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Inelastic squared form factors of the vibronic states of $B\ ^1\Sigma_u{}^+$, $C\ ^1\Pi_u$, and $EF\ ^1\Sigma_g{}^+$ for molecular hydrogen deuteride studied by fast electron scattering

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A joint experimental and theoretical investigation of the valence-shell excitations of hydrogen deuteride has been performed by the fast electron impact method at an incident electron energy of 1500 eV and the multireference single- and double-excitation configuration-interaction method. Momentum-transfer-dependent inelastic squared form factors for the vibronic states belonging to the $B\ ^1\Sigma_u{}^+$, $C\ ^1\Pi_u$, and $EF\ ^1\Sigma_g{}^+$ of molecular hydrogen deuteride have been derived with a high-energy resolution of 70 meV. Similar to the results of molecular hydrogen [L. Q. Xu, K. Xu, Y. G. Peng, X. Xu, Y. W. Liu, Y. Wu, K. Yang, N. Hiraoka, K. D. Tsuei, J. G. Wang, and L. F. Zhu, Phys. Rev. A **97**, 032503 (2018)], the present calculations do not satisfactorily reproduce the profiles of the inelastic squared form factors for the higher vibronic states of the $B\ ^1\Sigma_u{}^+$ of hydrogen deuteride. However, the discrepancies between the experimental and calculated results of the $B\ ^1\Sigma_u{}^+$ of hydrogen deuteride show a weaker dependence on the vibronic number than those of molecular hydrogen, i.e., the present experimental results for the $B\ ^1\Sigma_u{}^+$ of hydrogen deuteride are in better agreement with the calculated ones than those of the molecular hydrogen. It is very likely that the electronic-vibrational coupling effect in hydrogen deuteride is less important than that in molecular hydrogen. For the $C\ ^1\Pi_u$ state and some vibronic excitations of the $EF\ ^1\Sigma_g{}^+$ state, the present experimental results are lower than the present calculations, which may be due to the fact that the first Born approximation does not hold at an incident electron energy of 1500 eV.

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I. INTRODUCTION

Hydrogen deuteride (HD) is the third most abundant molecule in the interstellar medium and the planetary atmospheres, hence its energy-level structures and dynamic parameters of the valence-shell excitations have attracted a lot of interest from astrophysicists [1]. The Lyman ($B\ ^1\Sigma_u{}^+ \leftarrow X\ ^1\Sigma_g{}^+$) and Werner ($C\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g{}^+$) bands of interstellar HD, toward bright stars such as Zeta Ophiuchi [2,3], have been detected by the Copernicus satellite. More recently, using the Far Ultraviolet Spectroscopic Explorer satellite, several samples of these HD UV absorption transitions have also been detected in a variety of interstellar translucent clouds [4–7]. The strong electronic absorption spectra of the Lyman and Werner bands can be used to probe possible mass-variation effects on a cosmological time scale from the spectra observed at high redshift, not only in H_2 but also in the second most abundant hydrogen isotopomer HD [8]. In the solar system, HD has been observed in the atmospheres of all four giant planets (Jupiter, Saturn, Uranus, and Neptune) [9]. The HD density gives a measure of the H/D ratio in these giant planets, which is an efficient tracer of the universal star formation rate. So the H/D ratio has long been recognized as a powerful tool to understand the formation of the solar system from the primitive nebula [4]. Moreover, almost all D elements are bound in the HD molecule due to the high H/D ratio and the fact that D_2 has not been detected in the interstellar medium so far [10]. The electrons and ions in the ionospheres of planets can undergo elastic and inelastic collisions with the constituent species, such as HD, CH_3D, and C_2H_5D. So the electron impact cross sections for HD are needed to explain certain phenomena occurring in the planetary atmospheres and their ionospheres. Also, as an abundant composition in the edge region of fusion devices, the behavior of HD in the edge plasma of the tokamaks is crucial in understanding the boundary condition and the plasma-wall interaction in the fusion plasma [11]. Furthermore, the HD molecule is the simplest two-electron system after H_2 and therefore of interest for quantum-mechanical calculations beyond the Born-Oppenheimer approximation. The inelastic squared form factor (ISFF), which is traditionally presented in the form of the generalized oscillator strength (GOS), is a key quantity to connect the theoretical wave functions and the absolute excitation probabilities determined by experimental measurement. In order to interpret the astronomical observations and the complex behaviors of HD in the edge plasma, laboratory

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studies of the relevant physical processes of HD such as electron impact excitation are required.

