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Vibronic effect study of $^1A_2$ state of H_2O and D_2O

Bei-Yuan Zhang(张倍源)[1], Li-Han Wang(王礼涵)[1], Jian-Hui Zhu(朱剑辉)[1], Wei-Qing Xu(徐卫青)[2], Zi-Ru Ma(马子茹)[1], Xiao-Li Zhao(赵小利)[3], Yong Wu(吴勇)[4,5,6,†], and Lin-Fan Zhu(朱林繁)[1,‡]

[1] *Department of Modern Physics, University of Science and Technology of China, Hefei* 230026, *China*
[2] *Center for Transformative Science, ShanghaiTech University, Shanghai* 201210, *China*
[3] *Department of Physics, Yantai University, Yantai* 264005, *China*
[4] *Institute of Applied Physics and Computational Mathematics, Beijing* 100088, *China*
[5] *School of Physics and Information Technology, Shaanxi Normal University, Xi'an* 710119, *China*
[6] *HEDPS, Center for Applied Physics and Technology, Peking University, Beijing* 100084, *China*

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The generalized oscillator strengths of the dipole-forbidden excitations of the $^1A_2$ of H_2O and D_2O were calculated with the time dependent density functional theory, by taking into account the vibronic effect. It is found that the vibronic effect converts the dipole-forbidden excitation of the $^1A_2$ into a dipole-allowed one, which enhances the intensities of the corresponding generalized oscillator strength in the small squared momentum transfer region. The present investigation shows that the vibronic effect of H_2O is slightly stronger than that of D_2O, which exhibits a clear isotopic effect.

Keywords: water, heavy water, generalized oscillator strength, vibronic effect, isotope effect

PACS: 34.50.Gb, 34.80.Gs, 31.15.ee, 95.30.Ky **DOI:** 10.1088/1674-1056/ad24d9

1. Introduction

Vibronic effect, induced by the molecular vibration which distorts the molecular symmetry and couples the electronic and nuclear motions, has great influence on the molecular dynamic parameters, such as the generalized oscillator strengths (GOSs), optical oscillator strengths (OOSs), differential cross sections (DCSs), and integral cross sections (ICSs).[1–9] Furthermore, the vibronic effect can change the transition behaviors such as converting the dipole-forbidden transitions into the dipole-allowed ones, enhancing the intensities of the GOS in the small squared momentum transfer region, etc. Therefore, the influence of vibronic effect on the GOSs of the valence-shell excitations of atoms and molecules has attracted the interests of both experimentalists and theorists, and recently the vibronic effects for molecular CF_4,[1,2] NH_3,[3,4] N_2O,[5,6] CCl_4,[7,8] CH_3Cl,[9] CF_3Cl,[9] etc., have been studied extensively. The present paper focuses on the vibronic effect on the GOSs of the valence-shell excitations of H_2O and D_2O, and it is clearly elucidated that the isotopic substitution has an apparent influence on the vibronic effect.

Electron collision cross sections of H_2O and its isotopic substitutions are of great importance in many fields, such as atmosphere physics, astrophysics, radiation biology and medicine.[10–16] For example, the electronic excitation by electron collision is the main energy deposition channel[15–17] for radiation damage of biological tissues with H_2O as the main component, so the electronic excitation cross sections of H_2O and its isotopes are crucial for radiation damage simulation in biological tissues. Although electron collisional excitation cross sections for the low electronic states of H_2O have been extensively studied both theoretically[17–20] and experimentally,[17,21–26] the influence of the vibronic effect on them has not been considered while it has great influence on other molecules.[1–9]

This paper focuses on the vibronic effect and isotopic effects of the dipole-forbidden transition $^1A_2$ of H_2O and D_2O, and according to the previous investigations,[1–9] the vibronic effect on this transition should be prominent. The $^1A_2$ states of H_2O and D_2O were noticed in the electron energy loss spectra at the impact electron energies of 100 eV–200 eV,[25] 300 eV–500 eV,[27] and 1500 eV.[17,28] It should be pointed out that the $^1A_2$ has a large line width and is heavily overlapped with the strong dipole-allowed dissociative state of $\tilde{B}^1A_1$, so it is masked by $\tilde{B}^1A_1$ and can not be clearly resolved in the measured spectra. Therefore, a complex fitting procedure was previously used to derive its dynamic parameters such as the DCSs and GOSs.[17,28] Although all experimental and theoretical GOS profiles of H_2O and D_2O are in consistent,[17,28] while the absolute scales show apparent discrepancies. In this work, we will elucidate this difference with the time dependent density functional theory (TDDFT) simulation[7,29,30] by taking into account the vibronic effect.

