Optical oscillator strengths of the vibronic excitations of molecular deuterium determined by the dipole (γ, γ) method

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Absolute optical oscillator strengths of the Lyman and Werner bands of molecular deuterium are determined by a dipole(γ, γ) method with the high energy resolution of 25 meV. A comprehensive comparison shows that an excellent agreement between the present experimental results and the earlier theoretical calculations is achieved for both Lyman and Werner bands. In addition, the electronic transition dipole moments of D_2 are derived. The absolute optical oscillator strengths of the Lyman and Werner bands of D_2 reported in this work can serve as the benchmark to test calculations with different theoretical models and calculational codes and, also, be used in thermonuclear fusion plasma and other fields.

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I. INTRODUCTION

Hydrogen is the most abundant element in the universe, particularly in the stellar medium, interstellar medium, and planetary atmospheres. Deuterium, as one of the isotopes of hydrogen, is widely studied in astrophysics. Measurement of the D/H ratio is important in terms of the cosmological implications, and research on deuterium chemistry is of great interest in exploring the evolution of our universe [1]. Deuterium occurs in trace amounts naturally as D_2, with the most natural occurrence in the universe as HD. Thus, molecular deuterium is of less importance than HD in astrophysics. Nevertheless, the study of D_2 is a natural progression of works on molecular hydrogen and its isotopes. In addition, spectroscopic studies on D_2 specifically relate to detailed investigations in thermonuclear fusion plasma reactors such as the DIII-D reactor and JET fusion reactor, where D_2 is produced near the plasma-facing components [2]. Furthermore, the Born-Oppenheimer approximation may not be satisfied strictly due to the low nuclear masses of hydrogen and its isotopes, and the isotopic effect may be pronounced upon comparing the spectroscopies of H_2 and D_2 [3–5]. Since D_2 is a simple diatomic molecular system, relatively accurate numerical calculations can be achieved. It is significant to compare the theory and experiment quantitatively to evaluate the theoretical approaches [4]. Particularly, the Lyman band ($B^1\Sigma_u^+$-$X^1\Sigma_g^+$) and the Werner band ($C^1\Pi_u$-$X^1\Sigma_g$) have attracted much attention, since they are the strongest and dipole-allowed absorption systems originating from the electronic ground state [6–10]. The absolute optical oscillator strengths (OOSs) represent the transitional probability between the initial and the final states and are essential for describing and understanding the physical processes involving photon absorption and emission. The OOSs of D_2 are studied in this work.

Since the discovery of deterium in 1932 by Harold Urey [11], the energy level structures of D_2 have been investigated extensively using various methods [6,10,12–16]. However, there are few absolute experimental OOSs because of the difficulties in measurement of the absolute intensity [17], to the best of our knowledge. Absolute rotational absorption cross sections were obtained by Glass-Maujean *et al.* recently [18–20] for $n \geqslant 4$ by the photoabsorption method. But for the Lyman and Werner bands of D_2 considered here, the relative vibrational band strengths were determined only by an electron energy loss method by Geiger and Schmoranzer [16], then normalized by Allison and Dalgarno [21] to their theoretical calculations by multiplying a constant, and there is still a gap from the absolute experimental OOSs.

Due to the lack of experimental OOSs, the calculated OOSs are the only data available. It is customary to assume that the potential surface of each electronic state of a molecule is invariant to its isotopic substitution according to the Born-Oppenheimer approximation [3]. The potential curves and electronic transition dipole moments of H_2, systematically calculated by Wolniewicz and coworkers [22–28], were applied to calculate the absolute OOSs of D_2 [21,29]. Allison and Dalgarno [21] predicted the vibrational OOSs of the Lyman and Werner bands, and recently Fantz and Wünderlich [29] published the vibrational transition probabilities using the latest calculations of Wolniewicz and Staszewska [23,30], which can be transformed into OOSs. Both the calculations

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of Fantz and Wünderlich [29] and those of Allison and Dalgarno [21] are based on the numerical solution of the radial Schrödinger equation. In addition, Abgrall *et al.* [10] calculated the spontaneous Einstein emission coefficients for individual rotational transitions using a far more accurate coupled-equation approach. The experimental absolute OOSs are required to test the validity of these calculations, which is the purpose of this work.