In view of the above, it is clear that there is tremendous interest in the HD molecule in many fields. However, very few experimental measurements have been carried out to study excitation dynamic parameters such as the ISFFs or GOSs for the vibronic transitions of HD, due to the difficulties in resolving the heavily overlapped bands and determining the absolute values. Geiger and Schmoranzer [12] measured the electron energy-loss spectra of H_2, HD, and D_2 at an electron impact energy of 34 keV and obtained the Franck-Condon factors of the Lyman and Werner bands at near zero momentum transfer. Then a considerable isotope effect of H_2, HD, and D_2 was observed. The following electron impact experiments focus on the elastic scattering or the electron impact induced emission spectra of HD. Absolute elastic-scattering cross sections in the energy range 0.02–2 eV have been measured by Ferch *et al.* [13] for H_2, HD, and D_2 molecules. Electron impact dissociative excitation cross sections of HD have been studied at electron energies of 100–2000 eV by Möhlmann *et al.* [14]. Additionally, Ajello *et al.* [1] analyzed the high-resolution UV emission spectrum of the HD molecule measured by electron impact at 100 eV under optically thin single-scattering experimental conditions. In their work, absolute electron impact emission cross sections from the $B\,^1\Sigma_u{}^+$, $C\,^1\Pi_u$, $B'\,^1\Sigma_g{}^+$, and $D\,^1\Pi_u$ states were derived from a modeling analysis, and the dissociative excitation cross sections at 100 eV for the emission of Ly α lines at 1216 Å and Ly β lines at 1025 Å were also determined. To the best of our knowledge, the above-mentioned works are the only experimental electron impact cross sections reported for HD.

On the theoretical side, pure rotational excitations of HD by low-energy electron impact have been calculated by Hara [15], and vibrational excitations of HD have been analyzed theoretically by Kazanskii [16]. However, very few theoretical investigations on the valence-shell excitations of HD have been performed in the literature, and there are almost no vibrational excitation cross sections or ISFFs available for HD. As far as we know, only Kolos *et al.* [17] calculated the GOSs for the vibronic states of $B\,^1\Sigma_u{}^+$ beyond the commonly applied Franck-Condon approximation with the wave functions expanded in explicitly correlated Gaussian functions. In 2007, Fantz and Wünderlich [18] reported a systematic fundamental molecular database, i.e., the vibrational eigenvalues, Franck-Condon factors, and vibrationally resolved transition probabilities, for all isotopes of the hydrogen molecule, on the basis of the latest Born-Oppenheimer potential curves and electronic dipole transition moments of the hydrogen molecule.

Within the first Born approximation (FBA), the ISFF determined by the high-energy electron energy-loss spectroscopy (EELS) has the form [19–25]

$$\zeta(\boldsymbol{q},\omega_n) = \left|\langle\Psi_n\right|\sum_{j=1}^{N}\exp(i\boldsymbol{q}\cdot\boldsymbol{r}_j)\left|\Psi_0\rangle\right|^2, \tag{1}$$

where Ψ_0 and Ψ_n are the wave functions of the initial and final states, respectively. $\boldsymbol{q}$ is the momentum transfer in the scattering process. The sum is over all electrons and r_j is the position vector of the jth electron. Under the condition that the FBA is satisfied, the relationship between the ISFF and the experimental differential cross section (DCS) for the high-energy electron impact process is [21,22,26]

$$\zeta(\boldsymbol{q},\omega_n) = \frac{1}{4}\frac{k_i}{k_f}q^4\left(\frac{d\sigma}{d\Omega}\right)_e, \tag{2}$$

where k_i and k_f refer to the momenta of the incident and scattered electrons. $(\frac{d\sigma}{d\Omega})_e$ represents the DCS measured by the EELS method.

As mentioned above, although a few investigations of the ISFFs of HD have been carried out both experimentally and theoretically, the vibrationally resolved ones, especially for the experimental ones, are still scarce. In this paper, a joint experimental and theoretical study of the ISFFs for the vibronic excitations of the Lyman band, Werner band, and $EF\,^1\Sigma_g{}^+$ of HD is performed by the high-energy EELS and the multireference single- and double-excitation configuration-interaction (MRD-CI) methods. The present paper gives us a better understanding of and deeper insight into the elementary excitation process of HD, which will lead to more reliable explanations of phenomena in astronomical observations and fusion plasmas.

