Squared form factors for the $A\,^1\Pi$ and $B\,^1\Sigma^+$ vibronic bands of carbon monoxide studied by high-resolution inelastic x-ray scattering

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Using the inelastic x-ray scattering with a high resolution of 70 meV, squared form factors of molecular carbon monoxide have been determined from the ground state $X\,^1\Sigma^+$ to the vibronic states of $A\,^1\Pi$ and $B\,^1\Sigma^+$. Since the first Born approximation is satisfied in inelastic x-ray scattering, the inelastic squared form factors of the valence-shell excitations of carbon monoxide measured by this work not only provide the experimental benchmark data but also serve as the high-energy limit for the electron impact method. Based on the present experimental results, the validity conditions of the previous electron impact works are discussed. It is found that for the excitations of $A\,^1\Pi(v' = 0$–$6)$ the first Born approximation is reached in the region of $q^2 < 0.7$ a.u. at an impact electron energy of 1.5 keV, while for $B\,^1\Sigma^+(v' = 0)$ the first Born approximation does not fully hold at the impact electron energy of 1.5 keV except for the $q^2 < 0.15$ a.u. The large discrepancies between the present inelastic x-ray scattering results and the theoretical calculations for most transitions suggest that the formerly reported calculations are not accurate enough.

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I. INTRODUCTION

Carbon monoxide is not only a kind of fossil fuel of enormous significance but also the second most abundant interstellar molecule, which plays a crucial role in understanding the conditions and chemistry in the interstellar medium [1] and serves as a tracer of the large-scale distribution of molecular gas in the galaxy [2]. Moreover, accurate and reliable spectroscopic data of carbon monoxide will make the interpretation of new astrophysical observations available [2]. Consequently, the energy level structures and dynamic parameters of the valence-shell excitations of carbon monoxide have attracted the attentions of both theorists and experimentalists.

The inelastic squared form factor (ISFF), or the equivalent physical quantity, the generalized oscillator strength (GOS), is one of the most important dynamic parameters since these are directly related to the electronic structures, i.e., the wave functions of the initial and final states of atoms or molecules. Therefore, highly accurate experimental ISFFs or GOSs can be used to test theoretical models and calculational codes rigorously [3–12]. For carbon monoxide, most previous experiments concentrated mainly on measurements of differential cross sections (DCSs) or GOSs of valence-shell excitations utilizing the electron energy-loss spectroscopy (EELS) method. Among these, low impact energies (<100 eV) [13], moderate energies (100–500 eV) [14–19], and a high energy (1500 eV) [20] were used. Theoretical calculations have also received considerable attention, and the GOSs for the valence-shell excitations of carbon monoxide have been calculated with different methods [21–24]. Using the configuration-interaction treatment and including singly and doubly excited configurations with respect to a multireference description of a series of electronic states, Chantranupon and coworkers have reported theoretical calculations for the vibronic bands of $A\,^1\Pi$, $B\,^1\Sigma^+$, $C\,^1\Sigma^+$, and $E\,^1\Pi$ [21,22]. Dillon *et al.* [23] carried out the theoretical calculations for the vibronic bands of $A\,^1\Pi(v' = 0,1,2,4,7)$ and $B\,^1\Sigma^+(v' = 0,1)$, employing the Born approximation combined with the multireference single- and double-excitation configuration interaction methods. Rocha *et al.* [24] obtained results for the $B\,^1\Sigma^+$, $C\,^1\Sigma^+$, and $E\,^1\Pi$ on the condition that the target electronic states were determined using the configuration-interaction method, with a Hartree-Fock basis for the occupied molecular orbitals. Although it is generally believed that the first Born approximation (FBA) is satisfied and the GOSs for the valence-shell excitations of carbon monoxide can be transferred from the DCSs [16–20] for the moderate-energy [14–19] and high-energy electron impact [20], large differences are still observed between theoretical and experimental GOSs for $A\,^1\Pi$ and $B\,^1\Sigma^+$. There may be two reasons for these differences: (1) the CI calculations are not accurate enough and (2) the FBA is not satisfied in the region of the measured square momentum transfer. For the $A\,^1\Pi$ transition, the former reason seems to be reasonable considering the consistence of the GOSs measured at different impact electron energies, which means the FBA is reached in the measured q^2 region. While for the transition $B\,^1\Sigma^+$, the reason for the difference is unclear since the experimental GOSs increase with impact electron energies, and the validity condition of the FBA remains obscure. Since the FBA is nearly always valid in the inelastic x-ray scattering (IXS), measuring the ISFFs of the valence-shell excitations of carbon monoxide by IXS can provide the experimental