†Corresponding author. E-mail: wu_yong@iapcm.ac.cn
‡Corresponding author. E-mail: lfzhu@ustc.edu.cn

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2. Theoretical method

Under the first-order Born approximation (FBA), GOS is related to the differential cross section of an excited state as[31–33] (in atomic units: a.u.)

$$f(\boldsymbol{K},E_n)=\frac{E_n}{2}\frac{p_0}{p_\mathrm{a}}K^2\frac{\mathrm{d}\sigma_n}{\mathrm{d}\Omega}, \tag{1}$$

where p_0 and p_a are the momenta of the incident and scattered electrons, respectively. $\boldsymbol{K}$ is the momentum transfer vector, and E_n is the excitation energy. Considering molecular vibronic effect, the GOS for an electronic state n from the vibrational state v of the ground electronic state can be expressed as follows:

$$f_{n\leftarrow 0v}(\boldsymbol{K})=\frac{1}{4\pi}\sum_{v'}\frac{2E_{nv',0v}}{\boldsymbol{K}^2}\int \mathrm{d}\Omega_{\boldsymbol{K}}|\langle\chi_{nv'}(\boldsymbol{Q})|\varepsilon_{n0}(\boldsymbol{K},\boldsymbol{Q})|\chi_{0v}(\boldsymbol{Q})\rangle|^2. \tag{2}$$

Here, v and v' are the vibrational quantum numbers of the ground and excited state, respectively, $\chi_{0v}(\boldsymbol{Q})$ and $\chi_{nv'}(\boldsymbol{Q})$ represent the vibrational wavefunctions of the initial and final states of the target, respectively. $\boldsymbol{Q}$ is the internal vibrational coordinate. Due to the energy interval of the vibrational state is much larger than the kinetic energy of the H_2O molecule at room temperature, the initial vibrational state v should be only at the ground state of $v=0$. The electronic transition matrix element $\varepsilon_{n0}(\boldsymbol{K},\boldsymbol{Q})$ can be expressed as

$$\varepsilon_{n0}(\boldsymbol{K},\boldsymbol{Q})=\langle\Psi_n(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N;\boldsymbol{Q})|\sum_j\exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{r}_j)\times|\Psi_0(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N;\boldsymbol{Q})\rangle, \tag{3}$$

where Ψ_0 and Ψ_n are the initial and final electronic states wavefunctions with $\boldsymbol{r}_j$ being the coordinate vector of the j-th electron. Then under the Born–Oppenheimer approximation and with the closure relation of the vibrational eigenstates, the GOS with the vibronic effect being considered can be written as[2,7]

$$f_{n\leftarrow 0}(\boldsymbol{K})=\frac{2E_{n,0}}{\boldsymbol{K}^2}\int \mathrm{d}\boldsymbol{Q}\,|\chi_{00}(\boldsymbol{Q})|^2M_{n0}(\boldsymbol{K},\boldsymbol{Q}) \tag{4}$$

with

$$M_{n0}(\boldsymbol{K},\boldsymbol{Q})=\frac{1}{4\pi}\int|\varepsilon_{n0}(\boldsymbol{K},\boldsymbol{Q})|^2\mathrm{d}\Omega_{\boldsymbol{K}}. \tag{5}$$

Here, the integral over the solid angle Ω is a spherical average of the random orientation of the molecular axis in the $\boldsymbol{K}$ direction.

Under the harmonic approximation, the vibrational wave function can be expressed as the product of the harmonic oscillator functions

$$\chi_{00}(\boldsymbol{Q})=\prod_L\xi_L(Q_L), \tag{6}$$

where Q_L represents the displacement from the equilibrium geometry along the L-th normal coordinate.