II. EXPERIMENTAL AND CALCULATION METHODS

The present EELS measurement was performed at a high-resolution electron energy-loss spectrometer at University of Science and Technology of China, and details of the apparatus were described in our previous works [27–29]. For the present experiment, the spectrometer was set at an impact energy of 1500 eV and an energy resolution of about 70 meV. The experimental spectra were recorded at scattering angles from 1.5 to 8° and at room temperature. The standard relative flow technique [30–33] was utilized to simplify the normalization process and improve the accuracy of the experimental data. In the present measurement, the mixed gas of hydrogen deuteride and helium with individually controlled flowing rates flowed into the interaction chamber simultaneously and continuously through a jet nozzle, crossing with the monochromatic incident electron beam at an angle of 90°. The intensity ratios of the excited states of hydrogen deuteride to the $2\,^1$P of helium were measured at different scattering angles. Using these ratios and the accurate flow rates of hydrogen deuteride and helium, the absolute inelastic DCSs of hydrogen deuteride were determined by normalizing them to the inelastic DCS of the $2\,^1$P state of helium [34], which has been measured and calculated with a high accuracy [28,34–36]. Figure 1 shows a typical electron energy-loss spectrum measured by the present EELS, and it is clear that the measured vibronic bands belong to four electronic states in the investigated energy region according to Ref. [18].

In order to obtain the quantitative ISFFs for every vibronic excitation of the HD molecule, a least-squares fitting is used to fit the measured spectra. However, the traditional multipeak fitting method is insufficient to obtain reliable results, due to the heavy overlapping of different electronic states, especially in the energy region of the Werner band. Thus we have developed a least-squares fitting program based on the modified Franck-Condon approximation, which had been successfully applied to fit the spectra of molecular hydrogen. Details about this fitting program have been described in our recent work [37],

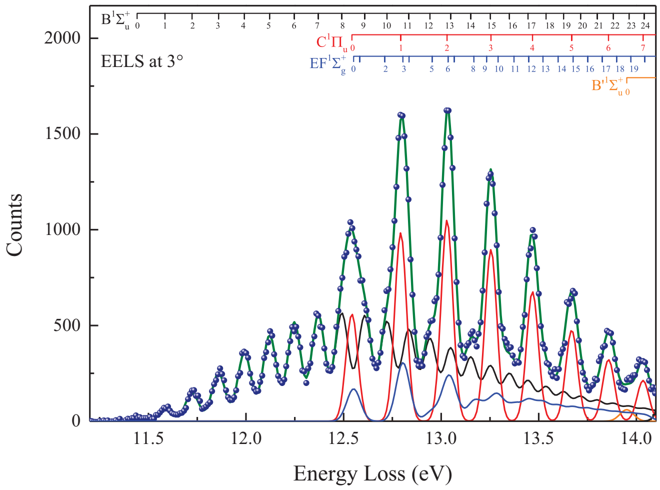

FIG. 1. A typical electron energy-loss spectrum of the HD molecule measured by the EELS at a scattering angle of 3°. The green fitted curve represents the sum of the black, red, and blue curves for the different excited vibronic states, and the details of the fitting procedure have been discussed in Sec. II.

and the same fitting method was used to fit all the measured spectra in this paper.

Momentum-transfer-dependent ISFFs for the vibronic states belonging to the $B\,^1\Sigma_u{}^+$, $C\,^1\Pi_u$, and $EF\,^1\Sigma_g{}^+$ of molecular hydrogen deuteride were calculated by using the MRD-CI method in the present paper. The same method has been described in detail in Refs. [38–43] and has been used to calculate the ISFFs of molecular hydrogen in our very recent work [37]. First, the adiabatic potential curves and wave functions of the electronic states were calculated with the MRD-CI method based on the Born-Oppenheimer approximation. Then, using the calculated adiabatic potential-energy curves, the nuclear vibronic energies and wave functions were obtained by solving the one-dimensional radial Schrödinger equation, where the discrete variable representation method [44] has been utilized. Finally, the vibronic ISFFs of molecular hydrogen deuteride were obtained on the basis of the calculated electronic and vibronic wave functions.

The experimental errors from the determination of the scattering angles as well as the absolutization procedures have been analyzed carefully [37]. The total experimental errors, as shown in the corresponding figures, are about 5–10% for most of the resolved states, and up to 10–30% for some unresolved states.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the EELS and calculated two-dimensional maps for the ISFF densities of HD versus the energy loss and squared momentum transfer. The EELS two-dimensional map was obtained by transferring the measured EELS spectra into the ISFF density scale. Moreover, the MRD-CI calculations were also plotted as a two-dimensional map by convolving the theoretical results with the present experimental energy resolution (70 meV). From Figs. 2(a) and 2(b), it is clear that qualitatively there is a good match between the EELS results and the theoretical calculations including their absolute scales and momentum transfer dependence behaviors.

The present experimental and theoretical ISFFs for some selected vibronic states of the $B\,^1\Sigma_u{}^+$, $C\,^1\Pi_u$, and $EF\,^1\Sigma_g{}^+$ excitations are shown in Figs. 3–5 along with the available previous results. Since there are no experimental vibronic ISFFs reported previously, only the previous theoretical results of Kolos *et al.* [17] are presented for comparison.

