Notes of the H_2O-H_2 Project

Toby Zeng

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I General Introduction of Matrix Elements

Under the assumption of adiabatic hindered rotor of H_2, the potential energy between H_2O and H_2 reads $V(R, \theta, \chi)$, and the total Hamiltonian of the H_2O-H_2 complex reads

$$\hat{H}(R, \alpha, \beta, \phi, \theta, \chi) \quad = \quad -\frac{\hbar^2}{2\mu}R^{-1}\frac{\partial^2}{\partial R^2}R + \frac{(\hat{\vec{J}} - \hat{\vec{j}})^2}{2\mu R^2} + \hat{H}_{\mathrm{H_2O}} + V(R, \theta, \chi), \tag{1}$$

where R specifies the distance between H_2O and H_2, $\hat{\vec{J}}$ the total angular momentum operator for the whole complex in the space-fixed frame, $\hat{\vec{j}}$ the angular momentum operator of H_2O in the body-fixed frame, and μ the reduced mass of the whose system: $\frac{1}{\mu} = \frac{1}{m_{\mathrm{H_2O}}} + \frac{1}{m_{\mathrm{H_2}}}$. The body-fixed frame has its z axis along $\vec{R}$, which has polar angles α and β in the space-fixed frame. The three Euler angles, ϕ, θ, and χ rotates the body-fixed frame to overlap with the H_2O-fixed frame, and consequently, the three angles describe the rotation of H_2O in the body-fixed frame. The first term in Eq. 1 is consistent with Eq. 1 of Ref [1] and Eq. 40 of Ref [2]. By using such a radial kinetic operator, radial wave functions, rather than distribution functions, are used in the basis set. Similarly to Wang and Carrington's work, we should use the uncoupled basis functions, $|jkK\rangle\,|JKM\rangle$ for the rotational motion, where

$$\langle \alpha, \beta, 0|JKM\rangle = \sqrt{\frac{2J+1}{4\pi}}D^J_{MK}(\alpha, \beta, 0)^* = \sqrt{\frac{2J+1}{4\pi}}e^{iM\alpha}d^J_{MK}(\beta); \tag{2}$$

$$\langle \phi, \theta, \chi|jkK\rangle = \sqrt{\frac{2j+1}{8\pi^2}}D^j_{Kk}(\phi, \theta, \chi)^* = \sqrt{\frac{2j+1}{8\pi^2}}e^{iK\phi}d^j_{Kk}(\theta)e^{ik\chi}. \tag{3}$$

The D^J_{MK} and d^j_{Kk} etc. are rotational matrix and Wigner d-matrix elements. Actually, in our H_2O-H_2 case, there is no difference between the coupled and uncoupled basis functions, because the angular momentum of the spherically-like hindered H_2 is zero and the dose not couple with the angular momentum of H_2O. Therefore, the angular momentum along the body-fixed z axis solely comes from H_2O and $|jkK\rangle$ and $|JKM\rangle$ take the same K value. With the orthonormal basis functions for the radial motion $\psi_n(R)$, the primitive basis functions of the totally six degrees of freedom read

$$|\psi_n\rangle\,|jkK\rangle\,|JKM\rangle\,. \tag{4}$$

The angular basis can be further contracted to be symmetry adapted with respect to the space inversion. The symmetry-adapted basis function reads

$$\left|\Theta_{jk}^{nJMKP}\right\rangle = |\psi_n\rangle \frac{1}{\sqrt{2(1+\delta_{K0}\delta_{k0})}} \Big[|jkK\rangle\,|JKM\rangle + (-1)^{J+k+P}\,|j\ -k\ -K\rangle\,|J\ -KM\rangle\Big], \tag{5}$$

where P indicates the parity of the function. Eq. 5 is the special form of Eq. 6 of Wang and Carrington's work when m_B, the angular momentum of H_2 along the body-fixed z-axis, is zero. Eq. 5 also has the same form as Eq. 4 of Ref [3]. With this basis set, the Hamiltonian matrix is divided into four symmetry blocks [3], with $\big((-1)^{J+P}, k\big) = (+1, \text{even}), (+1, \text{odd}), (-1, \text{even}), (-1, \text{odd})$. There should not be any off-block matrix elements for the Hamiltonian operator. Furthermore, because switching the two indistinguishable H of H_2O results in $(-1)^k\,|jkK\rangle$, the evenness and oddness of k specify para- or ortho-H_2O in the calculation. The restriction on the basis indices of Eq. 5 is $K \geq 0$ and k can be either negative or positive when $K > 0$, but only non-negative when $K = 0$. We should notice that the total parity depends on the value of $(-1)^P$, rather than the single value of $(-1)^{J+k+P}$. We should also notice that when $k = K = 0$, only $(-1)^{J+P} = 1$ retains the non-zero basis function. For the case of $(-1)^{J+P} = -1$ and $k = K = 0$, it would be wise to remove those null basis since the beginning. Despite the symmetry-adapted basis function, the calculation of matrix elements boils down to the calculation of

$$\left\langle JK'M\right|\left\langle j'k'K'\right|\langle\psi_m|\,\hat{H}\,|\psi_n\rangle\,|jkK\rangle\,|JKM\rangle\,, \tag{6}$$

where J and M are conserved because of the spatial isotropy in the absence of external magnetic or electric field.

The matrix element of the first term in Eq. 1 is straightforward:

$$\begin{aligned} &\left\langle JK'M\right|\left\langle j'k'K'\right|\langle\psi_m| -\frac{\hbar^2}{2\mu}R^{-1}\frac{\partial^2}{\partial R^2}R\,|\psi_n\rangle\,|jkK\rangle\,|JKM\rangle \\ =\ & -\frac{\hbar^2}{2\mu}\langle\psi_m|\,R^{-1}\frac{\partial^2}{\partial R^2}R\,|\psi_n\rangle\,\delta_{K'K}\delta_{j'j}\delta_{k'k}. \end{aligned} \tag{7}$$

With this formula, we have

$$\begin{aligned} &\left\langle\Theta_{j'k'}^{mJMK'P}\right| -\frac{\hbar^2}{2\mu}R^{-1}\frac{\partial^2}{\partial R^2}R\left|\Theta_{jk}^{nJMKP}\right\rangle \\ =\ & -\frac{\hbar^2}{4\mu}\frac{\delta_{j'j}}{\sqrt{(1+\delta_{K'0}\delta_{k'0})\,(1+\delta_{K0}\delta_{k0})}}\langle\psi_m|\,R^{-1}\frac{\partial^2}{\partial R^2}R\,|\psi_n\rangle\times \\ & \Big[\delta_{K'K}\delta_{k'k} + (-1)^{J+k+P}\delta_{k',-k}\delta_{K',-K} + (-1)^{J+k'+P}\delta_{-k',k}\delta_{-K',K} + (-1)^{k'+k}\delta_{-k',-k}\delta_{-K',-K}\Big] \\ =\ & -\frac{\hbar^2}{4\mu}\frac{\delta_{j'j}}{\sqrt{(1+\delta_{K'0}\delta_{k'0})\,(1+\delta_{K0}\delta_{k0})}}\langle\psi_m|\,R^{-1}\frac{\partial^2}{\partial R^2}R\,|\psi_n\rangle\times \\ & \Big[2\delta_{K'K}\delta_{k'k} + \Big((-1)^{J+k+P} + (-1)^{J+k'+P}\Big)\,\delta_{k',-k}\delta_{K',-K}\Big] \\ =\ & -\frac{\hbar^2}{2\mu}\langle\psi_m|\,R^{-1}\frac{\partial^2}{\partial R^2}R\,|\psi_n\rangle\,\frac{\delta_{j'j}}{\sqrt{(1+\delta_{K'0}\delta_{k'0})\,(1+\delta_{K0}\delta_{k0})}}\Big[\delta_{K'K}\delta_{k'k} + (-1)^{J+P}\delta_{k',0}\delta_{k,0}\delta_{K',0}\delta_{K,0}\Big] \\ =\ & -\frac{\hbar^2}{2\mu}\langle\psi_m|\,R^{-1}\frac{\partial^2}{\partial R^2}R\,|\psi_n\rangle\,\frac{\delta_{j'j}\delta_{K'K}\delta_{k'k}}{1+\delta_{K0}\delta_{k0}}\left(1 + (-1)^{J+P}\delta_{k0}\delta_{K0}\right) \end{aligned} \tag{8}$$

which is strictly diagonal in j, k, and K. When the null basis functions of $k = 0$, $K = 0$, and $J + P = odd$ are moved, the resultant matrix element would be

$$-\frac{\hbar^2}{2\mu} \langle\psi_m| R^{-1} \frac{\partial^2}{\partial R^2} R |\psi_n\rangle . \tag{9}$$

We may further simplify the situation by using radial distribution function, rather than the radial wave function in the integral. The radial distribution is defined as

$$P_n(R) = R\psi_n(R). \tag{10}$$

Substituting $\psi_n(R) = P_n(R)/R$ into Eq. 9, and replace the bra-ket notation with the integral form with the volume element of R^2dR, we have

$$\begin{aligned} -\frac{\hbar^2}{2\mu} \langle\psi_m| R^{-1} \frac{\partial^2}{\partial R^2} R |\psi_n\rangle &= \int R^2 dR \frac{P_m(R)}{R} R^{-1} \left(\frac{\partial^2}{\partial R^2} R \frac{P_n(R)}{R} \right) \\ &= \int dR P_m(R) \frac{\partial^2}{\partial R^2} P_n(R), \end{aligned} \tag{11}$$

which is easy to calculate using DVR equation (Eq. A6 of Ref [4]). In order to plot the radial wave function after calculation, one has to divide each gridded radial distribution function by the grid value, in order to be consistent with its definition in Eq. 10.

