_i - \rho_i')^2, \]

with \( \Delta V(t) = V(t) - \langle V \rangle \) and \( \omega_{ij} = \hbar (E_i - E_j) \) \( (E_i \) is eigenvalue of \( H_1 \) to the eigenstate \( \ket{i} \). \( \langle \cdot \rangle \) denotes the ensemble average over the lattice coordinates and their time evolution (in contrast to ref. [2], libra-
tion and translation of the molecule are contained in \( H_1 \)). It can be proved [10] that for calculation of the zero phonon line only adiabatic terms have to be considered (the zero phonon line is what is usually ob-
erved in IR matrix spectroscopy, the phonon wings are generally weak and dispersed over a broad range of frequencies, so that they are measured only in very thick matrices [11]). Summation over the terms with \( i \neq i' \) and \( f \neq f' \) will therefore be omitted in the following calculations. The main problem treated in this paper consists in the explicit calculation of the correlation functions of the matrix elements of \( V \), given by eq. (6). Correlation functions

\[ \langle u_{\alpha}(l, t) u_{\beta}^*(l', t') \rangle \quad (\alpha, \beta = x, y, z), \]

for the displacement operators of the lattice in the interaction representation are used and calculated in the Debye approximation in closed form (see appendix A). For the adiabatic terms in (9) a Taylor series expansion of \( V \) allows us immediately to see which terms contribute to line width and line shift. The poten-
tial has to contain even, nonzero powers of \( q \), otherwise the diagonal elements vanish and even pow-
ers of \( u \), otherwise the correlation functions oscillate rapidly without influence on the zero phonon line' (apart from a decrease in intensity). The harmonic contribution in \( V \) has been absorbed in \( H_1 \). Restricting the potential expansion to fourth order, only the terms quadratic in both \( q \) and \( u \) give a contribution to line width and a temperature dependent matrix shift. To this shift the influence of thermal expansion of the lattice, mainly caused by \( V^{(3)} \) has to be added.

Retaining only terms quadratic in \( q \) and \( u \) we get the interaction potential relevant for the zero phonon line width:

\[ V = \frac{1}{4} \sum_{j,l} V^{(4)}_{jl} \langle [u(l) - u(0)] \cdot e_j \rangle^2 \langle q_j \cdot e_{jl} \rangle^2, \]

and for the correlation function of the potential

\[ \langle V(l) V(0) \rangle = \frac{1}{4} \sum_{j,l} V^{(4)}_{jl} \langle d(l) \cdot e_j \rangle^2 \langle d(l', 0) \cdot e_{jl} \rangle^2, \]

with

\[ V^{(4)}_{jl} = V^{(4)}_{jl} (q_j \cdot e_j) (q_j \cdot e_{jl})^2, \]

and \( d(l, t) = u(l, t) - u(0, t) \) in the interaction representation. Making use of the properties of the correlation functions in the Debye approximation (see appendix B) this can be transformed to

\[ \langle \Delta V(t) \Delta V(0) \rangle = \frac{1}{8} \sum_{j,l} V^{(4)}_{jl} \langle q_j \cdot e_{jl} \rangle^2 \times \langle d_{\alpha}(l, t) d_{\alpha}(l', 0) \rangle^2. \]

In this and the following steps the assumption is made that all lattice points \( l \) appearing in the sum have the same distance \(|x(l)|\) from the center \( x(0) \) (nearest neighbours). All the space time correlation functions in the last equation can be expressed by the normalized space time correlation functions defined in appendix A:

\[ \langle u_{\alpha}(l, t) u_{\alpha}^* (l', 0) \rangle = (3\hbar/4M\omega_D) \varphi(R_{Hl}, \tau, \theta), \]

with \( R_{Hl} = |x(l) - x(l')| k_D^{-1}, \tau = t\omega_D, \)

\[ \langle d_{\alpha}(l, t) d_{\alpha}(l', 0) \rangle = (3\hbar/4M\omega_D) \psi(R_{Hl}, \tau, \theta), \]

\[ \varphi(R_{Hl}, \tau, \theta) = [\varphi(R_{Hl}, \tau, \theta) - 2\varphi(a, \tau, \theta) + \varphi(0, \tau, \theta)]^2, \]