For the $B\,^1\Sigma_u{}^+$, it is noted that the vibronic states of the $\nu' \leqslant 7$ do not overlap with other states as shown in Fig. 1, so their ISFFs are free from any systemic errors from the fitting procedure. Considering the clearly resolved features below 13.2 eV as shown in Fig. 1 and the improved fitting method, we have confidence in the present experimental results for the vibronic states of the $B\,^1\Sigma_u{}^+$ ($\nu' \leqslant 14$). It is clear from Fig. 3 that for the $B\,^1\Sigma_u{}^+$ the present MRD-CI calculations are in good agreement with the ones by Kolos *et al.* [17]. The present EELS results match the theoretical calculations very well for the lower vibronic excitations of $\nu' \leqslant 10$ while the discrepancies between them become larger with the increasing of the vibronic states. The same phenomenon has also been observed in molecular H_2 in our previous work [37]. However, the discrepancies between the experimental and calculational results of HD show a weaker dependence on the vibronic number than those of H_2, i.e., the present EELS results of HD are in better agreement with the calculational ones than those of the H_2. As discussed in our recent paper [37], this phenomenon may be attributed to the electronic-vibrational coupling, considering that H_2 and HD are very light molecules and the velocity of the nuclei increases with the higher vibronic state. In fact, HD is an isotopic molecule of H_2, and Buckman and Phelps [45] and de Heer [46] suggested that the electronic excitation cross sections of HD are almost the same as those with H_2. However, HD is heavier in comparison with H_2. As a result, the distribution of the Franck-Condon factors of the vibrational excitations is not the same for H_2 and HD. It is very likely that the electronic-vibrational coupling effect has less influence on the heavier isotopic molecule HD. Actually, the electronic-vibrational coupling effect has been studied by Wolniewicz *et al.* [47] and in the earlier work of Abgrall *et al.* [48], while the corresponding nonadiabatic rovibronic wave functions have not been used to predict scattering dynamic parameters such as the ISFFs or GOSs. More experimental and theoretical works on HD and H_2, especially high-resolution (higher than 20 meV) experimental studies and theoretical investigation taking the electronic-vibrational coupling effect into account, are needed for further explanations.

Figure 4 presents the ISFFs for the vibronic states of the $C\,^1\Pi_u$. Since there are no experimental or calculational vibronic ISFFs reported previously, only the present EELS and MRD-CI results are presented. It should be mentioned that random allocations of the intensities for the vibronic states of the $C\,^1\Pi_u$ and $EF\,^1\Sigma_g{}^+$, the energy positions of which nearly match [18], may bring somewhat larger experimental uncertainties in the fitting procedure. It is clear from Fig. 4 that the present EELS results are apparently lower than the MRD-CI calculations by about 25%. This is very different from the circumstance of H_2, where a reasonable agreement between the EELS results and the MRD-CI calculations was observed

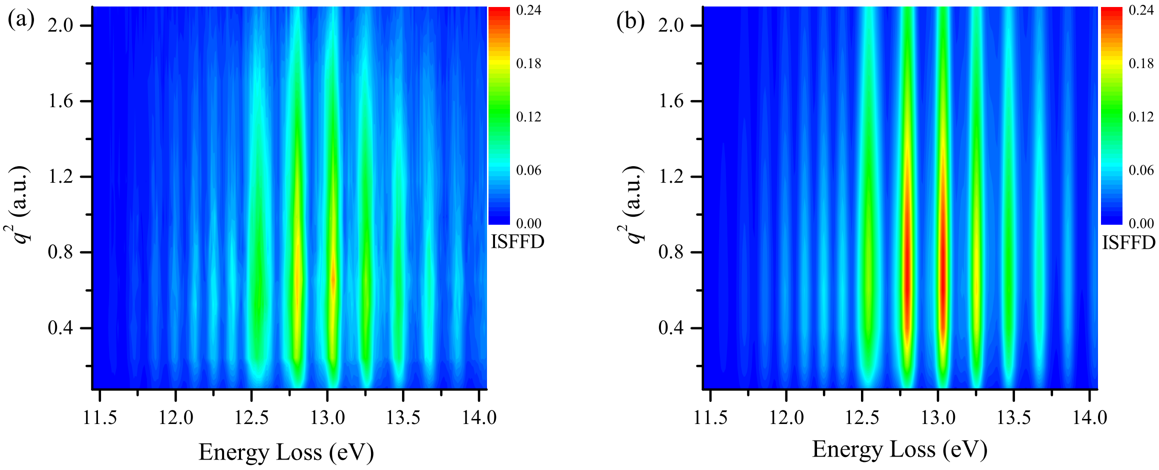

FIG. 2. The two-dimensional maps for the ISFF densities of the HD molecule vs the energy loss and squared momentum transfer: (a) measured by the present EELS and (b) calculated by the present MRD-CI method.

for the $C\,^1\Pi_u$, although the EELS results are slightly lower. However, at the present stage, we cannot give a clear explanation for the discrepancies among the results of experiments and calculations.

