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Dynamic corrections for neutron scattering of water in the free molecule approximation^{a)}

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We develop a quantum mechanical theory for the inelasticity or Placzek correction for an asymmetric top rigid rotator, and give a formula to compute this correction for neutron scattering. We have, however, used a sphericalized model which satisfies Mecke's sum rule to compute the correction for H₂O and D₂O. Since this rigid rotor model fails to satisfy the exact first sum rule, we introduce a form that does satisfy this condition. Good agreement with the large momentum exchange (k) behavior in the case of D₂O is obtained. However, for the H₂O this is not so and adjustable parameters have to be introduced to obtain the correction asymptotic behavior.

I. INTRODUCTION

The accurate determination of the relative hydrogen atom positions in liquid water is possible from neutron diffraction experiments with light and heavy water, described in an accompanying report.¹ The cross sections measured in these experiments contain large inelastic contributions. Therefore, an accurate calculation of these dynamic corrections is important.

Here, we present a method to compute the inelasticity corrections based on the assumption that the momentum transfers are sufficiently large, thus the water molecules behave like a gas. This assumption is implicit in all previous work on this correction.²⁻⁶ Models based on the moment expansion of Placzek² fail completely for molecules with light nuclides.⁵ We have shown⁶ that a model of quantum-mechanical spherical rigid rotators leads to realistic corrections for D₂O. However, the corrections are not completely consistent with experimental data for D₂O at large momentum transfers. We improve on the previous work in two ways: (1) We develop the theory for the asymmetric top rotator. However, the calculations are done using averages of the energy levels, which can be computed exactly from Mecke's sum rules.⁷ (2) We introduce a model with rotational stretching. The coefficients of the stretching are found by requiring that the scattering function satisfies an exact first moment sum rule.

It is clear, however, that the molecules of water are not free in the liquid, and that a model including the effect of collective modes has to be formulated, similar to Nelkin.⁸ However, in Nelkin's work the mass tensor formula was used, which in itself leads to large discrepancies in the asymptotic behavior of the correction at

large momentum transfer. We believe that in a comprehensive treatment of the correction, which includes collective motions, the kinetic part has to be calculated from the quantum-mechanical expression. This will be done in the future.

II. SCATTERING EXPERIMENT

Consider a neutron scattering experiment in which the incident neutrons have a wave vector k_0 and an energy

$$E_0 = \hbar\omega_0 = \hbar^2 k_0^2 / 2m_n, \quad (1)$$

where m_n is the neutron mass and ω_0 the angular frequency. The neutrons (Fig. 1) are scattered at an angle θ with wave vector k_s . The momentum transfer is

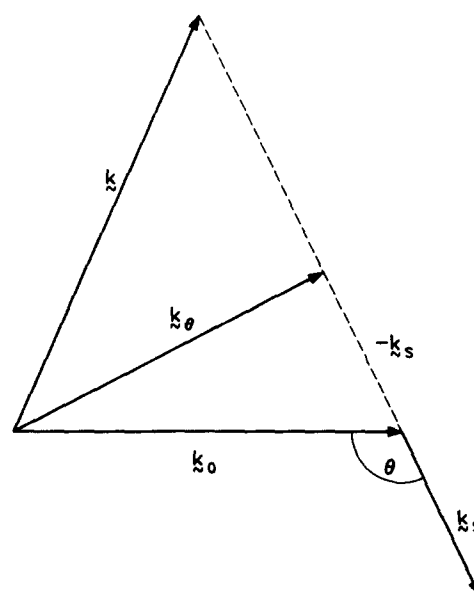


FIG. 1. Momentum exchange during collision. At a given angle θ the inelastic collision momentum exchange modulus k_θ is always less than the elastic value k . The incident neutron momentum is k_0 and the scattered one is k_s .

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$$\mathbf{k}_\theta = \mathbf{k}_s - \mathbf{k}_0, \quad (2)$$

and the energy transfer is

$$\Delta E = \hbar\omega = E_s - E_0. \quad (3)$$

The inelasticity correction⁶ is due to the difference between the energy integrated intensity at constant angle and the static scattering function $S(k)$:

$$\Delta(\theta) = \int_{-\infty}^{\omega_0} d\omega \epsilon(k_s)(k_s/k_0) S(k_\theta, \omega) - \epsilon(k_0) S(k), \quad (4)$$

where $\epsilon(k)$ is the detector efficiency, $S(k, \omega)$ is the frequency dependent inelastic scattering function, and k is the "elastic" momentum transfer [see Eq. (8) below]:

$$S(k, \omega) = \sum_{\alpha, \beta} (A_\alpha A_\beta + B_\beta^2 \delta_{\alpha\beta}) S_{\alpha\beta}(k, \omega), \quad (5)$$

with summation over all atoms α, β in the system, and A_α, B_α the coherent and incoherent scattering lengths.

The dynamic scattering function⁹ for atoms α, β is

$$S_{\alpha\beta}(k, \omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt e^{-i\omega t} \chi_{\alpha\beta}(k, t), \quad (6)$$

where $\chi_{\alpha\beta}(k, t)$ is the intermediate scattering function,

$$\begin{aligned} \chi_{\alpha\beta}(k, t) &= \langle \exp[-ik \cdot \mathbf{r}_\alpha(0)] \exp[ik \cdot \mathbf{r}_\beta(t)] \rangle \\ &= \text{Tr } e^{-\beta H} \{ \exp[-ik \cdot \mathbf{r}_\alpha(0)] \exp[ik \cdot \mathbf{r}_\beta(t)] \}, \end{aligned} \quad (7)$$

with $\mathbf{r}_\alpha(0)$ the position operator of atom α at time $t=0$, $\mathbf{r}_\beta(t)$ that of atom β at a later time t . The brackets in Eq. (7) indicate the quantum mechanical statistical average for an ensemble at temperature $\beta = (k_B T)^{-1}$, and H is the Hamiltonian of the system.

If there is no energy transfer during the scattering process,

$$k = 2k_0 \sin \theta / 2. \quad (8)$$

In general, the magnitude of the momentum transfer at constant angle θ is

$$k_\theta = k_0 [2 - \omega/\omega_0 - 2(1 - \omega/\omega_0)^{1/2} \cos \theta]^{1/2}, \quad (9)$$

where $\hbar\omega$ is the energy transfer

$$\hbar\omega = (\hbar^2/2m_n)(k_s^2 - k_0^2). \quad (10)$$

III. THEORETICAL MODELS

The purpose of this work is to evaluate the correction $\Delta(\theta)$ defined in Eq. (4); it is useful to consider the regions of small and large scattering angles separately.