\( R_{Hl} \) and \( a \) are the distances between lattice points in units of the Debye radius \( 1/k_D \). For a face centered cubic lattice \( R_{Hl} \) can assume the following values (for nearest neighbour shell) \( R_{Hl} \in [0, a, 3/2a, 2a] \), with \( a = 21/2(3\pi^2)^{1/3} \) \( (l, \tau = 1, 12) \). For the calculation of the zero phonon line shape we can replace the integral in the exponent of eq. (9) for large \( t \) by its asymptotic value \( |f|_{10}^\infty dr'(...) \) since the correlation functions in the bracket go to zero for \( t' \gg \tau_c \), the correlation time of the perturbing potential, which is of the order of the inverse Debye frequency for a solid. Since \( \varphi \) is already in a suitable integral form we can express the integral:

\[ \text{Re} \int_0^\infty d\tau \psi(R_{Hl}, \tau, \theta) = \frac{1}{2} \int_0^\infty d\tau \tilde{\psi}(R_{Hl}, \tau, \theta), \]
by the Fourier transform of \( \psi \) at \( x = 0 \) and remark that \( \tilde{\psi} \) is the convolution of the Fourier transform of a linear combination of functions \( \varphi(R_H', \tau, \Theta) \) with itself:

\[
\text{Re} \int_0^\infty \text{d}r \psi(R_H', \tau, \Theta) = \pi \tilde{\psi}(R_H', x, \Theta)
\]

\[
= 2\pi \int_0^1 \text{d}x \left[ \frac{\sin R_H' x}{R_H' a} - \frac{2 \sin ax}{a} + x \right]^2 \sinh \frac{x}{2\Theta} \frac{1}{2}
\]

\[
= 2\pi F(R_H', \Theta)
\]

(17)

(see fig. 1). We obtain finally, from eqs. (3), (9), (12), (14) and (17) inserting the matrix elements of \( Q_k^2 \) for the transition \( \nu_k = 0 \) to \( \nu_k = 1 \) (\( \nu_{k'} = 0 \) for \( k' \neq k \))

\[
I_{ff}(\omega) = \frac{I_0}{2\pi} \int_0^\infty \text{d}r e^{i[\omega - \omega_0(\Theta)] r} e^{-r/\Gamma}
\]

\[
= \frac{I_0}{\pi} \left[ \frac{I_0}{\omega - \omega_0(\Theta)} \right]^2 + \Gamma^2,
\]

with

\[
\Gamma = \frac{9\hbar^2 \pi}{64\omega_D^3 \omega_F^2 M^2 R_H^2 m_j^2} \sum_{jl} \frac{V_{jl}^{(4)}(1)}{m_j^2} (l_j^* \cdot e_{jl})^2
\]

\[
\times \int_0^1 \text{d}x \left[ \frac{\sin R_H' x}{R_H' a} - \frac{2 \sin ax}{a} + x \right]^2 \sinh \frac{x}{2\Theta} \frac{1}{2}
\]

\[
\omega_0(\Theta) = (E_f - E_F)/\hbar + \omega_{ph}(\Theta) + \omega_{te}(\Theta).
\]

(20)

The temperature dependent matrix shift consists of two distinct contributions:

\[
\omega_{ph}(\Theta) = \frac{3\hbar}{4M\omega_D \omega_{Fl}} \sum_{jl} V_{jl}^{(4)}(l_j^* \cdot e_{jl})^2 m_j^{-1}
\]

\[
\times \int_0^1 \text{d}x \left( x - \frac{\sin ax}{a} \right) \coth \frac{x}{2\Theta},
\]

\[
\omega_{ph} \text{ is the contribution of the phonons, calculated from eq. (9) with the aid of the expression for} \langle d_{\alpha}^2(l, 0) \rangle \text{ derived from (A.10)}
\]

\[
\omega_{te}(\Theta) = \frac{1}{2\omega_{Fl}} d_l(\Theta) \sum_{jl} V_{jl}^{(3)}(l_j^* \cdot e_{jl})^2/m_j
\]

\[
\omega_{te} \text{ is the contribution of the thermal expansion of the lattice which has not been included in the former equations but has been calculated separately.} \]

\[
\text{fig. (21)}
\]

\[
R_H' = 0 \text{ (for comparison T approximation; } \cdots \text{ R_H'} = a; \cdots \text{ R_H'} = 2a; \cdots \text{ R_H'} = 3a/2)
\]

\[
\times \sum_{jl} V_{jl}^{(3)}(l_j^* \cdot e_{jl})^2/m_j.
\]

(22)
atoms per unit volume) which relates thermal expansion and energy density of the lattice vibrations.