The second term in Eq. 1 can be expanded to be

$$\frac{1}{2\mu R^2} \left(\hat{J}^2 + \hat{j}^2 - 2\hat{J}_z\hat{j}_z - \hat{J}_+\hat{j}_+ - \hat{J}_-\hat{j}_- \right), \tag{12}$$

where

$$\hat{j}_\pm = \hat{j}_x \pm i\hat{j}_y; \tag{13}$$

$$\hat{J}_\pm = \hat{J}_x \mp i\hat{J}_y. \tag{14}$$

Eqs. 12 to 14 are taken from Eqs 40 and 41 of Ref [2]. The ladder operators have the normal actions on the operands, i.e.,

$$\hat{j}_\pm |jkK\rangle = \sqrt{j(j+1) - K(K\pm 1)}\, |jkK \pm 1\rangle ; \tag{15}$$

$$\hat{J}_\pm |JKM\rangle = \sqrt{J(J+1) - K(K\pm 1)}\, |JK \pm 1M\rangle . \tag{16}$$

Eq. 16 is the special form of Eq. B7 of Ref [2]. The $\hat{\vec{J}} \cdot \hat{\vec{j}}$ term in Eq. 12 couples the rotations of H_2O and the body-fixed frame, and it is the so-called Coriolis term. In this interaction, the $\hat{J}_+\hat{j}_+$ and $\hat{J}_-\hat{j}_-$ terms couple states with different K values, making K not a good quantum number. With all these relations, we have

$$\begin{aligned} & \langle JK'M| \langle j'k'K'| \langle\psi_m| \frac{(\hat{\vec{J}} - \hat{\vec{j}})^2}{2\mu R^2} |\psi_n\rangle |jkK\rangle |JKM\rangle \\ = \;& \frac{\hbar^2}{2\mu} \langle\psi_m| \frac{1}{R^2} |\psi_n\rangle \delta_{j'j}\delta_{k'k} \left\{ \left[J(J+1) + j(j+1) - 2K^2 \right] \delta_{K'K} \right. \\ & - \sqrt{J(J+1) - K(K+1)}\sqrt{j(j+1) - K(K+1)}\delta_{K',K+1} \\ & \left. - \sqrt{J(J+1) - K(K-1)}\sqrt{j(j+1) - K(K-1)}\delta_{K',K-1} \right\} . \end{aligned} \tag{17}$$

The matrix elements of $\hat{J}_+\hat{j}_+$ and $\hat{J}_-\hat{j}_-$ have wrong sign (+) in Eq. 42 of Ref [2] and I have confirmed with Doctor van der Avoird about that. Eq. 17 should be correct. Employing this expression and after some algebra, I obtain

$$\begin{aligned}
&\left\langle \Theta_{j'k'}^{mJMK'P} \right| \frac{(\hat{\vec{J}}-\hat{\vec{j}})^2}{2\mu R^2} \left| \Theta_{jk}^{nJMKP} \right\rangle \\
= \; & \frac{\hbar^2}{2\mu R_n^2} \frac{\delta_{j'j}}{\sqrt{(1+\delta_{K'0}\delta_{k'0})(1+\delta_{K0}\delta_{k0})}} \Big\{ E_{JjK}\delta_{K'K}\left(\delta_{k'k}+(-1)^{J+k+P}\delta_{-k',k}\delta_{K0}\right) \\
& -C_{J,K}^{+}C_{j,K}^{+}\delta_{K',K+1}\left(\delta_{k'k}+(-1)^{J+k+P}\delta_{-k',k}\delta_{K0}\right) - C_{J,K}^{-}C_{j,K}^{-}\delta_{K',K-1}\left(\delta_{k'k}+(-1)^{J+k+P}\delta_{-k',k}\delta_{K1}\right)\Big\}
\end{aligned} \tag{18}$$

where $E_{JjK} = J(J+1) + j(j+1) - 2K^2$ and $C_{J,K}^{+} = \sqrt{J(J+1)-K(K+1)}$.

The third term in Eq. 1 is the rotational Hamiltonian of the rigid H_2O, which conserves all basis labels except for k. Therefore, we have

$$\begin{aligned}
& \left\langle JK'M \right| \left\langle j'k'K' \right| \langle \psi_m | \hat{H}_{\mathrm{H_2O}} |\psi_n\rangle |jkK\rangle |JKM\rangle \\
= \; & \delta_{mn}\delta_{K'K}\delta_{j'j} \left\langle jk'K \right| \hat{H}_{\mathrm{H_2O}} |jkK\rangle
\end{aligned} \tag{19}$$

We choose the z'-axis of the H_2O-fixed frame to be along the C_2 axis, which is also the principal axis with the medium rotational constant (B), and the $x'z'$-plane is the H_2O-plane. With this selection, $\hat{H}_{\mathrm{H_2O}}$ has the following form:

$$\begin{aligned}
\hat{H}_{\mathrm{H_2O}} = \; & \left(\frac{A+C}{2}\right)\hat{j}^2 + \left[B - \left(\frac{A+C}{2}\right)\right]\hat{j}_{z'}^2 + \left(\frac{A-C}{4}\right)\left(\hat{j}_+^2+\hat{j}_-^2\right) \\
& -\Delta_j\hat{j}^4 - \Delta_k\hat{j}_{z'}^4 - \Delta_{jk}\hat{j}^2\hat{j}_{z'}^2 - 2\sigma_j\hat{j}^2\left(\hat{j}_+^2+\hat{j}_-^2\right) - \sigma_k\left[\hat{j}_{z'}^2\left(\hat{j}_+^2+\hat{j}_-^2\right)+\left(\hat{j}_+^2+\hat{j}_-^2\right)\hat{j}_{z'}^2\right].
\end{aligned} \tag{20}$$

Eq. 20 is taken from Eq. 2 of Ref [3] with typos being corrected and all the angular momentum operators are embedded in the H_2O-fixed frame, i.e., $\hat{j}_\pm = \hat{j}_{x'} \mp i\hat{j}_{y'}$. Be cautious that since the potential energy surface $V(R,\theta,\chi)$ contains the vibrational correction of the ground vibrational state of H_2O, the corresponding rotational constants and quartic centrifugal distortion parameters, i.e., A_0, B_0, C_0, etc., should be used. With the first three terms, we have the rigid rotor's matrix element:

$$\begin{aligned}
\left\langle jk'K \right| \hat{H}_{\mathrm{H_2O}} |jkK\rangle = \; & \delta_{k'k}\left\{\left(\frac{A+C}{2}\right)j(j+1) + \left(B-\frac{A+C}{2}\right)k^2\right\} \\
& + \left(\frac{A-C}{4}\right)\sqrt{j(j+1)-k(k+1)}\sqrt{j(j+1)-(k+1)(k+2)}\,\delta_{k',k+2} \\
& + \left(\frac{A-C}{4}\right)\sqrt{j(j+1)-k(k-1)}\sqrt{j(j+1)-(k-1)(k-2)}\,\delta_{k',k-2} \\
& .
\end{aligned} \tag{21}$$

This matrix element is consistent with Eq. 38b of Ref [2] and the rotational constants should have the unit of energy. The fourth to sixth terms of Eq. 20 brings about matrix element of

$$-\delta_{k'k}\left(\Delta_j j^2(j+1)^2 + \Delta_k k^4 + \Delta_{jk} j(j+1)k^2\right), \tag{22}$$

where the Δ should have unit of energy too. The last two terms in Eq. 20 give out

$$\left[-2\sigma_j j(j+1)-\sigma_k\left(k'^2+k^2\right)\right]\left(\sqrt{j(j+1)-k(k+1)}\sqrt{j(j+1)-(k+1)(k+2)}\delta_{k',k+2}\right.$$
$$\left.+\sqrt{j(j+1)-k(k-1)}\sqrt{j(j+1)-(k-1)(k-2)}\delta_{k',k-2}\right), \qquad (23)$$

where the σ should also have the unit of energy. Depending on different levels of corrections, Eqs 21 to 23 can be subsequently added to the total Hamiltonian matrix. If we want to assign $j_{K_aK_c}$ label to the final wave functions, the $\langle jk'K|\,\hat{H}_{\mathrm{H_2O}}\,|jkK\rangle$ matrix needs to be diagonalized separately. For the rigid H_2O rotor approximation, the matrix element in the symmetry-adapted basis reads

$$\begin{aligned}
&\left\langle\Theta^{mJMK'P}_{j'k'}\right|\hat{H}_{\mathrm{H_2O}}\left|\Theta^{nJMKP}_{jk}\right\rangle \\
=\;&\frac{\delta_{mn}\delta_{j'j}\delta_{K'K}}{\sqrt{(1+\delta_{K'0k'0})\left(1+\delta_{K0k0}\right)}}\left\{\left[\left(\frac{A+C}{2}\right)j\left(j+1\right)+\left(B-\frac{A+C}{2}\right)k^2\right]\left(\delta_{k'k}+(-1)^{J+k+P}\delta_{K0}\delta_{k',-k}\right)\right.\\
&+\frac{A-C}{4}\left[C^{+}_{j,k}C^{+}_{j,k+1}\left(\delta_{k',k+2}+(-1)^{J+k+P}\delta_{K0}\delta_{-k',k+2}\right)\right.\\
&\left.\left.+C^{-}_{j,k}C^{-}_{j,k-1}\left(\delta_{k',k-2}+(-1)^{J+k+P}\delta_{K0}\delta_{-k',k-2}\right)\right]\right\}. \qquad (24)
\end{aligned}$$