In this work, the dipole (γ, γ) method, which is inelastic x-ray scattering operated at a negligible momentum transfer, has been applied to measure the absolute OOSs of the Lyman and Werner bands of D_2. We provide the absolute OOSs of the Lyman and Werner bands with vibrational resolution. A comparison between the experimental results and the theoretical calculations is reported, and the validity of the Born-Oppenheimer approximation is discussed.

II. EXPERIMENTAL METHOD

The present experiment was carried out at the Taiwan Beamline BL12XU of SPring-8 with a high-energy resolution of about 25 meV, which was an improvement by a factor of 3 compared with the 75 meV used in our previous works [31–34], to resolve the heavily overlapped vibronic transitions of D_2. So the experimental setup used in this work is somewhat different. Synchrotron radiation from an undulator light source was first monochromatized by a Si (111) double-crystal monochromator at about 9890 eV, and the energy spread of the beam was then reduced down to $\leqslant 20\,\text{meV}$ by a postmonochromator of Si (800) four-bounce channel-cut crystals. The beam was focused by a platinum-coated toroidal mirror onto an $80 \times 120\,\mu\text{m}^2$ spot $(V \times H)$ in a sample position. Scattered x-rays were reflected by a diced Si (555) spherical crystal analyzer. The surface size of each dice was $1 \times 1\ \text{mm}^2$, making a footprint of $2 \times 2\ \text{mm}^2$ on a detector with an energy gradient along the axis perpendicular to the scattering plane. A Si strip detector was used to separate the focus into strips, with each strip having an energy window of 4 meV and independently recording the inelastic or elastic spectrum. The strip detector has a $4 \times 4\ \text{mm}^2$ active area with a 125-μm pixel (32 strips) [35]. In the experiment, we binned three strips into one channel, and five channels among them were used. Since the energy spread of the incident beam dominates the energy resolution, the binning procedure has little influence on the overall energy resolution, and finally, an overall energy resolution of 25 meV is achieved. In the measurement, the analyzer energy for the scattered photon was fixed, while the incident photon energy, from which the energy loss was determined, was varied. The deuterium and helium were sealed in a gas cell with kapton windows and put on the experimental platform for measurement in turn. Measurement was conducted at a scattering angle of 5°, as a compromise between the cost of the experimental time and the statistical counts. The pressures of deuterium and helium were about 1 MPa. Both deuterium and helium were measured twice and the final results are the average so as to reduce experimental errors. We summed the counts of five channels after calibrating their energy shifts to maintain the best energy resolution. In the measurement, the background was depressed to about 1 count per 100 s by shielding the detector from stray x-rays more efficiently. The summed energy loss spectrum of deuterium measured at 5° by inelastic x-ray scattering in the first round is shown in Fig. 1 after subtraction of a constant background of about 1.

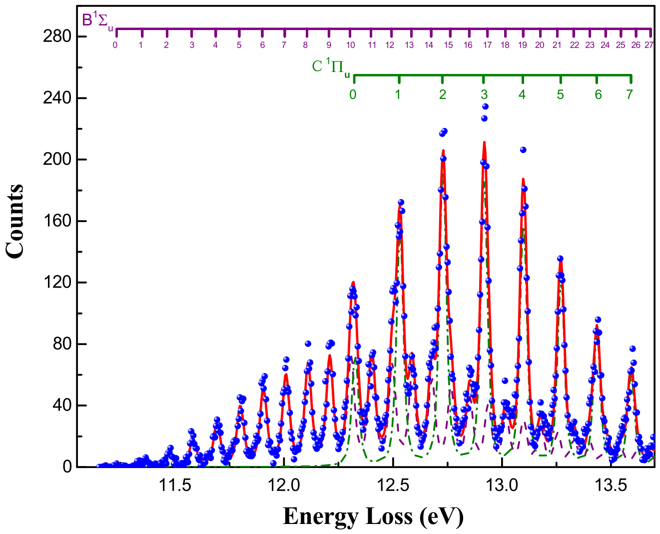

FIG. 1. Inelastic x-ray scattering spectrum for excitations to the Lyman and Werner bands of molecular deuterium at a scattering angle of 5°. Blue circles, experimental data; dashed purple line, fitted result for the Lyman band; dash-dotted olive line, fitted result for the Werner band; solid red line, fitted result in total.