A. Small-angle limit

For the case $\theta \rightarrow 0$ and $k \rightarrow 0$ we can safely assume that $S(k, \omega)$ will be a very narrow function of ω . Using the sum rule

$$S(k) = \int_{-\infty}^{\infty} d\omega S(k, \omega), \quad (11)$$

we rewrite Eq. (4) as

$$\Delta(\theta) = \Delta_s + \Delta_\epsilon - \int_{\omega_0}^{\infty} d\omega \epsilon(k_s)(k_s/k_0) S(k_\theta, \omega), \quad (12)$$

with

$$\Delta_s = \int_{-\infty}^{\infty} d\omega \epsilon(k_s)(k_s/k_0) [S(k_\theta, \omega) - S(k, \omega)], \quad (13)$$

$$\Delta_\epsilon = \int_{-\infty}^{\infty} d\omega [\epsilon(k_s)(k_s/k_0) - \epsilon(k_0)] S(k, \omega). \quad (14)$$

In the limit $\theta \rightarrow 0$, we can safely ignore the last term in Eq. (12). Furthermore, if $S(k, \omega)$ is a narrow function of ω , we can expand the term in the square brackets of Eq. (14). We get^{2,10} from Eqs. (9) and (10),

$$\begin{aligned} \epsilon(k_s)(k_s/k_0) - \epsilon(k_0) &= -1/2(k_0\epsilon_1 + \epsilon_0)x \\ &+ 1/8(k_0^2\epsilon_2 + \epsilon_1 k_0 - \epsilon_0)x^2 + \dots, \end{aligned} \quad (15)$$

where

$$x = \omega/\omega_0, \quad (16)$$

$$\epsilon_n = \frac{\partial^n}{\partial k^n} [\epsilon(k)]; \quad \epsilon_0 = \epsilon(k_0). \quad (17)$$

Therefore, we get for Eq. (14),

$$\Delta_\epsilon = \sum_{n=1}^{\infty} a_n \langle \omega^n \rangle, \quad (18)$$

where

$$\langle \omega^n \rangle = \int_{-\infty}^{\infty} d\omega \omega^n S(k, \omega)$$

and a_n are small coefficients. The first one is

$$a_1 = -\frac{1}{2} \frac{k_0}{\omega_0} [\epsilon_1 + \epsilon_0/k_0]. \quad (19)$$

For $n \geq 2$ they can be obtained from Eq. (15). The first moment is known exactly because of the sum rule^{2,11}

$$\langle \omega \rangle = \frac{\hbar k^2}{2} \sum_{\alpha\beta} (A_\alpha A_\beta + \delta_{\alpha\beta} B_\alpha^2) \frac{1}{m_\beta} S_{\alpha\beta}, \quad (20)$$

where m_β is the mass of atom β and $S_{\alpha\beta}(k)$ is the static structure function. It can be shown that the higher moments will be functions of k^n , with $n > 2$, so that when $k \rightarrow 0$,

$$\Delta_\epsilon = 0 \quad (21)$$

can be ignored.

Consider now Δ_s [Eq. (13)]. We have⁹

$$\begin{aligned} S(k_\theta, \omega) &= S(k, \omega) + (k_\theta^2 - k^2) \frac{\partial}{\partial (k^2)} S(k, \omega) \\ &+ \frac{1}{2}(k_\theta^2 - k^2)^2 \frac{\partial^2}{\partial (k^2)^2} S(k, \omega) + \dots \end{aligned} \quad (22)$$

By use of Eqs. (9), (10), and (15) we get

$$\begin{aligned} \Delta_s &= \epsilon_0 [k_0^2/4\omega_0^2] \langle \omega^2 \rangle' + \frac{k_0^2}{8\omega_0^4} \\ &\times [(\epsilon_0 - k_0\epsilon_1)\omega_0 \langle \omega^3 \rangle' + \frac{1}{8}(2\epsilon_2 k_0^2 - \epsilon_0) \langle \omega^4 \rangle'] \\ &+ \frac{k_0^2}{16\omega_0^4} \epsilon_0 \langle \omega^4 \rangle'' + \dots, \end{aligned} \quad (23)$$

where

$$\begin{aligned} \langle \omega^n \rangle' &= \frac{\partial}{\partial (k^2)} \langle \omega^n \rangle, \\ \langle \omega^n \rangle'' &= \frac{\partial^2}{\partial (k^2)^2} \langle \omega^n \rangle. \end{aligned} \quad (24)$$

The relevant moments for a fluid have been discussed by Rahman, Singwi, and Sjölander¹¹ who find

$$\begin{aligned}\langle \omega^2 \rangle &\sim O(k^2), \\ \langle \omega^3 \rangle &\sim O(k^2), \\ \langle \omega^4 \rangle &\sim O(k^4),\end{aligned}\quad (25)$$

so that the term in $\langle \omega^4 \rangle' \sim O(k^2)$. Using these results, we have finally

$$\Delta(0) = \epsilon_0/v_0^2 \langle \omega^2 \rangle' + (1/v_0^3)(\epsilon_0/k_0 - \epsilon_1) \langle \omega^3 \rangle' + \epsilon_0/v_0^4 \langle \omega^4 \rangle'' + \dots, \quad (26)$$

where we have used

$$k_0/2\omega_0 = m_n/\hbar k_0 = 1/v_0, \quad (27)$$

where v_0 is the neutron (wave packet) velocity.

B. Large-angle regime

1. Quasirigid rotator model

To compute the correction for high momentum exchange (or high angle θ) we need an expression for $S_{\alpha\beta}(k, \omega)$ in Eq. (6). To a first approximation,¹² we can write

$$S_{\alpha\beta}(k, \omega) = S_{\alpha\beta}^m(k, \omega) + S_{\alpha\beta}^d(k, \omega), \quad (28)$$

where $S_{\alpha\beta}^m$ is the molecular contribution (α, β belong to the same molecule) and $S_{\alpha\beta}^d$ is the different or intermolecular contribution (α, β belong to different molecules). The characteristic time of the neutron scattering process is much smaller than the collision time between molecules in the system so that the behavior of $S_{\alpha\beta}(k, \omega)$ is dominated by the short time behavior of $\chi_{\alpha\beta}(k, t)$ [Eqs. (6) and (7)], which is determined by the properties of individual molecules. We will thus neglect $S_{\alpha\beta}^d$. This approximation will be discussed in more detail in future work.