Neglecting the interactions between different vibration modes, equation (4) can be further reduced to

$$\begin{aligned}f_{n\leftarrow 0}(\boldsymbol{K})&=\frac{2E_{n,0}}{\boldsymbol{K}^2}\langle\chi_{00}(\boldsymbol{Q})|M_{n0}(\boldsymbol{K},\boldsymbol{0})+\sum_L\Delta M_{n0}(\boldsymbol{K},Q_L)|\chi_{00}(\boldsymbol{Q})\rangle\\&=\frac{2E_{n,0}}{\boldsymbol{K}^2}M_{n0}(\boldsymbol{K},\boldsymbol{0})+\frac{2E_{n,0}}{\boldsymbol{K}^2}\sum_L\langle\xi_L(Q_L)|\,M_{n0}(\boldsymbol{K},Q_L\hat{\boldsymbol{q}}_L)-M_{n0}(\boldsymbol{K},\boldsymbol{0})\,|\xi_L(Q_L)\rangle\,.\end{aligned} \tag{7}$$

It is reasonable to omit cross-terms between different normal coordinates, based on the assumption that $M_{n0}(\boldsymbol{K},\boldsymbol{Q})$ changes slowly with $\boldsymbol{Q}$ in the vicinity of the equilibrium geometry. Expanding M_{n0} using the power series and fitting the curve of M_{n0} by using the polynomial, equation (7) can be finally expressed as

$$f(\boldsymbol{K},E_n)=\frac{2E_n}{\boldsymbol{K}^2}\left[M_{n0}(\boldsymbol{K},0)+\sum_m\sum_L\frac{1}{(2m)!}\frac{\partial^{2m}M_{n0}}{\partial Q_L^{2m}}\bigg|_{\boldsymbol{Q}=0}\langle\xi_L(Q_L)|Q_L^{2m}|\xi_L(Q_L)\rangle\right]. \tag{8}$$

Thirteen molecular configurations with different disequilibrium internuclear distances were selected for calculating $M_{n0}(\boldsymbol{K},\boldsymbol{Q})$ in this work, so we considered the contributions of $m\leq 2$. It has been demonstrated that such a theoretical calculation procedure can successfully elucidate the momentum transfer dependence behaviors of GOSs for many molecules.[2,4,6–9]

In this work, the GOSs of the $^1\mathrm{A}_2\longleftarrow\tilde{\mathrm{X}}^1\mathrm{A}_1$ transitions of H_2O and D_2O were calculated by using Gaussian16 software, to elucidate the influence of the vibronic effect on this transition character. The vibrational normal coordinates and vibrational frequencies of H_2O and D_2O were calculated using

the basis set of aug-cc-pVTZ[34,35] at the treatment level of the second-order Møller–Plesset perturbation theory (MP2). The obtained frequencies of different vibration modes are shown in Table 1, which are in good agreement with the experimental measurements when a scale factor is taken into account.[36]

Table 1. Vibrational frequencies of H_2O and D_2O (in units : cm^{-1})

Mode	Descriptions	Calculated	Expt.
$\nu_1(H_2O)$	symmetric bending	1627.76	1649[a]
$\nu_2(H_2O)$	symmetric stretching	3824.70	3832[a]
$\nu_3(H_2O)$	asymmetric stretching	3950.61	3943[a]
$\nu_1(D_2O)$	symmetric bending	1191.33	1178[b]
$\nu_2(D_2O)$	symmetric stretching	2757.16	2672[b]
$\nu_3(D_2O)$	asymmetric stretching	2894.20	2788[b]

[a]Taken from Ref. [37]. [b] Taken from Ref. [38].

The wave functions of the ground and excited states were calculated by the TDDFT using the M06-2X functional[39] and the basis set of aug-cc-pVTZ.[34,35] The calculated energy intervals between the transition $^1A_2$ of H_2O and D_2O and the state $\tilde{A}^1B_1$ are identical 1.476 eV, which is in good agreement with the experimental measurements (H_2O 1.673 eV,[17] D_2O 1.765 eV[28]). With the obtained TDDFT wave functions, $(2E_{0,n}/\boldsymbol{K}^2)M_{0n}(\boldsymbol{K},\boldsymbol{Q})$ were calculated at several nuclear geometries from the equilibrium one along each normal coordinate, and the GOSs of the transition $^1A_2$ of both H_2O and D_2O molecules with molecular vibronic effects taken into account were calculated using Eq. (8).