The optical oscillator strength is described as

$$f_{v'v''} = \tfrac{2}{3}\omega_{v'v''} g |D_{v'v''}|^2. \tag{1}$$

g is the degeneracy of the final state. v' and v'' represent the vibrational quantum numbers in the upper and lower electronic states, respectively. $\omega_{v'v''}$ is the transition energy between two vibrational states in atomic units. $D_{v'v''}$ is the dipole transition moment, described as

$$\begin{aligned} |D_{v'v''}|^2 &= \left|\left\langle \chi_{v'}(R)\varphi_n^{\text{el}}(r_j)\right| \sum r_j \left|\chi_{v''}(R)\varphi_0^{\text{el}}(r_j)\right\rangle\right|^2 \\ &\approx q_{v'v''}|R_e(r_{v'v''})|^2, \end{aligned} \tag{2}$$

where $\chi_{v''}(R)$ and $\chi_{v'}(R)$ represent the vibrational wave functions, while $\varphi_0^{\text{el}}(r_j)$ and $\varphi_n^{\text{el}}(r_j)$ are the electronic wave functions for the initial and final states, respectively. R and r_j are the internuclear distance and the position vector of the jth electron. $q_{v'v''}$ is the Frank-Condon factor, and $R_e(r_{v'v''})$ is the electronic transition dipole moment at $r_{v'v''}$, the r-centroid internuclear distance, which may be considered the internuclear distance at which the transition $v' \leftarrow v''$ takes place.

Within the dipole (γ, γ) method [33,34,36,37], the relative optical oscillator strength is given as

$$f_0^{\gamma}(\omega_n) = B'_{\gamma}(\omega_n)\frac{N(\omega_n)}{N_0}\frac{1}{D_0\alpha}\frac{1}{l_{\text{eff}}}\frac{1}{n_0 P}, \tag{3}$$

where B'_{γ} is the so-called Bethe-Born conversion factor, which is determined accurately by simulating the actual arrangement of the light path considering the rectilinear propagation of the x-ray. $N(\omega_n)$ and N_0 stand for the counts of the scattered photons and the intensity of the incident photons, respectively. l_{eff}, n_0, and P are the collision length, the density of the target at 1 atm, and the pressure of the target in units of atm, respectively. D_0 is a constant determined by the detection efficiencies of the ionization chamber and the detector of the scattered photon, which includes the contributions from all channels and can be taken as a constant. The transmissivity α is determined by the sample species and its pressure, and it can be measured accurately with and without the sample gas in the gas cell by an ionization chamber after the gas cell. In order to obtain the absolute OOSs, a simple normalization method is used through

$$f_0(\omega_n) = \frac{B'_\gamma(\omega_n)}{B'_\gamma(2^1\mathrm{P})_{\mathrm{He}}} \frac{(N(\omega_n)/N_0)}{(N(2^1\mathrm{P})/N_0)_{\mathrm{He}}} \frac{\alpha_{\mathrm{He}}}{\alpha} \frac{P_{\mathrm{He}}}{P} f_0(2\,^1\mathrm{P})_{\mathrm{He}}, \tag{4}$$

where the $2\,^1\mathrm{P}$ of helium, whose OOS has been investigated with a high accuracy both experimentally [38] and theoretically [39], was measured at the same scattering angle and used to normalize the results of the deuterium.

In order to determine the intensity of the individual vibronic excitation, we wrote a fitting code based on the least-squares fitting method, and the details are reported in our recent work [40]. In the fitting procedure, the energy positions of the vibronic excitations were fixed to the ones calculated by Fantz and Wünderlich [29]. The individual vibronic excitation profile was described by a Voigt profile. The profiles of the Lyman and Werner bands were different due to the thermal distribution of initial rotational levels and the different intervals of the final rotational levels belonging to different excited electronic states, while the vibronic excitations belonging to a certain electronic state share the same profile, ignoring the slightly rotational effect. The fitted spectra for the first round are also shown in Fig. 1.

The final OOSs are the average of the results of both rounds. According to Eq. (4), the experimental errors of the OOSs come from the contributions of the Bethe-Born conversion factors, the fitting procedure including the statistical counts, the transmissivities, the pressures of deuterium and helium, and the OOS of the $2\,^1\mathrm{P}$ of helium, as well as the influences of the nonnegligible squared momentum transfer, which have been investigated carefully and are listed in Table I. Among them, the statistical error depends on the definite excitation and the systematic error due to the small but nonnegligible squared momentum transfer at 5° is estimated to be about 3%. Table I shows that the main experimental error contributions are due to statistical errors and systematic error. These errors can, in principle, be greatly reduced by accumulating the counts at a smaller angle, although it is hard to obtain a long beam time. The total experimental errors are also listed in Table I.