Indeed, the justification of this approximation is the consistency of the results: for high values of k , the corrected cross section $S(k)$ must approach asymptotically that of the free molecules (usually obtained from electron scattering). As we will see it below, this procedure yields good results for D_2O , but not for H_2O and HDO .

We write

$$S_{\alpha\beta}(k, \omega) \sim S_{\alpha\beta}^m(k, \omega) \quad (29)$$

and, furthermore, that $S_{\alpha\beta}^m(k, \omega)$ can be approximated by the free molecular function. The intermediate scattering function $\chi_{\alpha\beta}^m(k, t)$ can be written as the product of the translational and rovibrational parts,⁹

$$\chi_{\alpha\beta}^m(k, t) = \chi^{\text{trans}}(k, t) \chi_{\alpha\beta}^{\text{rv}}(k, t), \quad (30)$$

where the translational intermediate function is

$$\chi^{\text{trans}}(k, t) = \exp \left[-\frac{\hbar^2 k^2}{2\beta M_{\text{mol}}} (t^2 - i\hbar\beta t) \right], \quad (31)$$

with the total molecular mass and the Boltzmann factor $\beta = 1/k_B T$. The rovibrational part is by far the most difficult to compute,^{13,14}

$$\chi_{\alpha\beta}^{\text{rv}}(k, t) = \langle \exp[-ik \cdot r_\alpha(0)] \exp[ik \cdot r_\beta(t)] \rangle, \quad (32)$$

where $r_\alpha(0)$ is the position of atom α at time $t=0$ and $r_\beta(t)$ is that of atom β at a later time t . In the Heisenberg representation, the statistical average is

$$\begin{aligned}\chi_{\alpha\beta}^{\text{rv}}(k, t) &= \text{Tr} e^{-\beta H} \exp[-ik \cdot r_\alpha(0)] e^{iHt} \\ &\times \exp[ik \cdot r_\beta(0)] e^{-iHt} / \text{Tr} e^{-\beta H},\end{aligned}\quad (33)$$

where H is the vibration-rotation Hamiltonian of the molecule.

In Dirac's notation the eigenstates of the rovibrator are $\langle JKMn|$, where J, K, M are the rotational quantum numbers and n is the vibrational quantum number, corresponding to eigenvalues (energies)¹⁵ E_{JK}^n . Then, for formula (32) becomes

$$\begin{aligned}\chi_{\alpha\beta}^{\text{rv}}(k, t) &= \sum_{J'K'M'n'} \langle JKMn | \exp[-ik \cdot r_\alpha(0)] | J'K'M'n' \rangle \\ &\times \exp \left[-\beta E_{JK}^n + \frac{it}{\hbar} (E_{J'K'}^{n'} - E_{JK}^n) \right] \\ &\times \langle J'K'M'n' | \exp[ik \cdot r_\beta(0)] | JKMn \rangle / Z_\beta,\end{aligned}\quad (34)$$

where the partition function is

$$Z_\beta = \sum_{JKn} e^{-\beta E_{JK}^n}. \quad (35)$$

Using Rayleigh's expansion in Eq. (34)

$$\exp[ik \cdot r_\alpha(0)] = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr_\alpha) [C_l(\hat{k}) \cdot C_l(\hat{r}_\alpha)], \quad (36)$$

where $j_l(x)$ is the spherical Bessel function of order l , $C_l(\hat{k})$ is the Racah spherical harmonic with elements¹⁶

$$C_l^i(\hat{k}) = \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_{lm}(\theta_k, \phi_k), \quad (37)$$

and we are using the notation

$$\hat{k} \equiv \theta_k, \phi_k.$$

The spherical tensor dot product is defined by

$$a^i \cdot b^i = \sum_{m=-l}^l (-)^m a_m^i b_{-m}^i. \quad (38)$$

For isotropic fluids, $\chi_{\alpha\beta}^{\text{rv}}(k, t)$ does not depend on the direction of k . Therefore, after recoupling the angular tensor parts, we have for Eq. (34),

$$\begin{aligned}\chi_{\alpha\beta}^{\text{rv}}(k, t) &= \sum_{l=0}^{\infty} (2l+1) \frac{1}{Z_\beta} \sum_{J'K'M'n'} \exp \left[-\beta E_{JK}^n + \frac{it}{\hbar} (E_{J'K'}^{n'} - E_{JK}^n) \right] \\ &\times \sum_{\mu} (-)^{\mu} \langle JKMn | j_l(kr_\alpha) C_\mu^l(\hat{r}_\alpha) | J'K'M'n' \rangle \langle J'K'M'n' | j_l(kr_\beta) C_\mu^l(\hat{r}_\beta) | JKMn \rangle.\end{aligned}\quad (39)$$

For the water molecule, the vibrational frequencies are¹⁷ much higher than $k_B T$, and therefore, the molecules are in their vibrational ground state. Still, because of the centrifugal force and the anharmonicity of the potential, the distance b_α of atom α from the center of the molecule is a function of the rotational state of the molecule. This will lead to rovibrational corrections that will be discussed below. In the lowest approximation, we have

$$\langle JKM0 | j_i(kr_\alpha) C_\mu^l(\hat{r}_\alpha) | J'K'M'0 \rangle = j_i(kr_\alpha) e^{-1/2 k^2 r_\alpha^2} \langle JKM | C_\mu^l(\hat{r}_\alpha) | J'K'M' \rangle. \quad (40)$$

Replacing this expression into Eq. (39) and making use of

$$C_\mu^l(\hat{r}_\alpha) = \sum_m C_m^l(\hat{b}_\alpha) D_{m\mu}^l(\Omega), \quad (41)$$

where b_α is the coordinate of atom α in the molecular reference frame $D_\mu^l(\Omega)$ is the generalized spherical harmonic. Ω are the Euler angles ϕ, θ, ψ for the rotation of the laboratory to the molecular reference frame. We get^{12,18}

$$\chi_{\alpha\beta}^{r-v}(k, t) = \sum_l (2l+1) j_l(kr_\alpha) j_l(kr_\beta) \exp(-\frac{1}{2} k^2 \gamma_{\alpha\beta}) \times \sum_{mm'} (-)^m C_m^l(\hat{b}_\alpha) C_{-m}^l(\hat{b}_\beta) F_{mm'}^l(k, t) \quad (42)$$

is the Fourier transform of intermediate rotational relaxation function^{6,18}

$$F_{mm'}^l(R, t) = \langle D_{mm'}^l[\Omega(t) - \Omega(0)] \rangle, \quad (43)$$

which has been extensively discussed in the literature. $\gamma_{\alpha\beta}$ is the Debye-Waller factor.