3. Results and discussion

The presently calculated GOSs of the $^1A_2$ of H_2O and D_2O are shown in Fig. 1, where the calculations at the equilibrium geometry and with vibronic effects taken into account are compared. It is clear from Fig. 1 that although the $^1A_2$ state is a dipole-forbidden transition at the equilibrium geometry for both H_2O and D_2O, i.e., it has a zero intensity at $\boldsymbol{K}^2 = 0$, it becomes dipole-allowed when the vibronic effect is taken into account, i.e., it has an apparent enhanced intensity at $\boldsymbol{K}^2 = 0$. The theoretically calculated $^1A_2$ intensity of H_2O at $\boldsymbol{K}^2 = 0$ is 4% of the $\tilde{B}^1A_1$ transition when the vibronic effect is taken into account. Therefore, the $^1A_2$ should have considerable contribution in the photo-absorption spectra, which is neglected in the previous works.[17,25,27,28] Due to the same reason, in Refs. [17,25,27,28] the obtained peak profile of $\tilde{B}^1A_1$ of H_2O from photoabsorption spectrum may be problematic when the contribution of $^1A_2$ is neglected. Furthermore, the determined GOSs for the $^1A_2$ of H_2O may be influenced by the inaccurate profile of $\tilde{B}^1A_1$ used in the fitting procedure.[17,27]

In order to compare the present theoretical GOSs with the more accurate experimental data, we reanalyzed our previous electron energy loss spectra of H_2O to obtain accurate GOS of the $^1A_2$. The new peak profiles of the $^1A_2$ and $\tilde{B}^1A_1$ were determined from the high-resolution photo-absorption spectra[39] of H_2O with the $^1A_2$ contribution being taken into account. Here the transition energies of $\tilde{B}^1A_1$ and $^1A_2$ were fixed to the data determined by the high-resolution photo-absorption spectra[39] and electron energy loss spectroscopy experiment at large angles,[17] and the corresponding line widths were obtained by fitting the photo-absorption spectra.[39] New GOSs were obtained by refitting the electron energy loss spectra[17] with the peak profiles being fixed to the present ones.

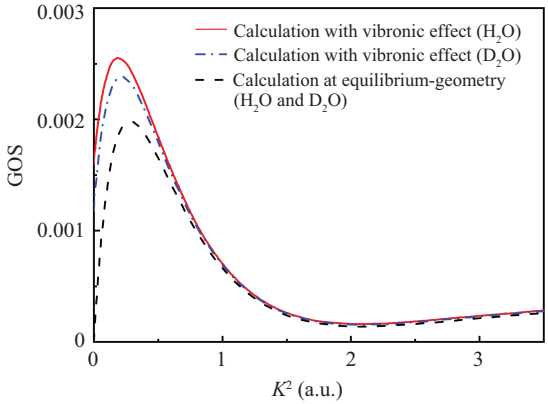


Fig. 1. Theoretical GOSs for the $^1A_2$ transitions of H_2O and D_2O. See text for details.

Figure 2 compares the presently calculated GOSs with the updated experimental results by this work and the ones in Ref. [17]. The contributions of three different normal modes are also plotted in Fig. 2 to elucidate the mechanism of the vibronic effect. It is clear that in Fig. 2 there is a large discrepancy in the small squared momentum transfer region between the present and previous[17] experimental data. This is due to the fact that previously the $^1A_2$ was neglected in determining the peak profile of $\tilde{B}^1A_1$ through fitting the photo-absorption spectra,[17] which results in the larger line width of $\tilde{B}^1A_1$ than its true value, and further bring about the intensity of $\tilde{B}^1A_1$ overestimated. Due to the heavy overlap of $^1A_2$ with the $\tilde{B}^1A_1$, the intensity of $^1A_2$ was underestimated in Ref. [17].

Figure 2 clearly shows that the calculated GOSs with and without the vibronic effect have apparent discrepancy, especially in the small $\boldsymbol{K}^2$ region. As mentioned above, the vibronic effect makes the $^1A_2$ become dipole-allowed, and the asymmetric stretching mode ν_3 is the main reason, as shown in Fig. 2. It is well-known that the H_2O molecule belongs to the C_{2v} point group and its asymmetric stretching vibration has the B_2 symmetry. The asymmetric stretching vibration couples with the dipole-forbidden transition $^1A_2$ and the direct product of A_2 and B_2 makes the total symmetry become B_1, which is dipole-allowed in the C_{2v} point group. This is the reason that the asymmetric stretching vibration has a considerable

contribution to $^1A_2$ intensity in the small squared momentum transfer region.