For the last term in Eq. 1, the potential term, since it does not depend on ϕ, i.e., it is invariant to the rotation about the body-fixed z-axis, it diagonalizes K, and we have

$$\left\langle JK'M\right|\left\langle j'k'K'\right|\langle\psi_m|\,V(R,\theta,\chi)\,|\psi_n\rangle\,|jkK\rangle\,|JKM\rangle=\delta_{K',K}\left\langle j'k'K\right|\langle\psi_m|\,V(R,\theta,\chi)\,|\psi_n\rangle\,|jkK\rangle\,. (25)$$

Notice that $V(R,\theta,\chi)$ makes the H_2O rotation anisotropic and different j and k values can be coupled. With the parity-adapted basis functions, the matrix element is:

$$\begin{aligned}
&\left\langle\Theta^{mJMK'P}_{j'k'}\right|V(R,\theta,\chi)\left|\Theta^{nJMKP}_{jk}\right\rangle \\
=\;&\frac{\delta_{K'K}}{4\pi}\sqrt{\frac{(2j+1)(2j'+1)}{(1+\delta_{K0}\delta_{k'0})(1+\delta_{K0}\delta_{k0})}}\int d\chi\int\sin\theta d\theta\,\langle\psi_m|\,V(R,\theta,\chi)\,|\psi_n\rangle\times\\
&\left[\cos[(k-k')\chi]d^{j'}_{Kk'}(\theta)d^{j}_{Kk}(\theta)+(-1)^{J+P}\delta_{K0}\cos[(k'+k)\chi]d^{j'}_{0k'}(\theta)d^{j}_{0k}(\theta)\right]. \qquad (26)
\end{aligned}$$

The detailed derivation of this formula follows.

$$\begin{aligned}
&\left\langle\Theta^{mJMK'P}_{j'k'}\right|V\left|\Theta^{nJMKP}_{jk}\right\rangle \\
=\;&\frac{\delta_{mn}}{2\sqrt{(1+\delta_{K'0}\delta_{k'0})(1+\delta_{K0}\delta_{k0})}}\left[\left\langle j'k'K'\right|\left\langle JK'M\right|+(-1)^{J+k'+P}\left\langle j'-k'-K'\right|\left\langle J-K'M\right|\right]V_n\times\\
&\left[|jkK\rangle\,|JKM\rangle+(-1)^{J+k+P}\,|j-k-K\rangle\,|J-KM\rangle\right], \qquad (27)
\end{aligned}$$

where $V_n(\theta,\chi)=V(R_n,\theta,\chi)$ because the radial basis $\{|\psi_n\rangle\}$ are eigenstates of $\hat{R}$ with eigenvalues $\{R_n\}$. The content in the square bracket becomes

$$\delta_{K'K}\left\langle j'k'K'\right|V_n\,|jkK\rangle+(-1)^{J+k+P}\delta_{K',-K}\left\langle j'k'K'\right|V_n\,|j-k-K\rangle+$$
$$(-1)^{J+k'+P}\delta_{-K',K}\left\langle j'-k'-K'\right|V_n\,|jkK\rangle+(-1)^{k+k'}\delta_{-K',-K}\left\langle j'-k'-K'\right|V_n\,|j-k-K\rangle\,. \quad (28)$$

With the equality of $(-1)^k = (-1)^{k'}$ and the restriction of $K; K' \geq 0$, the expression becomes

$$\begin{aligned} &\delta_{K'K} \left[\langle j'k'K | V_n | jkK \rangle + \langle j' - k' - K | V_n | j - k - K \rangle \right] + \\ &(-1)^{J+k+P} \delta_{K'K} \delta_{K0} \left[\langle j'k'0 | V_n | j - k0 \rangle + \langle j' - k'0 | V_n | jk0 \rangle \right] \end{aligned} \tag{29}$$

Let's focus on the first square bracket of Eq. 29. With Eq. 3, we have

$$\begin{aligned} &\langle j'k'K | V_n | jkK \rangle \\ = &\frac{\sqrt{(2j'+1)(2j+1)}}{8\pi^2} \int_0^{2\pi} d\phi \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta e^{-iK\phi} d^{j'}_{Kk'}(\theta) e^{-ik'\chi} V_n(\theta,\chi) e^{iK\phi} d^{j}_{Kk}(\theta) e^{ik\chi} \\ = &\frac{\sqrt{(2j'+1)(2j+1)}}{4\pi} \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta d^{j'}_{Kk'}(\theta) d^{j}_{Kk}(\theta) e^{i(k-k')\chi} V_n(\theta,\chi); \end{aligned} \tag{30}$$

$$\begin{aligned} &\langle j' - k' - K | V_n | j - k - K \rangle \\ = &\frac{\sqrt{(2j'+1)(2j+1)}}{8\pi^2} \int_0^{2\pi} d\phi \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta e^{iK\phi} d^{j'}_{-K,-k'}(\theta) e^{ik'\chi} V_n(\theta,\chi) e^{-iK\phi} d^{j}_{-K,-k} e^{-ik\chi} \\ = &\frac{\sqrt{(2j'+1)(2j+1)}}{4\pi} \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta d^{j'}_{-K,-k'}(\theta) d^{j}_{-K,-k}(\theta) e^{-i(k-k')\chi} V_n(\theta,\chi) \\ = &\frac{\sqrt{(2j'+1)(2j+1)}}{4\pi} \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta d^{j'}_{K,k'}(\theta) d^{j}_{K,k}(\theta) e^{-i(k-k')\chi} V_n(\theta,\chi). \end{aligned} \tag{31}$$

To obtain the last equality, the relation of $d^j_{-K,-k} = (-1)^{K-k} d^j_{K,k}$ (Zare's Eq. 3.70) is used. This relation is used several times in the following steps without specification. The summation of the last two equations gets the first square bracket of Eq. 29 to

$$\frac{\sqrt{(2j'+1)(2j+1)}}{2\pi} \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta d^{j'}_{K,k'}(\theta) d^{j}_{K,k}(\theta) \cos\left[(k-k')\chi\right] V_n(\theta,\chi). \tag{32}$$

Now let's look at the second square bracket of Eq. 29.

$$\begin{aligned} &\langle j'k'0 | V_n | j - k0 \rangle \\ = &\frac{\sqrt{(2j'+1)(2j+1)}}{8\pi^2} \int_0^{2\pi} d\phi \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta e^{-i0\phi} d^{j'}_{0,k'}(\theta) e^{-ik'\chi} V_n(\theta,\chi) e^{i0\phi} d^{j}_{0,-k}(\theta) e^{-ik\chi} \\ = &\frac{\sqrt{(2j'+1)(2j+1)}}{4\pi} \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta d^{j'}_{0,k'}(\theta) d^{j}_{0,-k}(\theta) e^{-i(k'+k)\chi} V_n(\theta,\chi) \\ = &(-1)^k \frac{\sqrt{(2j'+1)(2j+1)}}{4\pi} \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta d^{j'}_{0,k'}(\theta) d^{j}_{0,k}(\theta) e^{-i(k'+k)\chi} V_n(\theta,\chi); \end{aligned} \tag{33}$$

$$
\begin{aligned}
&\left\langle j'-k'0\right| V_n \left|jk0\right\rangle \\
= &\ \frac{\sqrt{(2j'+1)(2j+1)}}{8\pi^2}\int_0^{2\pi} d\phi \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta e^{-i0\phi} d^{j'}_{0,-k'}(\theta) e^{ik'\chi} V_n(\theta,\chi) e^{i0\phi} d^{j}_{0,k}(\theta) e^{ik\chi} \\
= &\ \frac{\sqrt{(2j'+1)(2j+1)}}{4\pi}\int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d^{j'}_{0,-k'}(\theta) d^{j}_{0,k}(\theta) e^{i(k'+k)\chi} V_n(\theta,\chi) \\
= &\ (-1)^{k'}\frac{\sqrt{(2j'+1)(2j+1)}}{4\pi}\int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta d^{j'}_{0,k'}(\theta) d^{j}_{0,k}(\theta) e^{i(k'+k)\chi} V_n(\theta,\chi).
\end{aligned} \tag{34}
$$

The summation of the last two equations gets the second square bracket of Eq. 29 to

$$
(-1)^k \frac{\sqrt{(2j'+1)(2j+1)}}{2\pi}\int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta d^{j'}_{0,k'}(\theta) d^{j}_{0,k}(\theta) \cos\left[(k'+k)\chi\right] V_n(\theta,\chi). \tag{35}
$$

Plugging Eqs. 32 and 35 in Eq. 29, and plugging the resultant Eq 29 in Eq. 27, we have

$$
\begin{aligned}
&\left\langle \Theta^{mJMK'P}_{j'k'}\right| V(R,\theta,\chi) \left|\Theta^{nJMKP}_{jk}\right\rangle \\
= &\ \frac{\delta_{K'K}\delta_{mn}}{4\pi}\sqrt{\frac{(2j+1)(2j'+1)}{(1+\delta_{K0}\delta_{k'0})(1+\delta_{K0}\delta_{k0})}}\int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta V_n(\theta,\chi) \times \\
&\left[\cos[(k-k')\chi] d^{j'}_{Kk'}(\theta) d^{j}_{Kk}(\theta) + (-1)^{J+P}\delta_{K0}\cos[(k'+k)\chi] d^{j'}_{0k'}(\theta) d^{j}_{0k}(\theta)\right].
\end{aligned} \tag{36}
$$

Let's switch to the discussion of Gauss quadrature of the integral $\int_{\chi=0}^{2\pi} d\chi f(\chi)$, where $f(\chi)$ is just a generic function without any assumption on symmetry and periodicity.