For an asymmetric top rotator (see Appendix A) this function is

$$F_{mm'}^l(t) = \frac{1}{Z_\beta} \sum_{J'K'} \exp \left[-\beta E_{J'K'} + \frac{it}{\hbar} (E_{J'K'} - E_{JK}) \right] \mathcal{L}_{mm'}^l(JK; J'K'), \quad (44)$$

with

$$\mathcal{L}_{mm'}^l(JK; J'K') = \sum_{N'L'} (-)^{N'+L'} a_N^{J,K} (a_L^{J,K})^* a_{L'}^{J',K'} (a_N^{J',K'})^* (2J'+1) \begin{pmatrix} J & l & J' \\ -N & m & N' \end{pmatrix} \begin{pmatrix} J & l & J' \\ L & -m' & -L' \end{pmatrix},$$

where we have used the standard notation for Wigner's 3- j symbols, and $a_N^{J,K}$ are the coefficients of the expansion of the asymmetric top rotator function in terms of the symmetric top ones

$$\langle JKM | = \sum_N a_N^{J,K} D_{NM}^J(\Omega). \quad (45)$$

Finally from Eqs. (6), (30), (31), (42), and (44) we get

$$S_{\alpha\beta}(k\omega) = \sum_l (2l+1) j_l(kr_\alpha) j_l(kr_\beta) \exp(-\frac{1}{2} k^2 \gamma_{\alpha\beta}) \sum_{mm'} (-)^m C_m^l(\hat{b}_\alpha) C_{-m}^l(\hat{b}_\beta) \tilde{F}_{mm'}^l(k\omega) \quad (46)$$

with

$$\tilde{F}_{mm'}^l(k, \omega) = \frac{1}{Z_\beta} \sum_{J'K'} \left(\frac{\beta M_{\text{mol}}}{2\pi \hbar^2 k^2} \right)^{1/2} \exp \left[-\beta E_{J'K'} - \frac{\beta M_{\text{mol}}}{2\hbar^2 k^2} \left(E_{J'K'} - E_{JK} - \hbar\omega + \frac{\hbar^2 k^2}{2M_{\text{mol}}} \right)^2 \right] \mathcal{L}_{mm'}^l(JK; J'K') \quad (47)$$

and finally, replacing into Eq. (5),

$$S(k, \omega) = \sum_{\alpha\beta} (A_\alpha A_\beta + \delta_{\alpha\beta} B_\beta^2) \sum_l (2l+1) j_l(kr_\alpha) j_l(kr_\beta) \exp(-\frac{1}{2} k^2 \gamma_{\alpha\beta}) \sum_{mm'} (-)^m C_m^l(\hat{b}_\alpha) C_{-m}^l(\hat{b}_\beta) \tilde{F}_{mm'}^l(k, \omega). \quad (48)$$

2. Rovibrational interactions and the moment conditions

The quasirigid rotator model of the previous section has a serious problem since it does not satisfy the exact sum rule for the first moment¹⁷

$$\langle \omega \rangle = \sum_{\alpha,\beta} \frac{\hbar k^2}{2m_\beta} (A_\alpha A_\beta + \delta_{\alpha\beta} B_\beta^2) \exp(-k^2 \gamma_{\alpha\beta}/2) j_0(kr_{\alpha\beta}), \quad (49)$$

but rather the sum rule for a rigid rotator. For a linear molecule

$$\langle \omega \rangle = \frac{\hbar k^2}{2} \sum_{\alpha,\beta} (A_\alpha A_\beta + \delta_{\alpha\beta} B_\beta^2) \frac{1}{I} [j_1(kr_{\alpha\beta})/kr_{\alpha\beta}] (r_\alpha - r_{\alpha\beta}) r_\alpha + \frac{1}{M_{\text{mol}}} j_0(kr_{\alpha\beta}), \quad (50)$$

where $r_{\alpha\beta}$ is the distance between atoms α and β . To account for the interaction between rotations and vibrations, we consider a spherical or linear rotator which is deformed by a small harmonic vibration of frequency ω . The deformation of the bond $r_{\alpha\beta}$ is called ξ , and satisfies the Schrödinger equation

$$\frac{\hbar^2}{2m} \frac{d^2}{d\xi^2} + \frac{1}{2} m \omega^2 \xi^2 + \frac{\hbar^2 J(J+1)}{2I(1+\xi/r_{\alpha\beta})^2} |Jn\rangle = E_J^n |Jn\rangle, \quad (51)$$

where the eigenstates $|Jn\rangle$ of energy E_J^n depend on both n and J . This equation can be solved by perturbations. While even for this oversimplified case the solution is quite complex, it can be shown that the rotational relaxation function's Fourier transform [Eq. (46)] is of the form

$$\tilde{F}_{mm'}^i(k, \omega) = \frac{1}{Z_\beta} \sum_{J, J'} \left(\frac{\beta M_{\text{mol}}}{2\pi \hbar^2 k^2} \right)^{1/2} \exp \left[-\beta E_J - \frac{\beta M_{\text{mol}}}{2\hbar^2 k^2} \left(E_{J'} - E_J - \hbar\omega + \frac{\hbar^2 k^2}{2M_{\text{mol}}} \right)^2 \right] \sum_n c_n \mathcal{H}_n \left[\sqrt{\frac{\beta M_{\text{mol}}}{2\hbar^2 k^2}} \left(E_J - E_{J'} + \hbar\omega - \frac{\hbar^2 k^2}{2M_{\text{mol}}} \right) \right], \quad (52)$$

where \mathcal{H}_n is the Hermite polynomial and c_n are coefficients obtained by solving a secular determinant.

Indeed, this is a very cumbersome procedure, so that we chose to find the coefficients c_n by simply requiring $S(k, \omega)$ to satisfy the first two moment conditions.