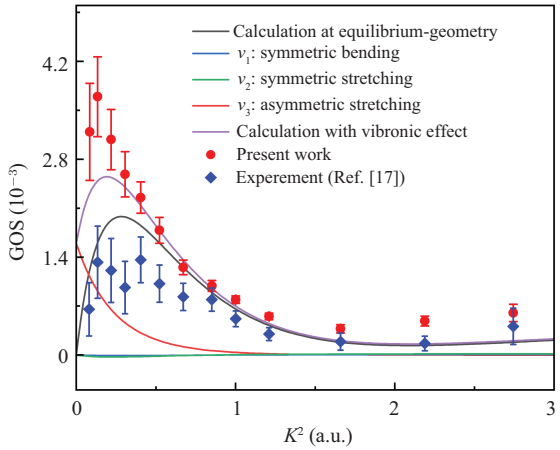


Fig. 2. Comparisons of the theoretical GOS profile of the present $^1A_2$ transition of H_2O with the experimental results updated by this work and the ones reported by Xu *et al.*[17] The contributions of the normal modes are also plotted.

It should be noted that even the agreement between the theoretical calculation and experimental measurement result is significantly improved by taking into account the vibronic effect, the discrepancies still exist in $\boldsymbol{K}^2 < 0.3$ a.u. and $\boldsymbol{K}^2 > 2$ a.u. There are several possible reasons for this discrepancy: non-harmonic effects of molecular vibrations, non-adiabatic effects, and interactions between different normal modes. The possible experimental errors from the fitting procedure can not be excluded.

Figure 3 shows the calculated GOS of the $^1A_2$ of D_2O with and without vibration effects being considered. Since D_2O and H_2O have the same molecular configuration, similar conclusion can be obtained: the vibronic effect makes $^1A_2$ dipole-allowed, and the asymmetric stretching mode ν_3 is the main reason as shown in Fig. 3. Furthermore, the slight difference of the theoretical and experimental GOS of D_2O in $\boldsymbol{K}^2 < 0.3$ a.u. may be due to the same reasons as those of H_2O, as discussed above.

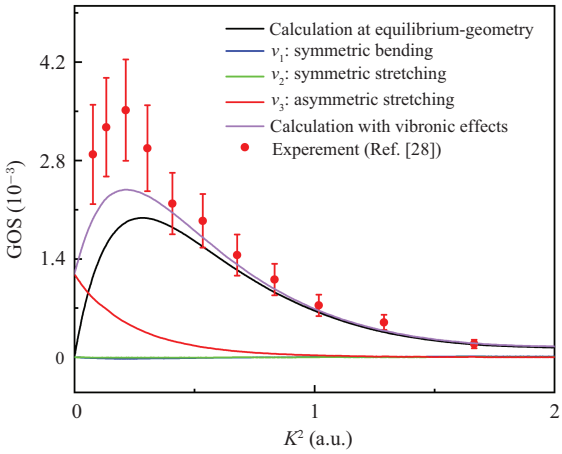


Fig. 3. Comparisons of the theoretical GOS profile of the $^1A_2$ transition of D_2O with the experimental results reported by Ma *et al.*[28] The contribution of each normal mode is also plotted in the figure. See text for details.

In the framework of the Born–Oppenheimer approximation, H_2O and D_2O have the same potential energy surface, so the GOSs for the same electronic excitation should be identical. However since D is heavier than H, the displacements of the nuclei from the equilibrium geometry in D_2O are less than those in H_2O, so it can be easily imaged that the vibrational effect has larger influence on H_2O than on D_2O. Figure 1 clearly elucidates the above analysis, i.e., the GOS of the $^1A_2$ of H_2O is larger than that of D_2O, especially in the small $\boldsymbol{K}^2$ region.

4. Conclusions

In this work, we studied the influence of the vibronic effect on the GOSs of the $^1A_2$ in H_2O and D_2O. Based on the TDDFT theory, we have calculated the GOSs of $^1A_2$ of H_2O and D_2O with and without considering vibronic effect. It is found that the vibronic effect converts the dipole-forbidden character of the $^1A_2$ into a dipole-allowed one, which has a significant influence on the GOS, especially in the small $\boldsymbol{K}^2$ region. The present calculation demonstrates that the ν_3 normal mode of $^1A_2$ contributes most to the vibronic effect, and the lighter mass of H makes the vibronic effect of H_2O be stronger than that of D_2O i.e., a clear isotropic effect is revealed.

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