TABLE I. Uncertainty budget.

Source	σ
$B'_\gamma(\omega_n)/B'_\gamma(2\,^1\mathrm{P})_{\mathrm{He}}$	$\leqslant$ 0.1%
$N(B\,^1\Sigma_u^+)\,(v'=2\text{–}27)$[a]	5%–12%
$N(C\,^1\Pi_u)\,(v'=0\text{–}7)$	3%–6%
$N(2\,^1\mathrm{P})_{\mathrm{He}}$	2%
$N_0(\omega_n)$, $N_0(2\,^1\mathrm{P})_{\mathrm{He}}$	0.3%
α_{D_2}, α_{He}	1%
P_{D_2}, P_{He}	1.5%
$f_0(2\,^1\mathrm{P})_{\mathrm{He}}$	10^{-6}
Systematic error	3%
$\mathrm{Total}(B\,^1\Sigma_u^+)(v'=2-27)$	10%–20%
$\mathrm{Total}(C\,^1\Pi_u)(v'=0-7)$	8%–11%

[a] The error of $N(B\,^1\Sigma_u^+)$ and the total error for $v'=0$ of the Lyman band are 46% and 63%, respectively, and they are 21% and 30% for $v'=1$, due to their very low intensities.

III. RESULTS AND DISCUSSION

In the measured energy region of 11.2–13.7 eV, only the Lyman band ($v'=0$–27) and Werner band ($v'=0$–7) exist. The absolute optical oscillator strengths for the Lyman and Werner bands of molecular deuterium are summarized in Tables II and III and shown in Figs. 2 and 3 along with the calculations of Allison and Dalgarno [21] and Fantz and Wünderlich [29] and the results of Abgrall *et al.* [10], which were obtained by summing the OOSs of the rotational states by taking the rotational thermal distribution of the ground state at $T = 300$ K into account, as well as the experimental results of Geiger and Schmoranzer [16]. Table II and Fig. 2 clearly show that the present results on the Lyman band are in agreement with the experimental ones of Geiger and

TABLE II. Absolute optical oscillator strengths of the Lyman band (amplified by a factor of 10^4).

v'	Present results	Allison and Dalgarno [21]	Fantz and Wünderlich [29]
0	1.7 ± 1.1	2.0	1.9
1	8.1 ± 2.5	9.5	9.2
2	21.9 ± 4.4	25.5	24.6
3	43.9 ± 6.7	50.4	48.7
4	72.3 ± 9.2	82.2	79.1
5	103.9 ± 11.8	116.8	112.0
6	134.6 ± 14.2	150.0	143.4
7	161.2 ± 16.1	177.9	169.4
8	181.3 ± 17.6	198.1	188.2
9	193.8 ± 18.5	209.0	198.7
10	198.7 ± 18.9	212.9	201.5
11	196.9 ± 18.8	209.1	197.4
12	189.7 ± 18.3	199.7	188.1
13	178.3 ± 17.6	186.2	175.1
14	164.4 ± 16.6	170.3	159.8
15	149.1 ± 15.5	153.2	143.5
16	133.2 ± 14.4	135.8	127.1
17	117.6 ± 13.2	119.1	111.3
18	102.9 ± 12.1	103.3	96.6
19	89.2 ± 11.0	89.0	83.1
20	76.8 ± 10.0	76.1	71.0
21	65.8 ± 9.1	64.7	60.4
22	56.0 ± 8.2	54.8	51.1
23	47.5 ± 7.4	46.3	43.1
24	40.2 ± 6.7	38.9	36.2
25	34.0 ± 6.1	32.7	30.4
26	28.6 ± 5.5	27.4	25.5
27	24.1 ± 5.0	23.0	21.4

TABLE III. Absolute optical oscillator strengths of the Werner band (amplified by a factor of 10^4).

v'	Present results	Allison and Dalgarno [21]	Fantz and Wünderlich [29]
0	201.5 ± 19.1	202.0	190.3
1	438.4 ± 34.9	441.8	416.2
2	559.9 ± 42.7	567.8	534.9
3	553.7 ± 42.4	565.4	533.2
4	472.1 ± 37.3	486.8	458.9
5	366.9 ± 30.6	382.8	360.4
6	268.6 ± 24.1	284.0	266.9
7	189.3 ± 18.7	203.2	190.5