For the asymmetric top rotator, the first moment condition is (Appendix B)

$$\exp(-\frac{1}{2}k^2\gamma_{\alpha\beta}) \langle \omega \rangle_{mm'}^i = \delta_{mm'} \frac{\hbar k^2}{m_\alpha} \exp(-\frac{1}{2}k^2\gamma_{\alpha\beta}), \quad (53)$$

because then, the first moment becomes

$$\begin{aligned} \langle \omega \rangle &= \sum_{\alpha, \beta} [A_\alpha A_\beta + \delta_{\alpha\beta} B_\beta^2] \exp(-\frac{1}{2}k^2\gamma_{\alpha\beta}) \frac{\hbar k^2}{m_\alpha} \sum_{l=0}^{\infty} (2l+1) j_l(kr_\alpha) j_l(kr_\beta) \sum_{mm'} (-)^{m'} C_m^l(b_\alpha) C_{-m}^l(b_\beta) \delta_{mm'} \\ &= \sum_{\alpha, \beta} (A_\alpha A_\beta + \delta_{\alpha\beta} B_\beta^2) \frac{\hbar k^2}{m_\alpha} \exp(-\frac{1}{2}k^2\gamma_{\alpha\beta}) j_0(kr_{\alpha\beta}). \end{aligned} \quad (54)$$

Here, we used a sum rule of the spherical Bessel functions. To satisfy Eq. (53), we assume that

$$\tilde{F}_{mm'}^i(k, \omega) = \frac{1}{Z_\beta} \sum_{J, J'} \mathcal{L}_{m, m'}^i(JK; J'K') \left(\frac{\beta M_{\text{mol}}}{2\pi \hbar^2 k^2} \right)^{1/2} \exp \left[-\beta E_{JK} - \frac{\beta M_{\text{mol}}}{2\hbar^2 k^2} \left(E_{J'K'} - E_{JK} - \hbar\omega + \frac{\hbar^2 k^2}{2M_{\text{mol}}} \right)^2 \right] [1 + (c_1^{\alpha i} \omega + c_0^{\alpha i}) + \dots], \quad (55)$$

which contains the parameters $c_1^{\alpha i}$ and $c_0^{\alpha i}$, which are found by requiring that

$$\langle F_{mm'}^i \rangle = \delta_{mm'}, \quad (56)$$

$$\langle \omega F_{mm'}^i \rangle = \hbar k^2 / 2m_\alpha. \quad (57)$$

IV. CALCULATED RESULTS

We now evaluate the dynamic corrections derived in Sec. III for D₂O, HDO, and H₂O molecules.

A. Small-angle limit

We note that Eq. (27) provides a way to estimate the zero-angle corrections directly from experiment. If we measure the limiting value of the differential scattering cross section $\theta \rightarrow 0$ at different values of k_0 , we can plot $S(0)$ against k_0^2 and find the coefficients $\langle \omega^2 \rangle'$, $\langle \omega^3 \rangle'$, and $\langle \omega^4 \rangle'$ in Eq. (26). We here estimate the values of $\Delta(0)$ from the computed frequency moments of classical rigid rotators.⁴ The expressions are

$$\langle \omega^2 \rangle' = A_s + A_d, \quad (58)$$

$$A_s = k_B T \sum_{\alpha} (A_\alpha^2 + B_\alpha^2) / m_{\alpha\alpha}^*, \quad (59)$$

TABLE I. Coefficients of the zero-angle corrections. Units are b Å² ps⁻².

	D ₂ O	HDO	H ₂ O
A_s	89.77	675.1	1703.1
A_d	-1.1378	0.5647	-0.688

$$A_d = k_B T \sum_{\alpha, \beta} A_\alpha A_\beta / m_{\alpha\beta}^*, \quad (60)$$

$$(m_{\alpha\beta}^*)^{-1} = M_{\text{mol}}^{-1} + 1/3 [\text{Tr}(\mathbf{b}_\alpha \mathbf{b}_\beta) \text{Tr} \mathbf{I}^{-1} - (\mathbf{b}_\alpha \mathbf{b}_\beta : \mathbf{I}^{-1})], \quad (61)$$

where \mathbf{b}_α is the position of atom α in the principal (moments of inertia tensor is diagonal) reference frame, \mathbf{I} is the inertia tensor, and M_{mol} is the molecular mass. From the numbers listed in Table I we see clearly that the self-part A_s dominates the corrections at small angles. We can write

$$\Delta(0) = \epsilon_0 v_0^{-2} \sum_{\alpha} \langle v_\alpha^2 \rangle (A_\alpha^2 + B_\alpha^2), \quad (62)$$

where v_0 is the velocity of the incident neutron and $\langle v_\alpha^2 \rangle$ is the mean-square (thermal) velocity of atom α .

The deviation from the free-molecule behavior can be estimated from a formula suggested by Rahman, Singwi, and Sjölander¹¹

$$\langle \omega^2 \rangle_T = \langle \omega^2 \rangle_R [1 + \theta_D(T)^2 / 20], \quad (63)$$

where $\langle \omega^2 \rangle_R$ is the classical and $\langle \omega^2 \rangle_T$ is the total moment. From thermodynamic data we estimate that the

TABLE II. Zero-angle corrections $\Delta(0)$ for 0.89 Å neutrons. Units are b sr⁻¹ molecule⁻¹.

	D ₂ O	HDO	H ₂ O
Rigid rotator	0.0507	0.3420	0.8580
Rahman correction	0.0019	0.013	0.0326
4th moment	0.0031	0.033	0.115
Total $\Delta(0)$	0.056	0.389	1.010

TABLE III. Rotational constants for water (Ref. 20).

	A (cm ⁻¹)	B (cm ⁻¹)	C (cm ⁻¹)	$\bar{B} = \frac{1}{3}(A+B+C)$ cm ⁻¹	$\frac{1}{3}(A+B+C) 10^{-16}$ erg
H ₂ O	27.8778	14.5092	9.2869	17.2246	34.2043
D ₂ O	15.3846	7.2716	4.8458	9.1673	18.2022
HDO	23.3786	9.1020	6.4173	12.9660	25.7476

Debye temperature $\theta_D \sim 260$ K for water. Finally, we can estimate the term $\langle \omega \rangle^{4''}$ in Eq. (26) from a result by Glass and Rice,¹⁹ namely,

$$\langle \omega^4 \rangle'' = 6(k_B T)^2 \sum_{\alpha} (A_{\alpha}^2 + B_{\alpha}^2)(m_{\alpha}^*)^{-2}. \quad (64)$$

For the experimental conditions described in Ref. (1), the results are listed in Table II.

B. Large-angle regime

We have calculated the dynamic corrections for the models described in Sec. III B. Instead of the individual energy levels, averages were used,

$$\bar{E}_J = (2J+1)^{-1} \sum_K E_{JK}, \quad (65)$$

The value of \bar{E}_J was obtained from the sum rule⁷

$$\bar{E}_J = (A+B+C)J(J+1)/3, \quad (66)$$

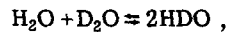
with

$$A = \hbar^2/2I_a, \quad B = \hbar^2/2I_b, \quad C = \hbar^2/2I_c.$$

The numerical values used^{17,20} are listed in Tables III and IV.