$$
\begin{aligned}
\int_{\chi=0}^{2\pi} d\chi f(\chi) &= \int_{\chi=0}^{2\pi} d\chi \sin\chi \frac{f(\chi)}{\sin\chi} \\
&= \int_{\chi=0}^{\pi} d\chi \sin\chi \frac{f(\chi)}{\sin\chi} + \int_{\chi=\pi}^{2\pi} d\chi \sin\chi \frac{f(\chi)}{\sin\chi} \\
&= \int_{\chi=0}^{\pi} d(-\cos\chi) \frac{f(\chi)}{\sqrt{1-\cos^2\chi}} + \int_{\chi=\pi}^{2\pi} d(-\cos\chi) \frac{f(\chi)}{-\sqrt{1-\cos^2\chi}} \\
&= \int_{\cos\chi=-1}^{1} d(\cos\chi) \frac{f(\cos^{-1}(\cos\chi))}{\sqrt{1-\cos^2\chi}} + \int_{\cos\chi=-1}^{1} d(\cos\chi) \frac{f(2\pi-\cos^{-1}(\cos\chi))}{\sqrt{1-\cos^2\chi}} \\
&= \int_{x=-1}^{1} dx \frac{f(\cos^{-1}x)}{\sqrt{1-x^2}} + \int_{x=-1}^{1} dx \frac{f(2\pi-\cos^{-1}x)}{\sqrt{1-x^2}} \\
&= \int_{x=-1}^{1} dx \frac{1}{\sqrt{1-x^2}} \left[f(\cos^{-1}x) + f(2\pi-\cos^{-1}x)\right] \\
&\approx \sum_i w_i^{GC} \left[f(\cos^{-1}x_i^{GC}) + f(2\pi-\cos^{-1}x_i^{GC})\right],
\end{aligned} \tag{37}
$$

where $\left\{w^{GC}\right\}$ and $\left\{x^{GC}\right\}$ are the Gauss-Chebyshev weights and grids. Obviously, if we only need n operations to obtain the result with $2n$ grids. If $f(\chi)$ is periodic with 2π period, then we can replace

$f(2\pi - \cos^{-1} x_i^{GC})$ by $f(-\cos^{-1} x_i^{GC})$. However, I prefer a more general formula and actually, calculating $f(2\pi - \cos^{-1} x_i^{GC})$ is not more time-consuming than $f(-\cos^{-1} x_i^{GC})$. Eq. 36 can be concisely written as

$$\begin{aligned}\left\langle \Theta_{j'k'}^{mJMK'P} \right| V \left| \Theta_{jk}^{nJMKP} \right\rangle &= \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta f\left(\theta, \chi; j', k', j, k, K, n, J, P\right) \\ &= \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta f\left(\theta, \chi; j', k', j, k\right), \end{aligned} \tag{38}$$

where the semicolon separates the true variables and quantum numbers. The quantum numbers without the primed pairs are conserved by V and in the second equality, I have hidden all the conserved quantum numbers for further conciseness. Now let's look at the matrix multiplication $\underline{u} = \underline{\underline{V}}\underline{v}$. In this note, single (double) underline denotes vector (matrix). The selection rule of V leads to

$$\begin{aligned} u_{j'k'}^{mK} &= \sum_{j,k} \left[\int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta f\left(\theta, \chi; j', k', j, k\right)\right] v_{jk}^{mK} \\ &= \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta d\theta \left[\sum_{j,k} f\left(\theta, \chi; j', k', j, k\right) v_{jk}^{mK}\right] \\ &= \int_0^{2\pi} d\chi \sum_l w_l^{GL} \left[\sum_{j,k} f\left(\cos^{-1}(y_l^{GL}), \chi; j', k', j, k\right) v_{jk}^{mK}\right] \\ &= \sum_i w_i^{GC} \sum_l w_l^{GL} \left\{\sum_{j,k} \left[f\left(\cos^{-1}(y_l^{GL}), \cos^{-1}(x_i^{GC}); j', k', j, k\right) + \right.\right. \\ &\quad \left.\left. f\left(\cos^{-1}(y_l^{GL}), 2\pi - \cos^{-1}(x_i^{GC}); j', k', j, k\right)\right] v_{jk}^{mK} \right\}, \end{aligned} \tag{39}$$

where $\left\{w^{GL}\right\}$ and $\left\{y^{GL}\right\}$ are the Gauss-Legendre weights and grids. For the conciseness in the following derivation, I define $\chi_i = \cos^{-1}\left(x_i^{GC}\right)$ and $\theta_l = \cos^{-1}\left(y_l^{GL}\right)$. With these definitions and Eq. 36, we have

$$\begin{aligned} & f\left(\theta_l, \chi_i; j', k', j, k\right) + f\left(\theta_l, 2\pi - \chi_i; j', k', j, k\right) \\ = \; & \frac{1}{4\pi} \sqrt{\frac{(2j+1)(2j'+1)}{(1+\delta_{K0}\delta_{k'0})(1+\delta_{K0}\delta_{k0})}} \Big\{ \\ & V_n(\theta_l, \chi_i) \left[\cos\left[(k-k')\chi_i\right] d_{Kk'}^{j'}(\theta_l) d_{Kk}^{j}(\theta_l) + (-1)^{J+P} \delta_{K0} \cos\left[(k'+k)\chi_i\right] d_{0k'}^{j'}(\theta_l) d_{0k}^{j}(\theta_l)\right] + \\ & V_n(\theta_l, 2\pi - \chi_i) \left[\cos\left[(k-k')(2\pi - \chi_i)\right] d_{Kk'}^{j'}(\theta_l) d_{Kk}^{j}(\theta_l) + \right. \\ & \left. (-1)^{J+P} \delta_{K0} \cos\left[(k'+k)(2\pi - \chi_i)\right] d_{0k'}^{j'}(\theta_l) d_{0k}^{j}(\theta_l)\right] \Big\}. \end{aligned} \tag{40}$$

Considering the C_{2v} symmetry of V, we have $V_n(\theta_l, 2\pi - \chi_i) = V_n(\theta_l, \chi_i)$. Also, the integer nature of $k - k'$ and $k + k'$ guarantees $\cos\left[(k-k')(2\pi - \chi_i)\right] = \cos\left[(k-k')\chi_i\right]$ and $\cos\left[(k'+k)(2\pi - \chi_i)\right] = \cos\left[(k'+k)\chi_i\right]$. With these equalities, the two terms in the curly bracket of Eq. 40 are identical and Eq. 52

reduces to

$$\begin{aligned}
& f\left(\theta_l, \chi_i; j', k', j, k\right) + f\left(\theta_l, 2\pi - \chi_i; j', k', j, k\right) \\
= \;& \frac{1}{2\pi}\sqrt{\frac{(2j+1)(2j'+1)}{(1+\delta_{K0}\delta_{k'0})(1+\delta_{K0}\delta_{k0})}} \times \\
& V_n(\theta_l,\chi_i)\left[\cos\left[(k-k')\chi_i\right] d^{j'}_{Kk'}(\theta_l) d^{j}_{Kk}(\theta_l) + (-1)^{J+P}\delta_{K0}\cos\left[(k'+k)\chi_i\right] d^{j'}_{0k'}(\theta_l) d^{j}_{0k}(\theta_l)\right] \\
= \;& 2f\left(\theta_l, \chi_i; j', k', j, k\right). \qquad (41)
\end{aligned}$$

Consequently, Eq. 39 becomes

$$u^{nK}_{j'k'} = \sum_i w^{GC}_i \sum_l w^{GL}_l \left[\sum_{jk} 2f\left(\theta_l, \chi_i; j', k', j, k\right) v^{nK}_{jk}\right]. \qquad (42)$$

By taking the $\sum_i w^{GC}_i \sum_l w_l$, we essentially evaluate $V_n(\theta, \chi)$ for each Gauss quadrature point (θ_l, χ_i) only once, and this fact decreases the computational resource substantially.

If desired, Eq. 42 can be written in a matrix form. Let's go back to the definition of $2f\left(\theta_l, \chi_i; j', k', j, k\right)$ in Eq. 41 and break the cos function to be

$$\cos\left[(k-k')\chi_i\right] = \cos(k\chi_i)\cos(k'\chi_i) + \sin(k\chi_i)\sin(k'\chi_i); \qquad (43)$$

$$\cos\left[(k+k')\chi_i\right] = \cos(k\chi_i)\cos(k'\chi_i) - \sin(k\chi_i)\sin(k'\chi_i). \qquad (44)$$

Substituting these two equalities into the square bracket in the first equality of of Eq. 41, we have

$$\begin{aligned}
& \cos(k'\chi_i)\cos(k\chi_i) d^{j'}_{Kk'}(\theta_l) d^{j}_{Kk}(\theta_l) + \sin(k'\chi_i)\sin(k\chi_i) d^{j'}_{Kk'}(\theta_l) d^{j}_{Kk}(\theta_l) \\
& + (-1)^{J+P}\delta_{K0}\cos(k'\chi_i)\cos(k\chi_i) d^{j'}_{0k'}(\theta_l) d^{j}_{0k}(\theta_l) - (-1)^{J+P}\delta_{K0}\sin(k'\chi_i)\sin(k\chi_i) d^{j'}_{0k'}(\theta_l) d^{j}_{0k}(\theta_l) \\
= \;& \cos(k'\chi_i)\cos(k\chi_i) d^{j'}_{Kk'}(\theta_l) d^{j}_{Kk}(\theta_l)\left(1 + (-1)^{J+P}\delta_{K0}\right) \\
& + \sin(k'\chi_i)\sin(k\chi_i) d^{j'}_{Kk'}(\theta_l) d^{j}_{Kk}(\theta_l)\left(1 - (-1)^{J+P}\delta_{K0}\right). \qquad (45)
\end{aligned}$$