Schmoranzer [16], while the latter are somewhat scattered. Compared with the theoretical calculations, Fig. 2 shows that our results agree with the results of both Allison and Dalgarno [21] and Fantz and Wünderlich [29] within the experimental uncertainties. It can be noted that the theoretical results of Fantz and Wünderlich [29] are more consistent with the present experimental data than the calculations of Allison and Dalgarno [21], particularly for the strong transitions of $v' = 8$–12. The discrepancies between the present OOSs and those calculated by Allison and Dalgarno [21] exceed the experimental errors slightly for $v' = 4$–7 of the Lyman band, while an excellent agreement is found for $v' \geqslant 15$. The vibronic OOSs of Abgrall *et al.* [10] are slightly higher than ours for $v' = 4$–12. For $v' \geqslant 10$, their results become scattered due to the localized rovibronic perturbations between Lyman and Werner bands, especially for $v' = 19$, which is not observed in this experiment due to the limitation of the least-squares fitting method [40]. As for the Werner band, it is clear in Fig. 3 that all experimental and theoretical results are in agreement within the experimental uncertainties. However, the present OOSs for the lower vibronic states of $v' = 0$–3 are in better agreement with those of Allison and Dalgarno [21] than those of Fantz and Wünderlich [29], while the situation is reversed for $v' = 5$–7. The effect of localized rovibronic perturbations between Lyman and Werner bands is weak for the Werner band, and our results fit well with the results of Abgrall *et al.* [10] in the whole range.

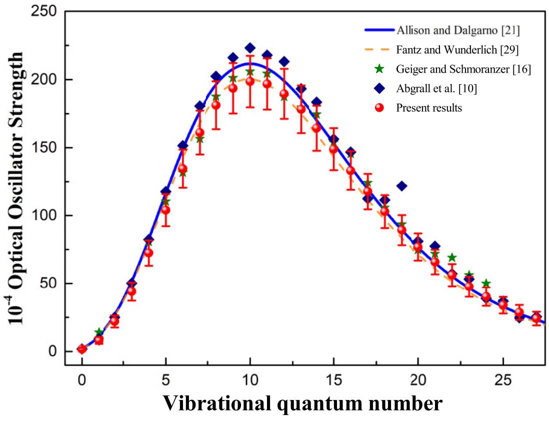

FIG. 2. Absolute optical oscillator strengths of the Lyman band. Red circles, present results; olive pentagrams, experimental results of Geiger and Schmoranzer [16]; dark-blue diamonds, results derived from the spontaneous Einstein emission coefficients calculated by Abgrall *et al.* [10]; solid blue line, calculated results of Allison and Dalgarno [21]; dashed orange line, calculated results derived by Fantz and Wünderlich [29].

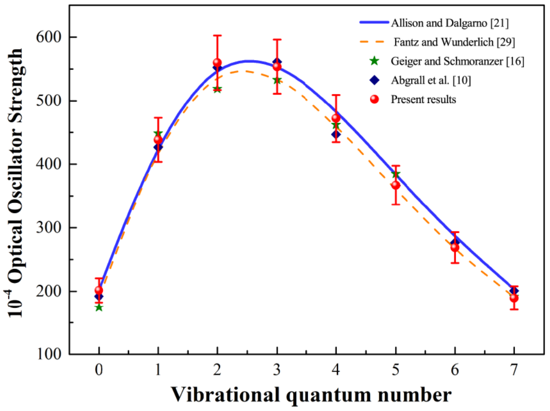

FIG. 3. Same as Fig. 2, but for the Werner band.

Since both Allison and Dalgarno's and Fantz and Wünderlich's calculations are based on the potential curves and electronic transition dipole moments of H_2 with the assumption of isotopic invariance in the framework of the Born-Oppenheimer approximation, the good agreement of the present experimental results and the theoretical calculations indicates that at the optical limit, i.e., where the squared momentum transfer approaches 0, the assumption is valid even for light nuclei such as the proton and deuteron, although electronic-vibrational coupling was observed in our recent study of momentum transfer dependence behaviors of the inelastic squared form factors of H_2 [40].