V. COMPARISON WITH EXPERIMENT

The neutron diffraction experiments¹ were carried out with four mixtures of light and heavy water containing 0.01%, 35.79%, 67.89%, and 99.75% D. To compute the corrections, we assumed that the mixtures were in chemical equilibrium according to



with an equilibrium constant²¹ of value $K = 3.94$. The total correction was then computed from

$$\Delta(\theta) = C_{\text{H}_2\text{O}} \Delta_{\text{H}_2\text{O}} + C_{\text{HDO}} \Delta_{\text{HDO}} + C_{\text{D}_2\text{O}} \Delta_{\text{D}_2\text{O}}, \quad (67)$$

with C_{α} the concentration and Δ_{α} the corrections for species α . The results are compared in Figs. 1–4.

Each of the figures shows four curves. The dotted curves are the measured differential scattering cross sections. The solid curves are computed cross sections, namely,

$$D(k) = \Delta(\theta) + \sum_{\alpha} (A_{\alpha}^2 + B_{\alpha}^2), \quad (68)$$

with A_{α} and B_{α} the coherent and incoherent scattering length of the atoms in a water molecule. Curves (a) are for the rigid rotator model, curves (b) for moment-adjusted rotator model, and curves (c) for the Placzek expansion. It is clear that the Placzek curves (c) are realistic only at small momentum transfers, where the models based on free molecules fail.

The curves (a) and (b) calculated for the gas models are a definite improvement on the Placzek model in that they do not predict negative cross sections at large momentum transfers. The curves (b) for the moment-adjusted rotator model are in better agreement with the experimental data than the curves (a) for the rigid rotator mode. For D₂O, the agreement is quite satisfactory, but for H₂O and the two mixtures large discrepancies remain.

VI. CONCLUSIONS

It is clear that we need to introduce corrections that take into account the interactions between rotations and vibrations. These interactions are complex in nature and require detailed knowledge of the forces of the water molecule. The effects are of three kinds; (a) stretching of the molecule due to centrifugal distortion, (b) the

TABLE IV. Average rotational energy for water in cm⁻¹ (expt. Ref. 20; calc., this work).

	H ₂ O		D ₂ O		HDO	
	\bar{E}_J expt.	\bar{E}_J calc.	\bar{E}_J expt.	\bar{E}_J calc.	\bar{E}_J expt.	\bar{E}_J calc.
$J=1$	34.43	34.45	18.33	18.33	25.97	25.93
$J=2$	103.16	103.34	54.96	55.00	77.78	77.79
$J=3$	205.93	206.69	109.85	110.01	155.30	155.59
$J=4$	342.35	344.59	182.81	183.35	258.10	259.32
$J=5$	512.00	516.73	273.76	275.02	386.53	388.98
$J=6$	714.24	723.43	382.54	385.03	539.69	544.57
$J=7$	948.58	964.58	509.04	513.36	717.40	726.09

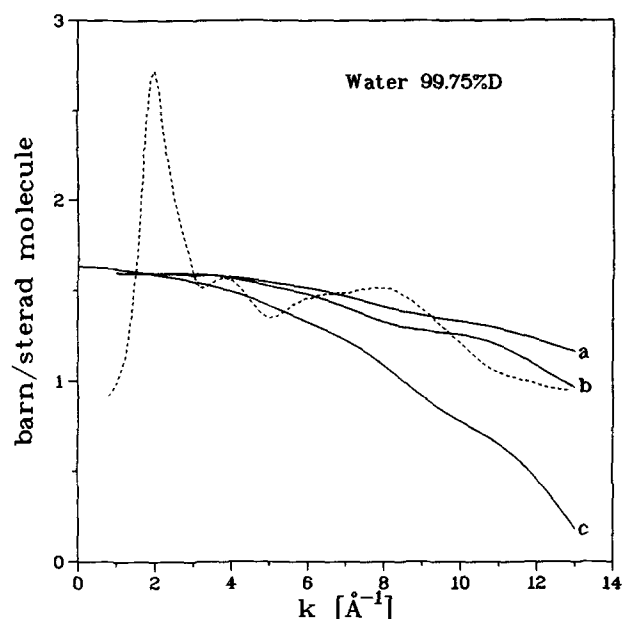


FIG. 2. Dynamic corrections for almost pure D_2O . Curve c has been obtained using Placzek's expansion. Curve a is the result for the rigid rotator model, and curve b is calculated by adjusting the first moment. The dotted curve is the measured differential scattering cross section (Ref. 1). $\lambda = 0.8899 \text{ \AA}$. The detector sensitivity function is $\epsilon(k) = 1 - e^{-\alpha/k}$. For the detector used in the experiments, $\alpha = 2.935 \text{ \AA}^{-1}$.

effect of zero-point motion, (c) Coriolis forces.

To a first approximation, we may simply require that the first moment condition is satisfied. This procedure is satisfactory for D_2O but does not yield good results for H_2O as shown in Figs. 1-4. Further corrections could be achieved by introducing shifts in the energy levels caused by distortions (D) and by the zero-point

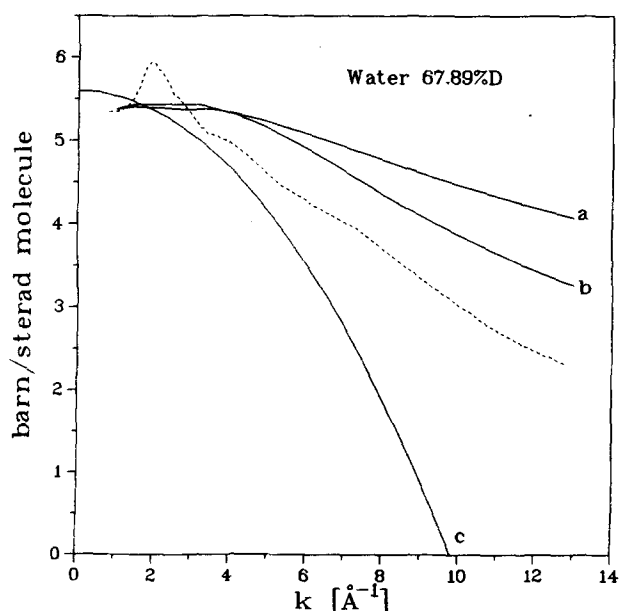


FIG. 3. Computed corrections and measured cross sections for water containing 67.89% D; for notation see Fig. 2.