4. Discussion of the result

The result obtained in eqs. (18)–(22) gives the contribution of the lattice modes to the vibrational line shape of the zero phonon transition of a matrix isolated molecule. If the molecule occupies a substitutional site in a face centered cubic lattice as was assumed above, line width as a function of temperature can be expressed as a sum over four simple integrals multiplied with interaction constants depending upon properties of the lattice ($\omega_D$) and the assumed geometry and normal modes of the molecule and the strength of the anharmonic interaction potential. The normalized integrals as a function of $T/\Theta_D$ are represented in fig. 1 for different values of $R_H$. As a Taylor series expansion shows, the calculated line width should be proportional to $T^7$, but only at very low temperatures as can be seen from the figure. The shift of the lines should be proportional to $T^4$ at low temperatures or in other words proportional to the thermal energy of the lattice ($T^3$ law for specific heat): This corresponds to the results in ref. [10] for an electronic transition.

Experimental evidence for the temperature dependent shift has been found recently in high resolution matrix spectra of acetaldehyde [13], an increase in line width was observed as well, but was masked by inhomogeneous broadening of $\approx 0.1$ cm$^{-1}$ line width.

Another check for the model would be the measurement of line shape. Our Debye model predicts a lorentzian profile, in contrast to the results of ref. [2] where with a different model (Einstein phonon spectrum) a gaussian line shape was predicted. The same problem as with line width arises also in the experimental determination of homogeneous line shape masked by inhomogeneous broadening. In the future double resonance experiments with tunable lasers might give an answer.

Appendix A: Space time correlation functions of $u(x, t)$ in the Debye approximation

In the Debye approximation the calculation of $\langle u_\alpha(x, t)u_\beta^*(0, 0) \rangle$ can be performed explicitly. We start from the usual equation for this correlation function [5]:

$$\langle u_\alpha(x, t)u_\beta^*(0, 0) \rangle = \frac{\hbar}{2NM} \sum_{k,p} e_{\alpha}(k, p) e_{\beta}^*(k, p) \frac{\omega_p(k)}{\omega_p(k)} e^{ikx} \times \left[ (n_{kp} + 1)e^{-i\omega_p(k)t} + n_{kp} e^{i\omega_p(k)t} \right], \quad (A.1)$$

with

$$n_{kp} = \left\{ \exp \left[ \frac{\hbar \omega_p(k)}{k_B T} \right] - 1 \right\}^{-1}. \quad (A.2)$$

The summation over $k$ can be replaced by an integration over the Debye sphere, the sum over $p$ can be performed making use of the closure relation of $e(k, p)$

$$\sum_p e_{\alpha}(k, p)e_{\beta}^*(k, p) = \delta_{\alpha\beta}. \quad (A.3)$$

Neglecting dispersion and the difference between longitudinal and transversal sound velocity we can introduce the “average” sound velocity $c$ by

$$c^{-3} = \frac{1}{3} c_l^{-3} + \frac{2}{3} c_t^{-3}, \quad \omega_p(k) = c|k|. \quad (A.4)$$

In spherical coordinates (axis in direction of $x$) integration over $\varphi$ and $\theta$ can be carried out and we obtain for the correlation function

$$\langle u_\alpha(x, t)u_\beta^*(0, 0) \rangle = \delta_{\alpha\beta} \frac{3\hbar}{2M\omega_D^3} \int_0^{\omega_D} d\omega \frac{\sin(\omega|x|/c)}{|x|/c} \times \left[ \frac{2\cos \omega t}{\exp \left( \frac{\hbar \omega}{k_B T} \right) - 1} + \exp \left( -i\omega t \right) \right]. \quad (A.5)$$

For the purpose of this study it is useful to express this correlation function in dimensionless parameters and normalize it appropriately. We introduce

(i) $\rho = |x|/k_D$, distance in units of the Debye radius $k_D^{-1}$,

(ii) $\tau = t\omega_D$, time in units of the inverse Debye frequency,

(iii) $\Theta = T/\Theta_D$, temperature in units of the Debye temperature and substitute $\omega$ by $x = \omega/\omega_D$,

$$\langle u_\alpha(x, t)u_\beta^*(0, 0) \rangle = \delta_{\alpha\beta} \langle u_\alpha^2(0) \rangle_{T=0} \varphi(\rho, \tau, \Theta), \quad (A.6)$$

with

$$\langle u_\alpha^2(0) \rangle_{T=0} = \frac{3\hbar}{4M\omega_D}, \quad (A.7)$$

$$\varphi(\rho, \tau, \Theta) = 2\int_0^1 \frac{\sin \rho x}{\rho} dx.$$
\[
\varphi(0, 0, 0) = 1. 
\] (A.9)

From these equations follow immediately the correlation functions for the relative displacements \( d_\alpha(l, t) = u_\alpha(l, t) - u_\alpha(0, t) \)

\[
\langle d_\alpha(l, t) d_\alpha(l', 0) \rangle = \left( 3h/4M\omega_D \right) \text{X} \left[ \varphi(R_H, \tau, \Theta) - 2\varphi(a, \tau, \Theta) + \varphi(0, \tau, \Theta) \right]. 
\] (A.10)

\( \varphi \) depends only on the dimensionless parameters \( \rho, \tau, \Theta \) and contains no other properties of the lattice. It can be used wherever the Debye approximation holds, especially at low temperatures.