Figure 5 shows the ISFFs of the vibronic states of the $EF\,^1\Sigma_g{}^+$. Since the ISFFs of some vibronic states ($\nu' = 1$, 2, 4, 5, 7, and 8) are negligibly small according to their calculated Franck-Condon Factors [18], their ISFFs are neglected and not shown in Fig. 5. For the higher vibronic states, selected results with even vibronic numbers are presented. Due to the irregular vibronic intensity distribution of the $EF\,^1\Sigma_g{}^+$ induced by its two minima of the double-well potential curve and the near match of its vibronic energy positions with those of $C\,^1\Pi_u$, the ISFFs for the vibronic states of $EF\,^1\Sigma_g{}^+$ are more scattered than those of the $B\,^1\Sigma_u{}^+$ and $C\,^1\Pi_u$. Generally speaking, for some vibronic states ($\nu' = 0,3,6,9$), the ISFFs of the EELS are in good agreement with the present MRD-CI calculations within the experimental errors, while for other vibronic states

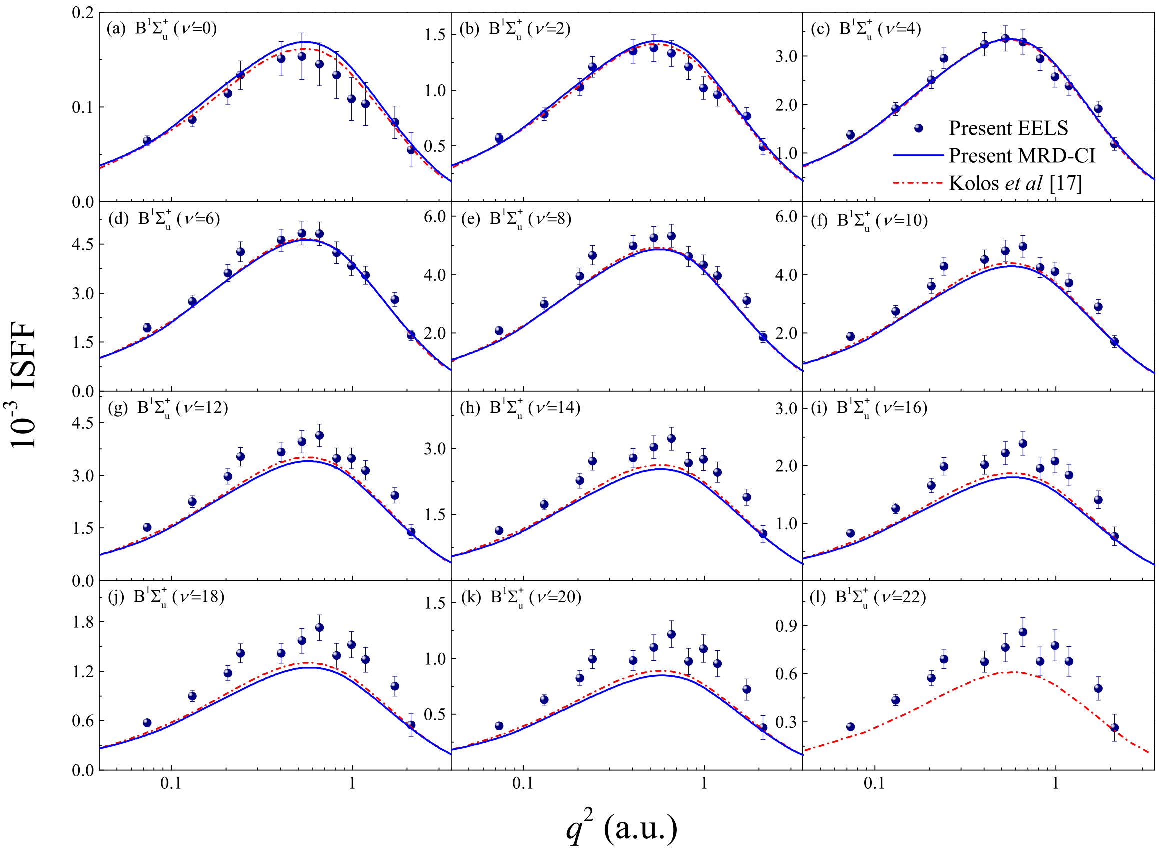

FIG. 3. (a)–(l) Selected ISFFs of $B\,^1\Sigma_u{}^+$ (even vibrational numbers). Blue spheres, the present EELS results; blue solid lines, the present MRD-CI calculations; red dash-dotted lines, the results of Kolos *et al*. [17].