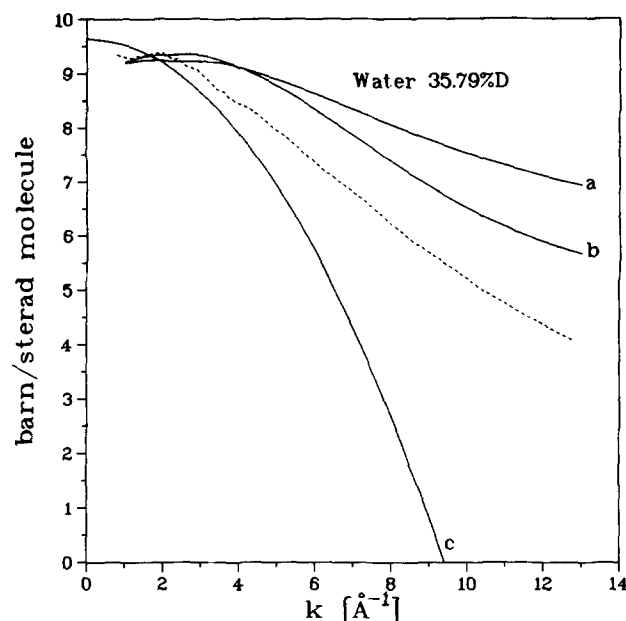


FIG. 4. Computed corrections and measured cross section for water containing 35.79% D; for notation see Fig. 2.

vibrations (α_0). The energy levels are, in that case, of the form¹⁵

$$\bar{E}_J = \bar{B}(J+1)J - \bar{D}J^2(J+1)^2,$$

where

$$\bar{B} = \frac{1}{3}(A+B+C),$$

$$\bar{D} = 4\bar{B}^3/\bar{\omega}^2,$$

$$\bar{\omega} = \frac{1}{2}(\omega_1 + \omega_2 + \omega_3),$$

where ω_1 , ω_2 , and ω_3 are the angular frequencies of the three vibration modes of water. With these we get the a

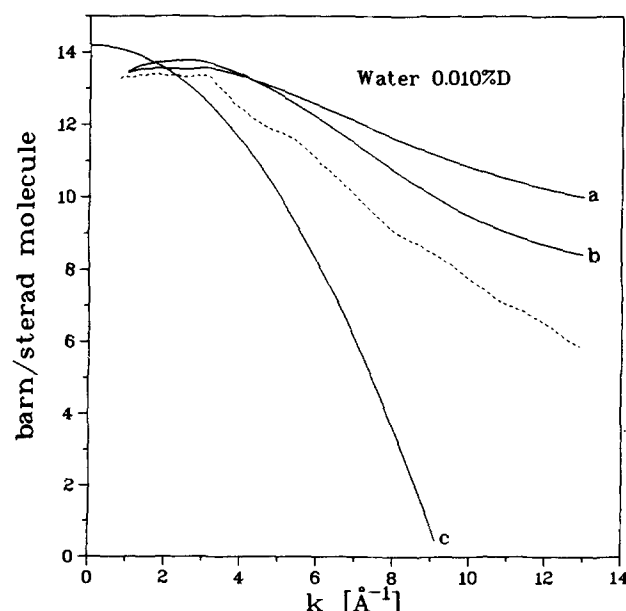


FIG. 5. Computed corrections and measured cross section for water containing 0.01% D; for notation see Fig. 2.

TABLE V. Average distortion constants.

\bar{D} (10^{-16} erg)	H ₂ O	D ₂ O	HDO
	4.4×10^{-3}	1.25×10^{-3}	2.78×10^{-3}

average distortion constants (Table V). The values are much too small to explain the discrepancy in the correction $\Delta(\theta)$ H₂O, but give a correct order of magnitude for the centrifugal distortion of water. (The level 11₁₁ of H₂O has a shift of 280 cm⁻¹, the formula gives 76.7.)

However, these corrections produce no noticeable change in the inelasticity corrections. We must remark, however, that the water molecules in the liquid have collective modes that are of energy comparable to those of the rotator, and which will influence the recoil correction. These bands are in the 60 to 300 cm⁻¹ range and are discussed in the book by Eisenberg and Kauzmann.¹⁸ Another unknown effect is due to the fact that the zero point motion of the atoms in the free molecule is not the same as in the liquid. The hydrogen bonding has a definite (but unknown) influence on the geometry of the water molecule, since the proton could tunnel between adjacent molecules. This effect should be much smaller in D₂O. Furthermore, the very large incoherent cross section of H makes the correction much more sensitive to these effects.

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APPENDIX A: ROTATIONAL RELAXATION FUNCTION OF THE FREE ASYMMETRIC TOP ROTATOR

We want

$$I = \sum_{M M' \mu} (-)^{\mu} \langle JKM | C_{\mu}^I(\hat{r}_{\alpha}) | J'K'M' \rangle \langle J'K'M' | C_{\mu}^I(\hat{r}_{\beta}) | JKM \rangle. \quad (A1)$$

Using Eq. (48), we get

$$I = \sum_{\mu} (-)^{\mu} \sum_{m m'} C_m^I(\hat{b}_{\alpha}) C_{m'}^I(\hat{b}_{\beta}) \times \langle JKM | D_{m\mu}^I(\Omega) | J'K'M' \rangle \langle J'K'M' | D_{m'\mu}^I(\Omega) | JKM \rangle. \quad (A2)$$

For the symmetric top rotator with principal moments of inertia I_a , I_b , and I_c the Hamiltonian is

$$H = -\frac{\hbar^2}{2} (\hat{P}_a^2/I_a + \hat{P}_b^2/I_b + \hat{P}_c^2/I_c), \quad (A3)$$

where \hat{P}_a is the angular momentum operator for axis a , etc. Define now the rotational constants

$$A = \frac{\hbar^2}{2I_a}, \quad B = \frac{\hbar^2}{2I_b}, \quad C = \frac{\hbar^2}{2I_c}. \quad (A4)$$