There are three cases for Eq. 45:

1. $K = 0$ and $J + P$ even, Eq. 45 becomes

$$2\cos(k'\chi_i)\cos(k\chi_i) d^{j'}_{Kk'}(\theta_l) d^{j}_{Kk}(\theta_l). \qquad (46)$$

   Plugging this back in Eq. 41 we have

$$2f\left(\theta_l, \chi_i; j', k', j, k\right) = \frac{1}{\pi}\sqrt{\frac{(2j+1)(2j'+1)}{(1+\delta_{K0}\delta_{k'0})(1+\delta_{K0}\delta_{k0})}} V_n(\theta_l,\chi_i)\cos(k'\chi_i)\cos(k\chi_i) d^{j'}_{Kk'}(\theta_l) d^{j}_{Kk}(\theta_l). \qquad (47)$$

   Putting this equation back in Eq. 42, taking $w^{GC}_i = \frac{\pi}{n_\chi}$, and with the definition of

$$T^{K,(\cos)}_{il,jk} = \sqrt{\frac{w^{GL}_l(2j+1)}{n_\chi(1+\delta_{K0}\delta_{k0})}}\cos(k\chi_i) d^{j}_{Kk}(\theta_l), \qquad (48)$$

we have

$$u^{n0}_{j'k'} = \sum_{il} T^{0,(\cos)}_{il,j'k'} V_n(\theta_l,\chi_i) \sum_{jk} T^{0,(\cos)}_{il,jk} v^{n0}_{jk}, \tag{49}$$

which has a matrix multiplication form. n_χ is the number of χ grid points.

2. $K=0$ and $J+P$ odd, Eq. 45 becomes

$$2\sin(k'\chi_i)\sin(k\chi_i) d^{j'}_{Kk'}(\theta_l) d^{j}_{Kk}(\theta_l). \tag{50}$$

With the definition of

$$T^{K,(\sin)}_{il,jk} = \sqrt{\frac{w^{GL}_l(2j+1)}{n_\chi(1+\delta_{K0}\delta_{k0})}} \sin(k\chi_i) d^{j}_{Kk}(\theta_l), \tag{51}$$

we have

$$u^{n0}_{j'k'} = \sum_{il} T^{0,(\sin)}_{il,j'k'} V_n(\theta_l,\chi_i) \sum_{jk} T^{0,(\sin)}_{il,jk} v^{n0}_{jk}, \tag{52}$$

which also has a matrix multiplication form.

3. $K \neq 0$, we have

$$u^{nK}_{j'k'} = \frac{1}{2}\left[\sum_{il} T^{K,(\cos)}_{il,j'k'} V_n(\theta_l,\chi_i) \sum_{jk} T^{K,(\cos)}_{il,jk} v^{nK}_{jk} + \sum_{il} T^{K,(\sin)}_{il,j'k'} V_n(\theta_l,\chi_i) \sum_{jk} T^{K,(\sin)}_{il,jk} v^{nK}_{jk}\right], \tag{53}$$

and it is also a matrix multiplication formula.

We may stick to the general Eq. 42 or the specific Eqs. 49, 52, and 53 for $\underline{\underline{V}}$ matrix manipulation. Based on the formulas above, we have a trick to use the FFT grids used by Wang and Carrington by seting

$$\chi_i = \frac{\pi(i-1)}{n_\chi} \text{ or } \chi_i = \frac{\pi(i-1/2)}{n_\chi}. \tag{54}$$

The following derivation is the attempt to use discrete cosine transform to evaluate the potential matrix. Let's start from Eq. 39 with the definition of $f(\theta,\chi;j',k',j,k)$ in Eq. 41, we have

$$\begin{aligned} u^{nK}_{j'k'} = & \sum_{jk} \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta \frac{1}{4\pi} \sqrt{\frac{(2j+1)(2j'+1)}{(1+\delta_{K0}\delta_{k'0})(1+\delta_{K0}\delta_{k0})}} \times \\ & V_n(\theta,\chi)\left[\cos\left[(k-k')\chi\right] d^{j'}_{Kk'}(\theta) d^{j}_{Kk}(\theta) + (-1)^{J+P}\delta_{K0}\cos\left[(k'+k)\chi\right] d^{j'}_{0k'}(\theta) d^{j}_{0k}(\theta)\right] v^{nK}_{jk} \end{aligned} \tag{55}$$

and considering only the case of $K \neq 0$, we have

$$
\begin{aligned}
u_{j'k'}^{nK} &= \sum_{jk} \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta \frac{1}{4\pi} \sqrt{\frac{(2j+1)(2j'+1)}{(1+\delta_{K0}\delta_{k'0})(1+\delta_{K0}\delta_{k0})}} V_n(\theta,\chi) \cos\left[(k-k')\chi\right] d_{Kk'}^{j'}(\theta) d_{Kk}^{j}(\theta) v_{jk}^{nK} \\
&= \sum_{jk} \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta \frac{1}{4\pi} \sqrt{\frac{(2j+1)(2j'+1)}{(1+\delta_{K0}\delta_{k'0})(1+\delta_{K0}\delta_{k0})}} V_n(\theta,\chi) d_{Kk'}^{j'}(\theta) d_{Kk}^{j}(\theta) \times \\
&\quad \left(\cos k'\chi \cos k\chi + \sin k'\chi \sin k\chi\right) v_{jk}^{nK}. \qquad (56)
\end{aligned}
$$

Let's first further narrow down the case of the $\cos$ term in the parenthesis:

$$
\sum_{jk} \int_0^{2\pi} d\chi \int_0^{\pi} \sin\theta \frac{1}{4\pi} \sqrt{\frac{(2j+1)(2j'+1)}{(1+\delta_{K0}\delta_{k'0})(1+\delta_{K0}\delta_{k0})}} V_n(\theta,\chi) d_{Kk'}^{j'}(\theta) d_{Kk}^{j}(\theta) \cos k'\chi \cos k\chi v_{jk}^{nK}. \quad (57)
$$

Using the same grid for χ as Wang and Carrington:

$$
\chi_\beta = \frac{2\pi}{n_\chi}\beta; \beta = 0, 1, \cdots, n_\chi - 1; w = \frac{2\pi}{n_\chi}, \quad (58)
$$

and the same Gauss-Legendre grid $\{\theta_\alpha\}$ and weights $\{w_\alpha\}$, Eq. 57 becomes

$$
\begin{aligned}
&\sum_{jk} \sum_{\alpha} \sum_{\beta} w_\alpha \frac{1}{2n_\chi} \sqrt{\frac{(2j+1)(2j'+1)}{(1+\delta_{K0}\delta_{k'0})(1+\delta_{K0}\delta_{k0})}} V_n\left(\theta_\alpha, \left(\frac{2\pi\beta}{n_\chi}\right)\right) \times \\
&d_{Kk'}^{j'}(\theta_\alpha) d_{Kk}^{j}(\theta_\alpha) \cos\left(\frac{2\pi k'\beta}{n_\chi}\right) \cos\left(\frac{2\pi k\beta}{n_\chi}\right) v_{jk}^{nK} \\
= &\sum_{\alpha} \sum_{\beta} w_\alpha \frac{1}{2n_\chi} \sqrt{\frac{2j'+1}{1+\delta_{K0}\delta_{k'0}}} V_n\left(\theta_\alpha, \left(\frac{2\pi\beta}{n_\chi}\right)\right) d_{Kk'}^{j'}(\theta_\alpha) \cos\left(\frac{2\pi k'\beta}{n_\chi}\right) \times \\
&\sum_j \sqrt{2j+1} \sum_{k=0 \text{ or } 1}^{j \text{ or } j-1} \cos\left(\frac{2\pi k\beta}{n_\chi}\right) \sqrt{\frac{1}{1+\delta_{K0}\delta_{k0}}} d_{Kk}^{j}(\theta_\alpha) v_{jk}^{nK} \qquad (59)
\end{aligned}
$$

In addition to the Hamiltonian matrix elements, we also need to calculate the dipole matrix elements in order to calculate the transition dipole moments, which are needed for the evaluation of the line strengths. I follow Wang and Carrington's derivation to calculate the matrix elements. Suppose the light is polarized along the space-fixed Z-axis and then, only μ_Z needs to be concerned. Here, μ stands for dipole moment operator and should not be misunderstood as the aforementioned reduced mass. We need to evaluate the following matrix element:

$$
\left\langle J'K'M' \right| \left\langle j'k'K' \right| \left\langle \psi_m \right| \mu_Z \left| \psi_n \right\rangle \left| jkK \right\rangle \left| JKM \right\rangle. \quad (60)
$$

Employing the knowledge of spherical tensor, $\mu_Z = \mu_0^{SF}$, where the superscript "SF" stands for space-fixed. μ_0^{SF} can be expanded as linear combination of the dipole moment components in the body-fixed frame:

$$
\mu_0^{SF} = \sum_{\sigma=-1}^{-1} D_{0,\sigma}^{1}(\alpha,\beta,0)^* \mu_\sigma^{BF}. \quad (61)
$$

Because H_2 does not contribute to dipole moment, μ_σ^{BF} can likewise be expanded as combination of the components in the H_2O-fixed frame as

$$\mu_\sigma^{BF} = \sum_{\sigma=-1}^{-1} D^1_{\sigma,\sigma'}(\phi,\theta,\chi)^* \mu_{\sigma'}^{\mathrm{H_2O}}. \tag{62}$$

Since the only non-zero dipole component is along the C_2 axis (H_2O-fixed z-axis), σ' can only be zero and we have

$$\mu_0^{SF} = \mu_{\mathrm{H_2O}} \sum_{\sigma=-1}^{-1} D^1_{0,\sigma}(\alpha,\beta,0)^* D^1_{\sigma,0}(\phi,\theta,\chi)^*. \tag{63}$$