To further study the isotope effect of D_2, according to Eqs. (1) and (2), the electronic transition dipole moments $R_e(r_{v'v''})$ were obtained from our OOSs. The r-centroid internuclear distances were determined by digitizing the data of Geiger and Schmoranzer [16] for both Lyman and Werner bands. The electronic transition dipole moments of D_2 versus the r-centroid internuclear distance for Lyman and Werner bands are shown in Figs. 4 and 5 along with the theoretical values of Allison and Dalgarno [21], Fantz and Wünderlich [29], and Wolniewicz and Staszewska for H_2 [23,30], as well as the experimental results of Geiger and Schmoranzer [16] for D_2 and Chan *et al.* for H_2 [41]. As shown in Figs. 4 and 5, the recent theoretical calculations by Fantz and Wünderlich [29] are systematically lower than other theoretical results [21,23,30], and the experimental results of Chan *et al.* on H_2 [41] fit well with the theoretical ones of Wolniewicz and Staszewska [23,30] for both Lyman and Werner bands. The present results for the Lyman band of D_2 are in better agreement with the calcualtions of Fantz and Wünderlich [29], while they are lower than those of Allison and Dalgarno [21] and Wolniewicz and Staszewska [23] in the larger r-centroid internuclear distances. In the smaller r-centroid internuclear distances, the present results of the Lyman band show better agreement with those of Allison and Dalgarno [21] and Wolniewicz and Staszewska [23]. Geiger and Schmoranzer's experimental results on the Lyman band [16] show a trend

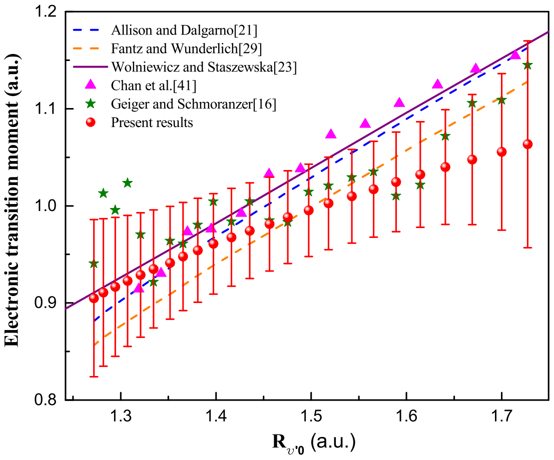

FIG. 4. The electronic transition moment as a function of the internuclear distance for the Lyman band ($\nu' = 2$–25). Red circles, present results; olive pentagram, experimental results of Geiger and Schmoranzer [16]; magenta triangles, experimental results on H_2 by Chan *et al.* [41]; solid purple lines,, calculated results of Wolniewicz and Staszewska [23]; dashed blue line, results derived by Allison and Dalgarno [21]; dash-dotted orange line, results derived by Fantz and Wünderlich [29].

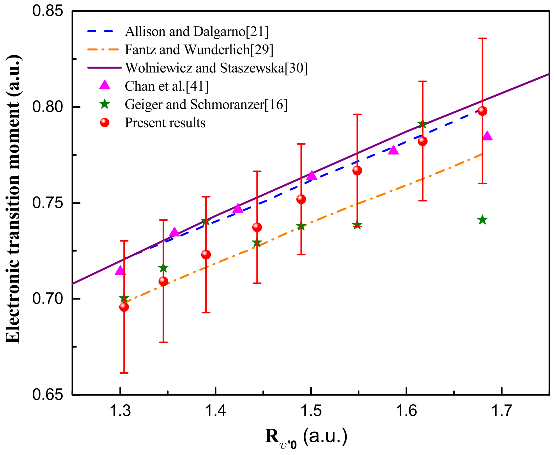

FIG. 5. Same as Fig. 4, but for the Werner band ($\nu' = 0$–7).

similar to ours. For the Werner band, this situation is reversed. The above comparison infers that the electronic transition dipole moments of D_2 and H_2 still show a slight difference.

IV. SUMMARY

Absolute optical oscillator strengths for the Lyman and Werner bands of D_2 have been determined experimentally by the dipole(γ, γ) method based on third-generation synchrotron radiation with the high energy resolution of 25 meV and the low background of about 0.01 cps. A comprehensive comparison shows that an excellent agreement among the present OOSs obtained with the dipole(γ, γ) method, the relative values of Geiger and Schmoranzer [16] with the EELS method, and the theoretical results of Allison and Dalgarno [21], Fantz and Wünderlich [29], and Abgrall *et al.* [10] is achieved. The derived electronic transition dipole moments show that there still exists a small difference between hydrogen and deuterium, though the isotope effect on the OOSs is slight. The present absolute optical oscillator strengths for the Lyman and Werner bands of D_2 provide experimental benchmarks to test different theoretical methods and for applications in thermonuclear fusion plasma.

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