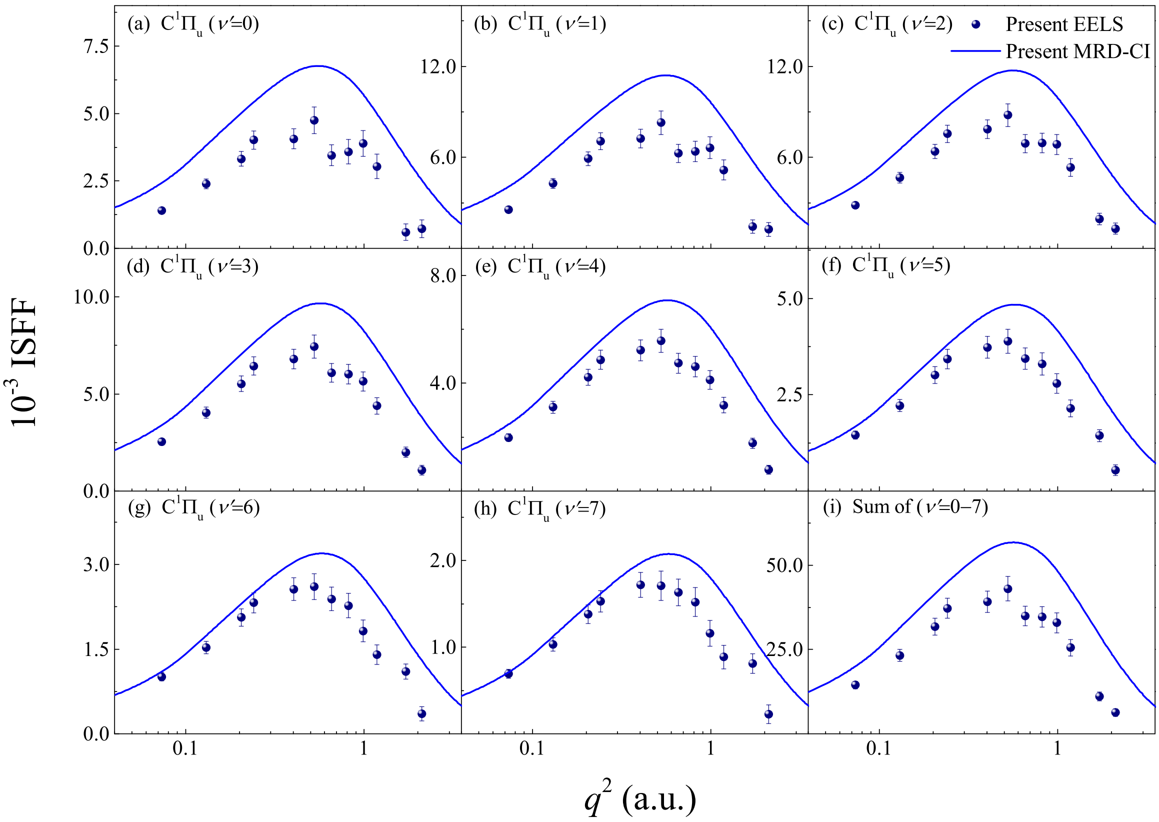

FIG. 4. (a)–(h) The ISFFs of $C\ {}^1\Pi_u$ ($v' = 0$–7). Blue spheres, the present EELS results; blue solid lines, the present MRD-CI calculations. (i) Sum of the ISFFs of $C\ {}^1\Pi_u$ ($v' = 0$–7).