Then Eq. 60 becomes

$$\begin{aligned}
& \mu_{\mathrm{H_2O}} \sum_{\sigma=-1}^{1} \left\langle J'K'M' \right| \left\langle j'k'K' \right| \langle \psi_m | D^1_{0,\sigma}(\alpha,\beta,0)^* D^1_{\sigma,0}(\phi,\theta,\chi)^* | \psi_n \rangle | jkK \rangle | JKM \rangle \\
= \; & \delta_{m,n} \mu_{\mathrm{H_2O}} \sum_{\sigma=-1}^{1} \left\langle J'K'M' \right| D^1_{0,\sigma}(\alpha,\beta,0)^* | JKM \rangle \left\langle j'k'K' \right| D^1_{\sigma,0}(\phi,\theta,\chi)^* | jkK \rangle \\
= \; & \delta_{m,n} \mu_{\mathrm{H_2O}} \sum_{\sigma=-1}^{1} (-1)^{k'+K'} \sqrt{2j+1}\sqrt{2j'+1} \begin{pmatrix} j' & 1 & j \\ -k' & 0 & k \end{pmatrix} \begin{pmatrix} j' & 1 & j \\ -K' & \sigma & K \end{pmatrix} \times \\
& \times (-1)^{K'+M'} \sqrt{2J+1}\sqrt{2J'+1} \begin{pmatrix} J' & 1 & J \\ -K' & \sigma & K \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -M' & 0 & M \end{pmatrix}.
\end{aligned} \tag{64}$$

Employing the basis as Eq. 5 and after some algebra, we obtain

$$
\begin{aligned}
\left\langle \Theta^{J'M'P'}_{j'k'K'm} \right| \mu^{SF}_{Z} \left| \Theta^{JMP}_{jkKn} \right\rangle &= \frac{\mu_{\mathrm{H_2O}}\delta_{mn}}{2\sqrt{(1+\delta_{k'0}\delta_{K'0})(1+\delta_{k0}\delta_{K0})}} \delta_{M'M}(-1)^{k'+M}[j][j'][J][J'] \begin{pmatrix} J' & 1 & J \\ -M & 0 & M \end{pmatrix} \times \\
&\sum_{\sigma=-1}^{1} \left\{ \begin{pmatrix} j' & 1 & j \\ -k' & 0 & k \end{pmatrix} \begin{pmatrix} j' & 1 & j \\ -K' & \sigma & K \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -K' & \sigma & K \end{pmatrix} + \right. \\
&(-1)^{J+P+k} \begin{pmatrix} j' & 1 & j \\ -k' & 0 & -k \end{pmatrix} \begin{pmatrix} j' & 1 & j \\ -K' & \sigma & -K \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -K' & \sigma & -K \end{pmatrix} + \\
&(-1)^{J'+P'+k'} \begin{pmatrix} j' & 1 & j \\ k' & 0 & k \end{pmatrix} \begin{pmatrix} j' & 1 & j \\ K' & \sigma & K \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ K' & \sigma & K \end{pmatrix} + \\
&\left. (-1)^{J+J'+P+P'+k+k'} \begin{pmatrix} j' & 1 & j \\ k' & 0 & -k \end{pmatrix} \begin{pmatrix} j' & 1 & j \\ K' & \sigma & -K \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ K' & \sigma & -K \end{pmatrix} \right\} \\
&= \delta_{M'M}(-1)^{M} \begin{pmatrix} J' & 1 & J \\ -M & 0 & M \end{pmatrix} \mu_{\mathrm{H_2O}} A_{J'JP'Pj'jk'kK'Kmn}, \qquad (65)
\end{aligned}
$$

where $[j] = \sqrt{2j+1}$ etc. and the definition of $A_{J'JP'Pj'jk'kK'Kmn}$ is

$$
\begin{aligned}
A_{J'JP'Pj'jk'kK'Kmn} &= \frac{\delta_{mn}}{2\sqrt{(1+\delta_{k'0}\delta_{K'0})(1+\delta_{k0}\delta_{K0})}} (-1)^{k'}[j][j'][J][J'] \times \\
&\sum_{\sigma=-1}^{1} \left\{ \begin{pmatrix} j' & 1 & j \\ -k' & 0 & k \end{pmatrix} \begin{pmatrix} j' & 1 & j \\ -K' & \sigma & K \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -K' & \sigma & K \end{pmatrix} + \right. \\
&(-1)^{J+P+k} \begin{pmatrix} j' & 1 & j \\ -k' & 0 & -k \end{pmatrix} \begin{pmatrix} j' & 1 & j \\ -K' & \sigma & -K \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -K' & \sigma & -K \end{pmatrix} + \\
&(-1)^{J'+P'+k'} \begin{pmatrix} j' & 1 & j \\ k' & 0 & k \end{pmatrix} \begin{pmatrix} j' & 1 & j \\ K' & \sigma & K \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ K' & \sigma & K \end{pmatrix} + \\
&\left. (-1)^{J+J'+P+P'+k+k'} \begin{pmatrix} j' & 1 & j \\ k' & 0 & -k \end{pmatrix} \begin{pmatrix} j' & 1 & j \\ K' & \sigma & -K \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ K' & \sigma & -K \end{pmatrix} \right\}. \qquad (66)
\end{aligned}
$$

According to Wang and Carrington's definition, the transition line strength is defined as

$$
S_{i'i} = 3 \left| \sum_{M,M'} \left\langle \Psi^{J'M'P'}_{i'} \right| \mu^{SF}_{0} \left| \Psi^{JMP}_{i} \right\rangle \right|^2 . \qquad (67)
$$

The $\delta_{M'M}$ in Eq. 65 leads to

$$S_{i'i} = 3\left|\mu_{\mathrm{H_2O}}\sum_{M=-J_{min}}^{J_{min}}(-1)^M\begin{pmatrix} J' & 1 & J \\ -M & 0 & M\end{pmatrix}\sum_{j'k'K'n}\sum_{jkK}C_{j'k'K'n}^{J'MP'i'}C_{jkK}^{JMPi}A_{J'JP'Pj'jk'kK'Knn}\right|^2, \tag{68}$$

where $J_{min} = min\,(J', J)$.

II Wave function analysis

Like what Wang and Carrington did, we should assign K and $j_{K_aK_c}$ values to the resultant wave functions. For the $j_{K_aK_c}$ values, we only consider the four cases of 0_{00}, 1_{10}, 1_{01}, and 1_{11}, since they comprise most of Wang and Carrington's assignments. With

$$\begin{aligned} |0_{00}\rangle &= |000\rangle\,; \\ |1_{11}\rangle &= |10K\rangle\,; \\ |1_{10}\rangle &= \frac{1}{\sqrt{2}}\left[|11K\rangle + |1-1K\rangle\right]; \\ |1_{01}\rangle &= \frac{1}{\sqrt{2}}\left[|11K\rangle - |1-1K\rangle\right], \end{aligned} \tag{69}$$

we have

$$\begin{aligned} \langle 0_{00}|jkK\rangle &= \delta_{j0}\delta_{k0}\delta_{K0}; \\ \langle 1_{11}|jkK\rangle &= \delta_{j1}\delta_{k0}; \\ \langle 1_{10}|jkK\rangle &= \frac{1}{\sqrt{2}}\left(\delta_{j1}\delta_{k1} + \delta_{j1}\delta_{k-1}\right); \\ \langle 1_{01}|jkK\rangle &= \frac{1}{\sqrt{2}}\left(\delta_{j1}\delta_{k1} - \delta_{j1}\delta_{k-1}\right). \end{aligned} \tag{70}$$

For the last three equalities, $K = -1, 0, 1$ only. The eigen function in the symmetry-adapted basis reads

$$\begin{aligned} \left|\Psi^{JMP}\right\rangle &= \sum_{jkKn}\left|\Theta_{jk}^{nJMKP}\right\rangle \\ &= \sum_{jkKn}\frac{C_{jkKn}\,|R_n\rangle}{\sqrt{2\left(1+\delta_{k0}\delta_{K0}\right)}}\Big[|jkK\rangle\,|JKM\rangle + (-1)^{J+k+P}\,|j\ -k\ -K\rangle\,|J\ -KM\rangle\Big] \end{aligned} \tag{71}$$

Left-multiply the corresponding bra and sum over the square of the coefficients of the orthonormal basis functions in the resultant ket, we obtain the following contribution formulas for the H_2O-rigid rotor ket. The coefficients have the format of C_{jkKn}

1. $|0_{00}\rangle$:

$$\frac{1+(-1)^{J+P}}{2}\sum_n C_{000n}^2; \tag{72}$$

2. $|1_{11}\rangle$:

$$\frac{1+(-1)^{J+P}}{2}\sum_n C_{100n}^2+\sum_n C_{101n}^2; \tag{73}$$

3. $|1_{01}\rangle$:

$$\frac{1+(-1)^{J+P}}{2}\sum_n C_{110n}^2+\frac{1}{2}\sum_n\left(C_{111n}-C_{1-11n}\right)^2; \tag{74}$$

4. $|1_{10}\rangle$:

$$\frac{1-(-1)^{J+P}}{2}\sum_n C_{110n}^2+\frac{1}{2}\sum_n\left(C_{111n}+C_{1-11n}\right)^2. \tag{75}$$