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benchmark data, serve as the high-energy limit of the electron impact method, as well as clarify the existing difference between theoretical calculations and preceding experiments.

The ISFF determined by the IXS or high-energy EELS is defined as

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

where $\boldsymbol{q}$ denotes the momentum transfer. Ψ_0 and Ψ_n stand for the wave functions of the initial and final states respectively. The sum is over all electrons and $\boldsymbol{r}_j$ is the position vector of the jth electron. The ISFF can be determined from the DCSs measured by the IXS or high-energy EELS under the condition that the FBA is reached:

$$\begin{aligned}\zeta(\boldsymbol{q},\omega_n) &= \frac{1}{r_0^2}\frac{\omega_i}{\omega_f}\frac{1}{|\boldsymbol{\epsilon}_i\cdot\boldsymbol{\epsilon}_f^*|^2}\left(\frac{d\sigma}{d\Omega}\right)_\gamma,\\ &= \frac{1}{4}\frac{k_i}{k_f}q^4\left(\frac{d\sigma}{d\Omega}\right)_e,\\ &= \frac{q^2}{2\omega_n}f(\boldsymbol{q},\omega_n). \quad (2)\end{aligned}$$

$(\frac{d\sigma}{d\Omega})_\gamma$ and $(\frac{d\sigma}{d\Omega})_e$ represent the DCSs measured by the IXS and EELS, and $f(\boldsymbol{q},\omega_n)$ symbolizes the GOS. The factor $|\boldsymbol{\epsilon}_i\cdot\boldsymbol{\epsilon}_f^*|^2$ is the product of the polarized directions of incident and scattered photons, and r_0 is the classical electron radius. ω_i, ω_f and $\omega_n = \omega_i - \omega_f$ represent the energies of the incident photon, scattered photon, and the loss between them. k_i and k_f denote the momenta of the incident and scattered electrons.

In the present work, using the high-resolution inelastic x-ray scattering method, we measured the inelastic squared form factors for the vibronic states of $A\,^1\Pi$ and $B\,^1\Sigma^+$ of carbon monoxide with the squared momentum transfer q^2 ranging from nearly 0 to 6 a.u. Comparisons are also made between the present results and previously published data.

II. EXPERIMENTAL METHOD

The present experiment was performed at the Taiwan Beamline BL12XU at SPring-8 and the experimental procedures employed are similar to those used in our previously reported works for the noble gases [25,26,29,30] and the diatomic molecule nitrogen [27]. Accordingly, only a brief description will be given here. In this experiment, the energy of the scattered photon was fixed at 9889.43 eV, while the incident photon energy varied, from which the energy loss can be easily deduced. The energy resolution is about 70 meV, with which the vibronic states $A\,^1\Pi$ and $B\,^1\Sigma^+$ can be resolved. A typical IXS spectrum of carbon monoxide is shown in Fig. 1 together with the vibronic states assigned. The excitation from the ground state to the 2^1P state of helium, whose GOS has been measured and calculated with high accuracy and proven to be credible [26–29] was measured at small scattering angles and utilized to normalize the results of carbon monoxide. In addition, in order to acquire the absolute value of $\zeta(\boldsymbol{q},\omega_n)$ for carbon monoxide, the pressures and the actual transmission rates of both carbon monoxide and helium were recorded to normalize the experimental data under the same experimental conditions. The experimental errors of ISFF derived mainly from the statistics of counts, the fitting procedure, as well as the normalizing process, which are shown in Table I and the corresponding figures.