**Appendix B: Some properties of phonon correlation functions in the Debye approximation**

In the calculation of the line shape the following expression has to be evaluated

\[
C(t) = \langle [d(l, t) \cdot e_{\parallel}]^2 [d(l', 0) \cdot e_{\parallel}]^2 \rangle - \langle [d(l, t) \cdot e_{\parallel}]^2 \langle [d(l', 0) \cdot e_{\parallel}]^2 \rangle,
\] (B.1)

with \( d(l, t) = u(l, t) - u(0, t) \), under the assumptions \( |x(l)| = |x(l')|, x(0) = 0, \cos \chi = e_{\parallel} \cdot e_{\parallel} \). By proper choice of the coordinate system, taking advantage of the fact that these correlation functions are invariant under rotations, the above expression can be written in components

\[
C(t) = \langle d^2_\alpha(l, t) d^2_\alpha(l', 0) \rangle \sin \chi \\
+ d^2_\alpha(l', 0) \cos \chi \rangle^2 - \langle d^2_\alpha(l, 0) \rangle^2. 
\] (B.2)

This can be simplified with the orthogonality relation (A.6) to

\[
C(t) = \langle d^2_\alpha(l, t) \rangle^2 \langle d^2_\alpha(l', 0) \rangle \cos^2 \chi \\
+ \langle d^2_\alpha(l, 0) \rangle^2 (\sin^2 \chi - 1) \\
= \langle d^2_\alpha(l, t) \rangle^2 \langle d^2_\alpha(l', 0) \rangle - \langle d^2_\alpha(l, 0) \rangle^2 (\langle e_{\parallel} \cdot e_{\parallel} \rangle)^2 
\] (B.3)

containing only one component \( (x, y \text{ or } z) \) of the displacements. It has to be expressed in correlation functions linear in \( u_\alpha(l, t) \) respectively in \( u_\alpha(0, t) \), so that the results of appendix A can be used. For this purpose we write \( d_\alpha(l, t) \) in terms of phonon creation and destruction operators, in analogy with eq. (5) but with the summation somewhat rearranged

\[
d_\alpha(l, t) = (h/2NM)^{1/2} \sum_{k,p} D(k, p, l, t), 
\] (B.4)

with

\[
D(k, p, l, t) = \left[ \omega(k) \right]^{-1/2} e_\alpha(k, p) \\
\times \left[ \langle a_{kp} \exp(-i\omega t) \rangle - \langle b_{kp} \exp(i\omega t) \rangle \right], 
\] (B.5)

\[
\langle d^2_\alpha(l, t) d^2_\alpha(l', 0) \rangle = \left( h/2NM \right)^2 \\
\times \sum_{k_1,...,k_4} \langle D(k_1, p_1, l, t) D(k_2, p_2, l, t) \rangle \times D(k_3, p_3, l', 0) D(k_4, p_4, l', 0). 
\] (B.6)

The correlation functions can be expressed by cumulants [9], lower order correlation functions and expectation values, noting that

\[
(k_1, p_1), (k_2, p_2), (k_3, p_3), (k_4, p_4) 
\]

have to be pairwise identical to give nonvanishing contributions. The sum over terms with pair correlation functions gives

\[
\langle d^2_\alpha(l, t) \rangle \langle d^2_\alpha(l', 0) \rangle + 2 \langle d_\alpha(l, 0) d_\alpha(l', 0) \rangle^2.
\]

To this has to be added the contribution of the cumulants. These are different from zero only if the operators \( D \) are statistically connected. This is the case for

\[
(k_1, p_1) = (k_2, p_2) = (k_3, p_3) = (k_4, p_4).
\]

There are only \( 3N \) terms of this kind. Their contribution to the total correlation function (B.6) is of the order \( O(1/N) \) for \( N \rightarrow \infty \) as an explicit calculation shows. They can therefore be neglected for the correlation functions in the Debye approximation but have to be included in the treatment of localized modes where they do not vanish. Therefore we get

\[
\langle d^2_\alpha(l, t) d^2_\alpha(l', 0) \rangle - \langle d^2_\alpha(l, 0) \rangle^2 \\
= 2 \langle d_\alpha(l, t) d_\alpha(l', 0) \rangle^2 + O(1/N). 
\] (B.7)

**References**

[1] M. Dubs and HsH. Günthard, to be published.