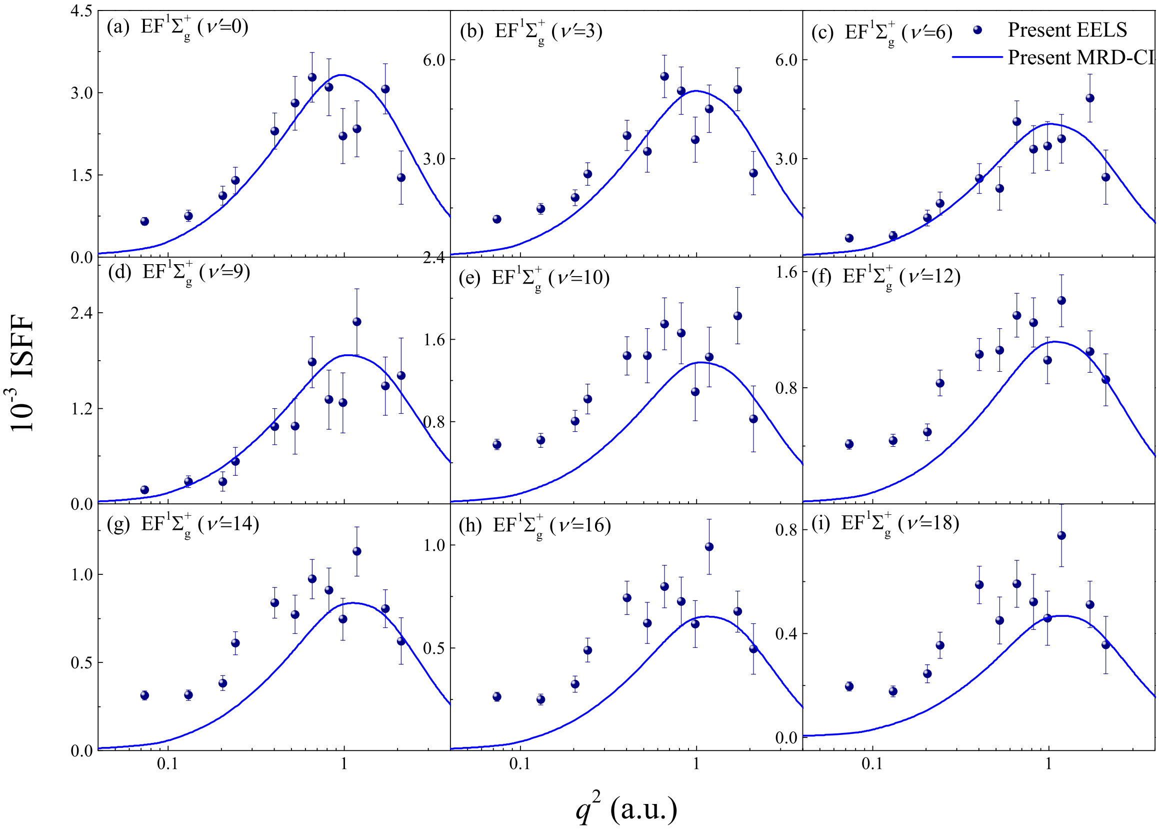

FIG. 5. (a)–(i) Selected ISFFs of $EF\ {}^1\Sigma_g{}^+$ ($v' = 0,3,6,9,10,12,14,16,18$). Blue spheres, the present EELS results; blue solid lines, the present MRD-CI results.