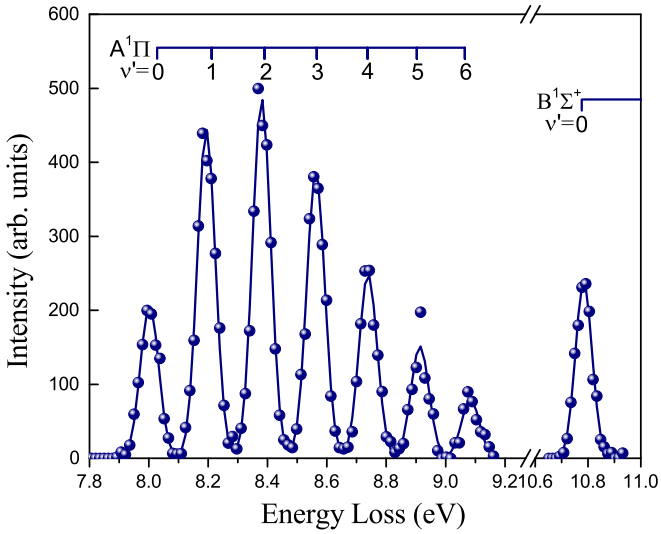

FIG. 1. (Color online) Typical IXS spectrum of the valence-shell excitations of molecular carbon monoxide measured at 15° ($q^2 \approx 0.48$ a.u.). The solid line is the fitted curve to guide the eye.

III. RESULTS AND DISCUSSION

The present ISFFs are presented in Figs. 2–4 along with previous experimental results and theoretical calculations. Figure 2 shows the present ISFF for the excitation to $A\,^1\Pi(\nu'=2)$ along with EELS values measured at different incident electron energies [14,19]. It is clear that the EELS results at impact energies of 300, 400, and 500 eV are in good agreement with the present IXS one, but at impact energies of 100 and 200 eV, the EELS values deviate from the present IXS with increasing momentum transfer. This phenomenon means that the FBA is satisfied at impact electron energies of more than 300 eV in the measured q^2 region, but does not hold for impact electron energies below 200 eV in the region $q^2 > 0.1$ a.u. Excellent agreement is observed between the present results and the data by Zhong *et al.* [20] at an impact electron energy of 1500 eV in the region $q^2 < 0.7$ a.u. However, the results of Zhong *et al.* disagree with the current measurement around the maximum,which may result from the inadequacy of the FBA when q^2 is beyond 0.7 a.u. even at the impact electron energy of 1500 eV. The present results show good consistency with respect to theoretical calculations by Chantranupong *et al.* [21] and Dillon *et al.* [23] in small momentum transfer square region of $0 < q^2 < 0.4$ a.u. when experimental errors are taken into consideration.

Figure 3 shows the inelastic squared form factors of $A\,^1\Pi(\nu' = 0,1,3,4,5,6)$ determined in the present work along with the theoretical calculations [21,23] and EELS values [14,20] converted from the reported GOSs. It is obvious that the experimental results of Zhong *et al.* [20] and the present IXS ones are in good agreement with each other in the region $q^2 < 0.7$ a.u., but the present results are slightly larger in the region $q^2 > 0.7$ a.u. This may be attributed to

TABLE I. The present ISFFs determined by the IXS. The listed data are multiplied by a factor of 10^3. Data in the parentheses represent the corresponding experimental uncertainties. For simplicity, $A(0)$ is short for $A\,^1\Pi(v'=0)$, and similarly for the rest.