Given the eigen function of Eq. 71, taking its modular square and perform the integration of $\int_0^\pi \sin\alpha d\alpha \int_0^{2\pi} d\beta \int_0^{2\pi} d\phi$, we have the distribution density in the space of R, θ, χ as

$$\begin{aligned}\rho(R,\theta,\chi) \;=\; & \sum_{jkj'k'Kn} \frac{C_{jkKn}C_{j'k'Kn}}{4\pi}\sqrt{\frac{(2j+1)(2j'+1)}{(1+\delta_{k0}\delta_{K0})(1+\delta_{k'0}\delta_{K0})}}\{ \\ & \cos k'\chi \cos k\chi d^{j'}_{Kk'}(\theta) d^{j}_{Kk}(\theta)\left(1+(-1)^{J+P}\delta_{K0}\right)+ \\ & \sin k'\chi \sin k\chi d^{j'}_{Kk'}(\theta) d^{j}_{Kk}(\theta)\left(1-(-1)^{J+P}\delta_{K0}\right)\Big\}. \end{aligned} \tag{76}$$

One should notice that the R-dependence is hidden in the running index n, which is for the DVR radial basis $\{|R_n\rangle\}$. It is wise to follow Hui Li's method to calculate the densities at the Gaussian quadrature and DVR grid points and then use Gaussian distribution at each grid points to obtain the density at any arbitrary coordinate. The matrices $T^{K,\sin}_{il,jk}$ and $T^{K,\cos}_{il,jk}$ can be used in calculating the grid density. After some algebra, I obtain the following expression for the density at the grid point (R_n, θ_l, χ_i):

1. $J+P$ odd:

$$\begin{aligned}\rho\left(R_n,\theta_l,\chi_i\right) \;=\; & \frac{n_\chi}{w_l^{GL}2\pi}\Bigg[\sum_{jkj'k'} C_{jk0n}C_{j'k'0n}T^{0,\sin}_{il,j'k'}T^{0,\sin}_{il,jk}+ \\ & \frac{1}{2}\sum_{jkj'k'K} C_{jkKn}C_{j'k'Kn}\left(T^{K,\cos}_{il,j'k'}T^{K,\cos}_{il,jk}+T^{K,\sin}_{il,j'k'}T^{K,\sin}_{il,jk}\right)\Bigg]; \end{aligned} \tag{77}$$

2. $J+P$ even:

$$\begin{aligned}\rho\left(R_n,\theta_l,\chi_i\right) \;=\; & \frac{n_\chi}{w_l^{GL}2\pi}\Bigg[\sum_{jkj'k'} C_{jk0n}C_{j'k'0n}T^{0,\cos}_{il,j'k'}T^{0,\cos}_{il,jk}+ \\ & \frac{1}{2}\sum_{jkj'k'K} C_{jkKn}C_{j'k'Kn}\left(T^{K,\cos}_{il,j'k'}T^{K,\cos}_{il,jk}+T^{K,\sin}_{il,j'k'}T^{K,\sin}_{il,jk}\right)\Bigg]. \end{aligned} \tag{78}$$

III Adiabaticity Analysis

The true total Hamiltonian operator of the H_2O-H_2-system reads

$$\begin{aligned}\hat{H}_{\text{total}} &= \hat{T}_{H_2O} + \hat{T}_{H_2} - \frac{\hbar^2}{2\mu}R^{-1}\frac{\partial^2}{\partial R^2}R + \frac{\hbar^2}{2\mu R^2}\left[\hat{\vec{J}} - \left(\hat{\vec{j}}_{H_2O} + \hat{\vec{j}}_{H_2}\right)\right]^2 + V(R,\theta,\chi,\theta_2,\phi) \\ &= \hat{T}_{H_2O} + \hat{T}_{H_2} - \frac{\hbar^2}{2\mu}R^{-1}\frac{\partial^2}{\partial R^2}R + \frac{\hbar^2}{2\mu R^2}\left[\hat{J}^2 + \hat{j}^2_{H_2O} + \hat{j}^2_{H_2} + 2\hat{\vec{j}}_{H_2O}\cdot\hat{\vec{j}}_{H_2} - 2\hat{\vec{J}}\cdot\hat{\vec{j}}_{H_2O} - 2\hat{\vec{J}}\cdot\hat{\vec{j}}_{H_2}\right] \\ &\quad + V(R,\theta,\chi,\theta_2,\phi).\end{aligned} \tag{79}$$

Our adiabatic separation of the H_2 motion from the rest is equivalent to writing the total wave function as

$$\Phi(\alpha,\beta,R,\theta,\chi,\theta_2,\phi) = \phi(\theta_2,\phi;R,\theta,\chi)\Psi^{JMP}(R,\theta,\chi,\alpha,\beta), \tag{80}$$

and decouple the relative motions. We have actually suppressed the dependence of the hydrogen function on the overall Euler angles α and β because the hydrogen's coupling with the dimer frame (implicitly through the $\hat{\vec{j}}_{H_2}\cdot\hat{\vec{J}}$ term of Eq. 79) is much weaker than with H_2O (explicitly through $V(R,\theta,\chi,\theta_2,\phi)$ and implicitly through the $\hat{\vec{j}}_{H_2}\cdot\hat{\vec{j}}_{H_2O}$ term). The adiabatic H_2 function is obtained through solving the following equation:

$$\left(\hat{T}_{H_2} + \frac{\hbar^2}{2\mu R^2}\hat{j}^2_{H_2} + V(R,\theta,\chi,\theta_2,\phi)\right)\phi(\theta_2,\phi;R,\theta,\chi) = V^{ad}(R,\theta,\chi)\phi(\theta_2,\phi;R,\theta,\chi). \tag{81}$$

The presumption for such an equation is that H_2 moves much faster than H_2O and the dimer frame and the action of the other coordinates is just to exert a potential for the fast motion of H_2. Consequently, the eigen function ϕ parametrically depends on the position and orientation of H_2 with respect to H_2O. The adiabatic energy of the whole system reads

$$\langle\Phi|\hat{H}_{\text{total}}|\Phi\rangle = \left\langle\Psi^{JMP}\right|\langle\phi|\hat{H}_{\text{total}}|\phi\rangle\left|\Psi^{JMP}\right\rangle \tag{82}$$

and the effective Hamiltonian operator for Ψ^{JMP} is

$$\begin{aligned}\langle\phi|\hat{H}_{\text{total}}|\phi\rangle &= -\frac{\hbar^2}{2\mu}\langle\phi|R^{-1}\frac{\partial^2}{\partial R^2}R|\phi\rangle + \langle\phi|\hat{T}_{H_2O}|\phi\rangle + \frac{\hbar^2}{2\mu R^2}\left[\hat{J}^2 + \langle\phi|\hat{j}^2_{H_2O}|\phi\rangle + \right. \\ &\left. 2\langle\phi|\hat{\vec{j}}_{H_2O}\cdot\hat{\vec{j}}_{H_2}|\phi\rangle - 2\hat{\vec{J}}\cdot\langle\phi|\hat{\vec{j}}_{H_2O}|\phi\rangle - 2\hat{\vec{J}}\cdot\langle\phi|\hat{\vec{j}}_{H_2}|\phi\rangle\right] + V^{ad}(R,\theta,\chi),\end{aligned} \tag{83}$$

where the superscript "ad" denotes the adiabaticity of the potential. The comparison of Eq. 83 and Eq. 1 shows that further approximations have been made in order to get to the Bohn-Oppenheimer approximation:

$$\begin{aligned}\langle\phi|R^{-1}\frac{\partial^2}{\partial R^2}R|\phi\rangle &\approx R^{-1}\frac{\partial^2}{\partial R^2}R; \\ \langle\phi|\hat{T}_{H_2O}|\phi\rangle &\approx \hat{T}_{H_2O}; \\ \langle\phi|\hat{j}^2_{H_2O}|\phi\rangle &\approx \hat{j}^2_{H_2O}; \\ \langle\phi|\hat{\vec{j}}_{H_2O}\cdot\hat{\vec{j}}_{H_2}|\phi\rangle &\approx 0; \\ \hat{\vec{J}}\cdot\langle\phi|\hat{\vec{j}}_{H_2O}|\phi\rangle &\approx \hat{\vec{J}}\cdot\hat{\vec{j}}_{H_2O}; \\ \hat{\vec{J}}\cdot\langle\phi|\hat{\vec{j}}_{H_2}|\phi\rangle &\approx 0.\end{aligned} \tag{84}$$

The fifth and seventh (the two nullification) approximations are based on the rationalization that $|\phi\rangle$ is the ground state of a para-H_2 molecule and it is mainly of zero angular momentum nature, and the seventh should be exact because of the hermiticity of $\hat{\vec{j}}_{\mathrm{H}_2}$ and the real-valued nature of $|\phi\rangle$. The other four approximations are based on the assumption that $|\phi\rangle$ changes slowly with respect to R, θ, and χ (through the coefficients of the spherical harmonic basis functions) and therefore, the corresponding derivatives are negligibly small. One should notice that $\hat{j}_{\mathrm{H}_2\mathrm{O}}$ explicitly contains $\frac{\partial}{\partial\theta}$ and $\frac{\partial}{\partial\chi}$. This assumption should be OK for para-H_2, since the ground state and the first excited state of Eq. 81 are energetically well separated (by more than 100 cm^{-1}) and usually the derivatives are only large at the crossing or avoided crossing areas of PES. However, the approximation should not work for the ortho-H_2 as near-degeneracy (at the order of hundredths of cm^{-1}) is observed. Also the two nullification approximations are absolutely wrong for the ground state of ortho-H_2 (mainly $l = 1$). Therefore, the Bohn-Oppenheimer approximation used in this project cannot be employed for ortho-H_2. This explains the poor ortho-H_2 results obtained so far. Calculating the exact matrix elements in Eq. 84 is the starting point for the diagonal adiabatic correction.