Then, if $A > B > C$ we have¹⁶

$$E_{JK} = \frac{1}{2}(B+C)J(J+1) + [A - \frac{1}{2}(B+C)]f_{JK}(b), \quad (A5)$$

$$b = \frac{1}{2}(C-B)/[A - \frac{1}{2}(B+C)]. \quad (A6)$$

The eigenfunctions of the asymmetric rotator are

$$\langle JKM | = \sum_N a_N^{JK} D_{NM}^J(\Omega), \quad (A7)$$

where the coefficients a_N^{JK} are obtained from the eigenvector of the matrix of the secular determinant. Now, using Eq. (A7) we write

$$\langle JKM | D_{m\mu}^I(\Omega) | J'K'M' \rangle = \sum_{N N'} a_N^{JK} (a_{N'}^{J'K'})^* \times \frac{1}{8\pi^2} \int d\Omega D_{NM}^J(\Omega) D_{m\mu}^I(\Omega) [D_{N'M'}^{J'}(\Omega)]^* = [(2J+1)(2J'+1)]^{1/2} \sum_{N N'} a_N^{JK} (a_{N'}^{J'K'})^* (-)^{N'-M'} \begin{pmatrix} J & l & J' \\ N & m & -N' \end{pmatrix} \begin{pmatrix} J & l & J' \\ M & \mu & -M' \end{pmatrix}, \quad (A8)$$

so that

$$I = \sum_{m m'} C_m^I(\hat{b}_{\alpha}) C_{m'}^I(\hat{b}_{\beta}) \sum_{N' L' L} a_N^{JK} (a_{N'}^{J'K'})^* a_{L'}^{J'K'} (a_L^{JK})^* \times (-)^{N'+L} (2J'+1) \begin{pmatrix} J & l & J' \\ N & m & -N' \end{pmatrix} \begin{pmatrix} J' & l & J \\ L' & m' & -L \end{pmatrix} \sum_{M M' \mu} (-)^{M-M'} (-)^{J'+l+J} (2J+1) \begin{pmatrix} J' & l & J \\ -M' & \mu & M \end{pmatrix}^2. \quad (A9)$$

But the last sum is just equal to one so that using well-known symmetry relations of the 3- j symbols we get

$$I = \sum_{m m'} (-1)^{m'} C_m^I(\hat{b}_{\alpha}) C_{m'}^I(\hat{b}_{\beta}) \mathcal{E}_{mm'}^I(JK; J'K'), \quad (A10)$$

which is the desired result. The symbol $\mathcal{E}_{mm'}^I(JK; J'K')$ has a sum rule. Because of the orthogonality of the asymmetric top eigenfunctions

$$\langle JKN | J'K'N' \rangle = \delta_{JJ'} \delta_{KK'} \delta_{NN'}, \quad (A11)$$

the coefficients a_N^{JK} must satisfy

$$\sum_N a_N^{JK} (a_N^{JK'})^* = \delta_{KK'} , \quad (\text{A12})$$

$$\sum_K a_N^{JK} (a_N^{JK})^* = \delta_{NN'} . \quad (\text{A13})$$

Therefore, we can derive the interesting sum rule

$$\begin{aligned} \sum_{J'K'} \mathcal{L}_{mm'}^i(JK; J'K') &= \sum_{N'L'} \sum_{J'K'} (-)^{N'+L'} a_{L'}^{J'K'} (a_{N'}^{J'K'})^* a_N^{JK} (a_L^{JK})^* \begin{pmatrix} J & l & J' \\ N & m & N' \end{pmatrix} \begin{pmatrix} J & l & J' \\ L & -m' & -L' \end{pmatrix} (2J'+1) \\ &= \sum_{N'L} a_N^{JK} (a_L^{JK})^* \sum_{J'L'} \begin{pmatrix} J & l & J' \\ N & m & L' \end{pmatrix} \begin{pmatrix} J & l & J' \\ L & m' & L' \end{pmatrix} (2J'+1) \\ &= \delta_{mm'} \sum_{N'L} a_N^{JK} (a_L^{JK})^* \delta_{NL} , \end{aligned}$$

$$\sum_{J'K'} \mathcal{L}_{mm'}^i(JK; J'K') = \delta_{mm'} . \quad (\text{A14})$$

APPENDIX B

The first moment of $S(q, \omega)$ is

$$\langle \omega \rangle = \int_{-\infty}^{\infty} d\omega \omega S(k, \omega) \quad (\text{B1})$$

using Eq. (55), we have

$$\begin{aligned} \langle \omega \rangle &= \sum_{\alpha, \beta} (A_{\alpha} A_{\beta} + \delta_{\alpha\beta} B_{\beta}^2) \sum_l (2l+1) j_l(kr_{\alpha}) j_l(kr_{\beta}) \exp(-\frac{1}{2} k^2 \gamma_{\alpha\beta}) \\ &\times \sum_{mm'} (-)^{m'} C_m^l(\hat{b}_{\alpha}) C_{-m'}^l(\hat{b}_{\beta}) \int_{-\infty}^{\infty} d\omega \omega \tilde{F}_{mm'}^i(k, \omega) . \end{aligned} \quad (\text{B2})$$

Using Eq. (54) and the fact that

$$\frac{1}{\sqrt{2\pi a}} \int_{-\infty}^{\infty} d\omega e^{-a(\Delta-\omega)^2} (\omega - \Delta) = 0 \quad (\text{B3})$$

and

$$\frac{1}{\sqrt{2\pi a}} \int_{-\infty}^{\infty} d\omega \omega e^{-a(\Delta-\omega)^2} = \Delta , \quad (\text{B4})$$

so that

$$\begin{aligned} \langle \omega \rangle &= \frac{1}{\hbar} \sum_{\alpha, \beta} [A_{\alpha} A_{\beta} + \delta_{\alpha\beta} B_{\beta}^2] \sum_{l=0}^{\infty} (2l+1) j_l(kr_{\alpha}) j_l(kr_{\beta}) \\ &\times \exp(-\frac{1}{2} k^2 \gamma_{\alpha\beta}) \sum_{mm'} (-)^{m'} C_m^l(\hat{b}_{\alpha}) C_{-m'}^l(\hat{b}_{\beta}) \langle \omega \rangle_{mm'}^i , \end{aligned} \quad (\text{B5})$$

with

$$\begin{aligned} \langle \omega \rangle_{mm'}^i &= \frac{1}{Z_{\beta}} \sum_{J'K'} \left(E_{J'K'} - E_{JK} + \frac{\hbar^2 k^2}{2M_{\text{mol}}} \right) \\ &\times \exp(-\beta E_{JK}) \mathcal{L}_{mm'}^i(JK; J'K') . \end{aligned} \quad (\text{B6})$$

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