q^2 (a.u.)	$A(0)$	$A(1)$	$A(2)$	$A(3)$	$A(4)$	$A(5)$	$A(6)$	$B(0)$
0.05	1.62(0.12)	3.07(0.19)	3.36(0.21)	2.77(0.18)	1.93(0.14)	1.01(0.10)	0.49(0.09)	1.56(0.29)
0.11	2.90(0.20)	5.86(0.35)	6.65(0.39)	5.39(0.32)	3.61(0.24)	2.27(0.18)	1.15(0.14)	2.14(0.27)
0.21	5.81(0.39)	10.8(0.7)	12.7(0.8)	9.93(0.60)	6.75(0.44)	3.97(0.31)	1.80(0.23)	5.44(0.50)
0.33	7.21(0.46)	14.2(0.8)	16.4(0.9)	13.6(0.75)	8.78(0.53)	5.37(0.38)	2.46(0.28)	9.58(0.76)
0.48	9.22(0.65)	19.8(1.1)	21.7(1.2)	17.2(1.0)	11.1(0.7)	6.76(0.56)	3.54(0.46)	11.3(0.9)
0.69	12.2(0.8)	25.3(1.4)	27.8(1.5)	22.6(1.3)	14.1(0.9)			12.4(1.0)
1.03	12.7(1.0)	26.2(1.6)	31.6(1.8)	22.5(1.4)	15.5(1.1)			10.4(0.7)
1.54								10.5(0.7)
1.65	14.2(1.0)	27.6(1.6)	28.26(1.6)	23.4(1.4)	14.8(1.0)			
2.28	11.1(0.9)	20.8(1.3)	25.18(1.5)	19.3(1.23)	11.7(0.9)			
2.99	7.77(0.69)	16.0(1.0)	18.04(1.1)	13.3(0.9)	8.2(0.70)			
3.96	5.12(0.63)	11.6(0.8)	12.7(0.8)	9.78(0.74)	5.70(0.64)			
6.01	2.79(0.81)	5.24(1.5)	6.36(1.9)	4.86(1.41)	2.94(0.85)			

the breakdown of the FBA in the region $q^2 > 0.7$ a.u. as for $A\,^1\Pi(v'=2)$ mentioned above. The results by Kato *et al.* match fairly well the current IXS values only in very small momentum transfer squared region, i.e., $q^2 < 0.1$ a.u., and gradually diverge from one another in the large momentum transfer squared region of $q^2 > 0.2$ a.u. This shows that impact electron energies of 100 and 200 eV are still not high enough to meet the requirements of the FBA in the region of $0.13 < q^2 < 0.6$ a.u. It is apparent that except for the vibronic states $A\,^1\Pi(v'=1)$ where the theoretical results are in good agreement with the present ones, great deviations are observed between theoretical calculations and the present IXS results. Moreover, there exists the trend that discrepancies between the IXS results and theoretical calculations tend to increase with increasing momentum transfer and vibrational quantum number. The fact that the EELS results by Zhong *et al.* [20] are consistent with the present IXS ones as a crosscheck not only proves the reliability of the results but provides further solid evidence that the preceding calculations are inappropriate for the comprehensive description of ISFFs of all vibronic states over the whole momentum transfer region as well.

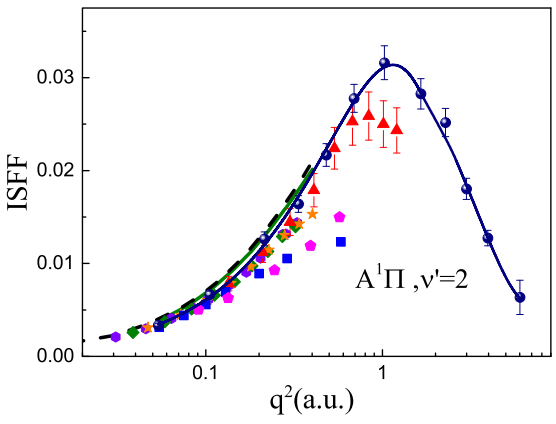

FIG. 2. (Color online) The ISFF for the excitation to $A\,^1\Pi(v'=2)$. The dots are the present IXS results. The EELS results are as follows: squares, 100 eV [14]; pentagons, 200 eV [14]; hexagons, 300 eV [19]; diamonds, 400 eV [19]; stars, 500 eV [19]; and triangles, 1500 eV [20]. The olive (gray) solid line and black dashed line are theoretical calculations by Chantranupong *et al.* [21] and Dillon *et al.* [23] respectively. The blue (gray) solid line is a fitted result to guide the eye.