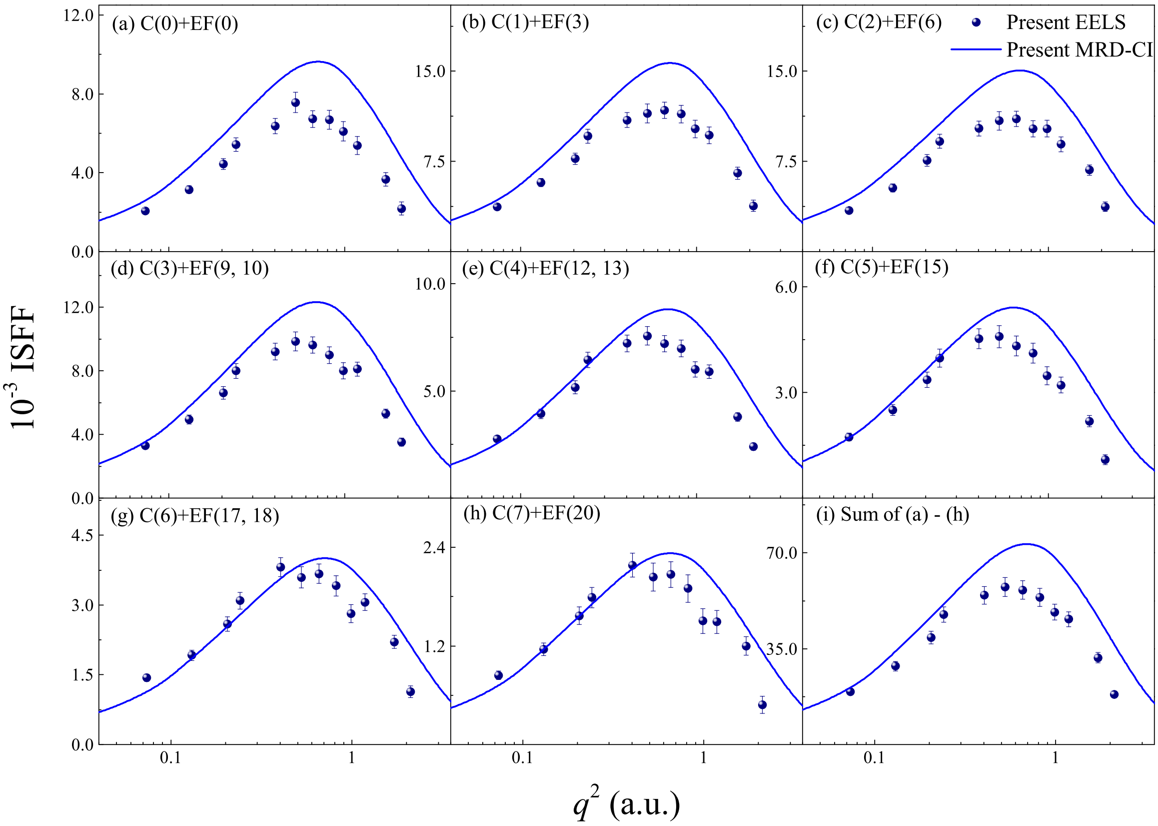

FIG. 6. (a)–(h) Sum of the ISFFs of unresolved vibronic states belonging to the Werner band and EF states ranging from 12.45 to 13.90 eV. Blue spheres, the present EELS results; blue solid lines, the present MRD-CI calculations. (i) Sum of the ISFFs of panels (a)–(h).

($v' = 10, 12, 14, 16, 18$) the experimental ISFFs are somewhat higher than the calculated results.

In Fig. 6, we present the sum ISFFs of the vibronic excitations of the $C\,^1\Pi_u$ and $EF\,^1\Sigma_g{}^+$ which cannot be clearly resolved in the EELS spectra, to avoid the possible systematic errors from the fitting procedures for the heavily overlapped states in the energy region larger than 12.44 eV. From Fig. 6, we can clearly see that the present EELS results are apparently lower than the MRD-CI calculations by about 25% in the squared momentum transfer region of $q^2 > 0.5$ a.u. However, for the results in the momentum transfer region of $q^2 < 0.5$ a.u., the EELS results are in reasonable agreement with the MRD-CI calculations except for those shown in Figs. 6(a)–6(c). Moreover, for the sum ISFFs of the vibronic excitations of the $C\,^1\Pi_u$ and $EF\,^1\Sigma_g{}^+$ of molecular hydrogen [37], although the experimental results and the MRD-CI calculations are in reasonable agreement within the experimental uncertainties, the EELS results are still slightly lower than the inelastic x-ray scattering results and the MRD-CI calculations in $q^2 > 0.2$ a.u. This may imply that for HD the FBA has also not been reached even at a high electron impact energy of 1500 eV in the larger q^2 region.

IV. SUMMARY

In this paper, a joint experimental and theoretical investigation of the valence-shell excitations of molecular hydrogen deuteride has been performed by the fast electron impact method and the MRD-CI method. The high-energy resolution of about 70 meV resolves the vibronic states. Momentum-transfer-dependent ISFFs for the vibronic states belonging to the $B\,^1\Sigma_u{}^+$, $C\,^1\Pi_u$, and $EF\,^1\Sigma_g{}^+$ of HD have been derived. Similar to the results of molecular hydrogen, the present calculations cannot satisfactorily reproduce the inelastic squared form factor profiles for the higher vibronic states of the $B\,^1\Sigma_u{}^+$ of HD. However, light is shed on this phenomenon: the discrepancies between the experimental and calculated results of HD show a weaker dependence on the vibronic number than those of molecular hydrogen, which may be due to the fact that the electronic-vibrational coupling effect in the heavier HD molecule is less important than that in molecular hydrogen. As for the $C\,^1\Pi_u$, the experimental ISFFs are apparently lower than the MRD-CI calculations by about 25%, especially in the larger q^2 region. The sum ISFFs of the $C\,^1\Pi_u$ and the $EF\,^1\Sigma_g{}^+$, which excluded the fitting uncertainties, are still lower than the calculational ones in the larger q^2 region, which may be due to the invalidity of the FBA at an incident electron energy of 1500 eV.

Considering that the H_2 and HD are the simplest diatomic molecules, we initially expected that their experimental results could be reproduced by the theoretical calculations very well. However, obvious discrepancies are observed for both HD and H_2 in the present paper and previous works [37]. Therefore, further high-resolution experimental studies and more accurate calculations including the electronic-vibrational coupling effect are greatly recommended.

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