IV Units, Constants, and Parameters

It would be wise to use atomic units in the calculation and convert the final energetic results to have the unit of cm^{-1}. The mass of H and O atoms are 1.007826 and 15.994915 u. The reduced mass μ of the total complex is 1.812775 u. With the conversion factor of 1 u=1822.88839 a.u., we have $\mu = 3304.486$ a.u. With this reduced mass, we calculate the energy prefactor $\frac{\hbar^2}{2\mu} = 1.513094 \times 10^{-4}$ a.u$= 33.20859\ \mathrm{cm}^{-1}$. The rotational constants of H_2O are taken from van der Avoird's paper: $A = 27.8806\ \mathrm{cm}^{-1}$, $B = 14.5216\ \mathrm{cm}^{-1}$, and $C = 9.2778\ \mathrm{cm}^{-1}$. They are converted to be in the unit of Hartree as: $A = 1.27033 \times 10^{-4}$ a.u., $B = 6.61653 \times 10^{-5}$ a.u., and $C = 4.2273 \times 10^{-5}$ a.u.

V The number of Basis Functions

If we do not consider the spin statistics of the two hydrogens in H_2O, we have the following conditions for the quantum numbers j, k, and K, given specific J and j_{max}:

$$0 \le j \le j_{max}; 0 \le k \le j, 0 \le K \le min(j, J). \tag{85}$$

The j index must run from 0 to j_{max} and we have $J < j_{max}$ as a guaranteed condition. When $j < J$, the range of K is determined by j and the number of K values is $j + 1$. Otherwise, the range of K is determined by J and the number of K is $J + 1$. The range of k is only determined by j and the number of k is always $j + 1$. Therefore, we have the numbers of basis functions for the two ranges of j as:

1. j from 0 to J:

$$N^{j\le J}_{Jj_{max}} = \sum_{j=0}^{J}(j+1)^2 = \frac{1}{6}J(J+1)(2J+1) + (J+1)^2; \tag{86}$$

2. j from $J + 1$ to j_{max}:

$$N^{j>J}_{Jj_{max}} = \sum_{j=J+1}^{j_{max}} (J+1)(j+1) = \frac{1}{2}(J+1)\left[j_{max}(j_{max}+3) - J(J+3)\right]. \tag{87}$$

The summation of the two terms gives

$$(J+1)\left\{\frac{1}{6}J(2J+1)+(J+1)+\frac{1}{2}\left[j_{max}(j_{max}+3)-J(J+3)\right]\right\}. \tag{88}$$

I have tested this formula for the case of $J = 1$ and $j_{max} = 5$ and the correct number of terms, 41, is obtained.

Now let's consider the evenness and oddness of k, i.e., the ortho- and para-H_2O. Depending on the oddness and evenness of j, the numbers of even and odd k can be classified into the following four categories:

1. For an even j, the number of even k is $\frac{j}{2}+1$;
2. For an even j, the number of odd k is $\frac{j}{2}$;
3. For an odd j, the number of even k is $\frac{j+1}{2}$;
4. For an odd j, the number of odd k is $\frac{j+1}{2}$.

These four formulas are extensively used in the following calculation of basis function numbers. The basis function numbers depend on the evenness and oddness of k, J, and j_{max}, and therefore, we have the following eight cases, under the condition of $J < j_{max}$:

1. k even, J even, and j_{max} even, the number of basis functions is

$$\frac{1}{2}\left[\frac{1}{6}J(J+1)(2J+1)+\frac{5}{4}J^2+3J+2\right]+(J+1)(j_{max}-J)\left[\frac{1}{4}(J+j_{max})+1\right]. \tag{89}$$

The first summand is the number of basis functions for $j \le J$ while the second is for $J < j \le j_{max}$. The same convention is used below;

2. k odd, J even, and j_{max} even:

$$\frac{1}{2}\left[\frac{1}{6}J(J+1)(2J+1)+\frac{3}{4}J^2+J\right]+\frac{1}{4}(J+1)(j_{max}-J)(J+j_{max}+2); \tag{90}$$

3. k even, J odd, and j_{max} even:

$$\frac{1}{4}(J+1)\left[\frac{1}{3}J(2J+1)+\frac{5}{2}(J+1)\right]+\frac{1}{4}(J+1)\left[(J+j_{max}+1)(j_{max}-J)+3(j_{max}-J)+1\right]; \tag{91}$$

4. k odd, J odd, and j_{max} even:

$$\frac{1}{4}(J+1)\left[\frac{1}{3}J(2J+1)+\frac{3}{2}(J+1)\right]+\frac{1}{4}(J+1)\left[(j_{max}+J+1)(j_{max}-J)+j_{max}-J-1\right]; \tag{92}$$

5. k even, J even, and j_{max} odd:

$$\frac{1}{2}\left[\frac{1}{6}J(J+1)(2J+1)+\frac{5}{4}J^2+3J+2\right]+\frac{1}{4}(J+1)\left[(j_{max}+J+1)(j_{max}-J)+3(j_{max}-J)-1\right]; \tag{93}$$

6. k odd, J even, j_{max} odd:

$$\frac{1}{2}\left[\frac{1}{6}J(J+1)(2J+1)+\frac{3}{4}J^2+J\right]+\frac{1}{4}(J+1)\left[(J+j_{max}+1)(j_{max}-J)+j_{max}-J+1\right]; \tag{94}$$

7. k even, J odd, and j_{max} odd:

$$\frac{1}{4}(J+1)\left[\frac{1}{3}J(2J+1)+\frac{5}{2}(J+1)\right]+\frac{1}{4}(J+1)(j_{max}-J)\left[j_{max}+J+4\right]; \tag{95}$$

8. k odd, J odd, and j_{max} odd:

$$\frac{1}{4}(J+1)\left[\frac{1}{3}J(2J+1)+\frac{3}{2}(J+1)\right]+\frac{1}{4}(J+1)(j_{max}-J)(j_{max}+J+2). \tag{96}$$

I have tested these formulas and they turn out to be correct.

VI Construction of $V(R,\theta,\chi)$

Valiron et al. [5] defined the coordinates for the H_2O-H_2 potential as follows. Symbols identical to the previous section are used but for different notations. They should not be misunderstood. The H_2O-fixed frame has its z-axis along the C_2 axis and its x-axis in the H_2O-plane. The mass of centre of H_2O is chosen to be the origin. The mass of centre of H_2 is defined by spherical coordinates R, θ, and ϕ. θ is the angle between $\vec{R}$ and the z-axis and ϕ the angle between the projection of $\vec{R}$ on the xy-plane and the x-axis. The centre of mass of H_2 is chosen to be the origin of the frame that describe the H_2-rigid rotor motion, and two solid angles θ' and ϕ' are used to describe the orientation of H_2. This coordinate arrangement is clearly illustrated in Fig. 1 of Ref [5], with the same symbols. The fitted 5-dimensional $V(R,\theta,\phi,\theta',\phi')$ potential has been obtained and it read five random values and give a potential energy in the unit of cm^{-1}. To obtain the hindered rotor potential, we need to solve the following rotor Schrödinger equation for a grid of R, θ, and ϕ:

$$\left(\frac{\hat{l}^2}{2\mu_{H_2}r_0}+V(R,\theta,\phi,\theta',\phi')\right)\psi(\theta',\phi')=E(R,\theta,\phi)\psi(\theta',\phi'), \tag{97}$$

where $\psi(\theta',\phi')$ is expanded in the spherical harmonic basis $|lm\rangle$, with only even l to account for the nature of para-H_2, and r_0 is the averaged H_2 bond length in the ground vibrational state. The symmetry of H_2O leads to the following relation: $E(R,\theta,\phi)=E(R,\theta,\pi-\phi)=E(R,\theta,\pi+\phi)=E(R,\theta,2\pi-\phi)=E(R,\theta,-\phi)$, and therefore, only $0\le\phi\le\pi/2$ should be considered in the grid. To convert $E(R,\theta,\phi)$ to $V(R,\theta,\chi)$, we should be careful of the relations between angles in different frames. θ in this section denotes and angle that the $\vec{R}$ vector rotates away from the H_2O-C_2 axis, while the θ in Sec. I denotes the angle that the H_2O-C_2 axis rotates away from $\vec{R}$. Therefore, the two θ should be converted to each other by a "$-$" sign. Following the same argument, χ in Sec. I is $-\phi$ in this section. However, with the symmetry relation, we still have $V(R,\theta,\chi)=E(R,-\theta,-\chi)=E(R,-\theta,\chi)$. Now let's go back to θ. In spherical coordinates, taking $-\theta$ is equivalent to taking θ and $\phi+\pi$, and we have $V(R,\theta,\chi)=E(R,\theta,\chi+\pi)$. Using the symmetry property of χ we have $V(R,\theta,\chi)=E(R,\theta,\chi)$. We also need to shift $V(R,\theta,\chi)$ to have zero energy at the infinite R.

VII Watch Out!

There are several things I am not certain in Sec. I. A possible wrongness lies in Eq. 5. I do not have enough background about inversion symmetry of the rotational functions and I simply adapted Eq. 4 of Ref [3] to our case without any derivation. As said above, Eq. 6 of Wang and Carrington's preprint paper reduces to Eq. 5 when all the angular momentum quantum numbers of H_2 are set to be zero. Also, Eq. 16 of van der Avoird and Nisbitt's preprint paper also reduces to Eq. 5 when H_2's angular momentum quantum numbers are set to be zero. This raises my confidence but still, carefulness should be put on it. In the last step of Eq. 64, I did not derive the integrals, but simply adapt Wang and Carrington's Eq. 14 to our case. The relation of $V(R,\theta,\chi) = E(R,\theta,\chi)$ in the previous section also worth checking.

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