The ISFFs for the excitation to $B\,^1\Sigma^+(v'=0)$ are presented in Fig. 4. It is notable that the experimental data reported by Lassettre *et al.* [19] at impact electron energies of 300, 400, and 500 eV show great deviations with respect to the present IXS ones. The experimental results by Zhong *et al.* [20], though in reasonable agreement with the present IXS values, taking experimental uncertainties into consideration, are generally lower in magnitude. Furthermore, there exists a distinct trend that the difference between the IXS and EELS values tends to decrease with increasing impact electron energy. This phenomenon indicates that incident electron energies of 300–500 eV are not high enough to approach the FBA, including impact electron energy as high as 1500 eV. The situation is strikingly different from the state $A\,^1\Pi(v'=2)$ where the FBA is already satisfied at impact electron energies of more than 300 eV in the region $q^2 < 0.3$ a.u. This may be due to the fact that the FBA depends on the electronic states, i.e., it is more difficult to satisfy the FBA for $B\,^1\Sigma^+$. It can be seen that the present experimental ISFFs deviate sharply from the theoretical calculations by Chantranupon *et al.* [21] and Dillon *et al.* [23], in the large momentum transfer region. Theoretical data by Rocha *et al.* [24] is lower in magnitude than the results of Zhong *et al.* [20] at small momentum transfer squared even taking experimental uncertainties into consideration, especially at $q^2 \approx 0$ where the calculated optical oscillator strength is lower than the EELS one by about 25% [20]. This makes us believe the theoretical results by Rocha *et al.* [24] may be generally lower in the whole region, and the good agreement between the theoretical data [24] and the EELS [20] in the large q^2 region may be fortuitous since the FBA is believed to be better satisfied in the small q^2 region.

IV. SUMMARY AND CONCLUSION

Based on the high-resolution IXS method, the state-resolved squared form factors of vibronic states $A\,^1\Pi(v'=0$–$6)$ and $B\,^1\Sigma^+(v'=0)$ of carbon monoxide were determined at an incident photon energy of about 10 keV and

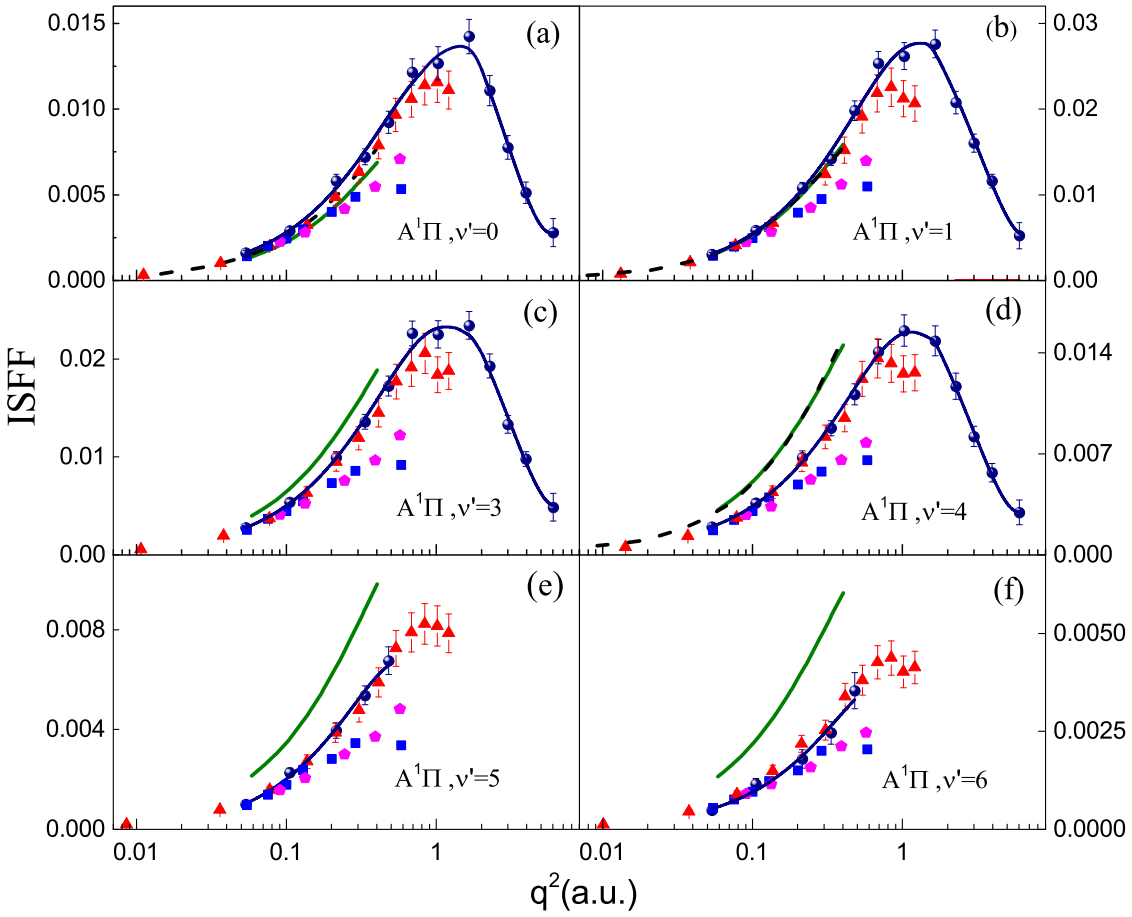

FIG. 3. (Color online) Same as for Fig. 2 but for $A\ ^1\Pi(v' = 0,1,3,4,5,6)$.

a target pressure of 9.6 atm. By comparing the present IXS results with preceding EELS results [13–20] and theoretical calculations [21–24], some meaningful conclusions can be reached. At the photon energy involved in the inelastic x-ray scattering experiment, the FBA is satisfied. The ISFFs of the valence-shell excitations of carbon monoxide measured by IXS thus can not only provide experimental benchmark data but also can serve as the high-energy limit for the electron impact method. The good agreement between the present IXS results and the EELS ones by Zhong *et al.* [20] for $A\ ^1\Pi(v' = 0–6)$ in the region $q^2 < 0.7$ a.u. indicates the adequacy of the FBA at an impact electron energy of 1500 eV for $A\ ^1\Pi(v' = 0–6)$ in this q^2 region, but the FBA is not applicable for the region $q^2 > 0.7$ a.u. where the present results are slightly higher in magnitude. For $B\ ^1\Sigma^+(v' = 0)$, the experimental data of Zhong *et al.* [20], though in reasonable agreement with the present IXS data, are generally lower in the whole momentum transfer squared region. This may be attributed to the inadequacy of the FBA even at an impact electron energy of 1500 eV. Finally, there exist large discrepancies between the present IXS results and theoretical calculations, suggesting that the formerly reported calculations are not accurate enough, and more comprehensive theoretical calculations are highly needed and recommended.

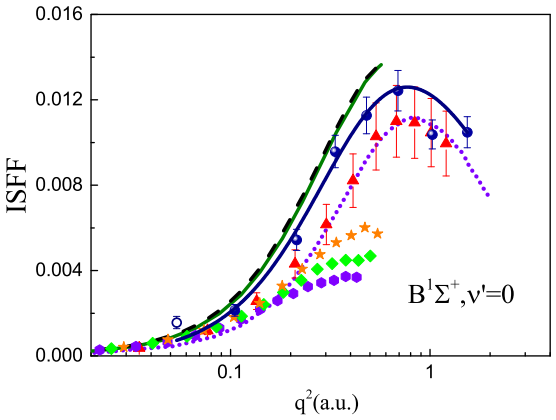

FIG. 4. (Color online) Same as Fig. 2 but for $B\ ^1\Sigma^+(v' = 0)$. The open circle point is less reliable due to the very lower counts for $B\ ^1\Sigma^+$ and higher background at the very small scattering angle of 5°. The violet (gray) short dots are the theoretical results by Rocha *et al.* [24].

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