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Selection rules for electric multipole transition of triatomic molecule in scattering experiments*

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In the electron or x-ray scattering experiment, the measured spectra at larger momentum transfer are dominated by the electric dipole-forbidden transitions, while the corresponding selection rules for triatomic molecules have not been clearly elucidated. In this work, based on the molecular point group, the selection rules for the electric multipolarities of the electronic transitions of triatomic molecules are derived and summarized into several tables with the variation of molecular geometry in the transition process being considered. Based on the summarized selection rules, the electron energy loss spectra of H_2O, CO_2, and N_2O are identified, and the momentum transfer dependence behaviors of their valence-shell excitations are explained.

Keywords: electric multipole transition, selection rule, molecular point group, electron scattering

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1. Introduction

As an usual experimental method differing from optical spectroscopy, scattering experiment is a powerful tool to explore the properties for the energy level structures and dynamic parameters of atoms and molecules,[1–6] in which the former can be identified by measuring the energy difference of the incident and scattered particles while the latter can be determined by measuring the intensity variation with the scattering angle. Although the energy resolution of the scattering experiment is generally lower than that of optical spectroscopic experiment, the scattering experiment has an unique advantage that the energy transfer and the momentum transfer are not a one-to-one correspondence, i.e., the momentum transfer of a definite excited state increases with the scattering angle increasing. Therefore, the scattering experiment can be used to reveal the electronic structures of the ground and excited states of atoms and molecules, i.e., the distribution information of the wave functions of the ground and excited states in the momentum space. Furthermore, unlike the optical spectroscopic experiment dominated by the electric dipole transitions, the scattering experiment can excite the dipole-forbidden transitions, such as electric monopole-, quadrupole-, and octapole-allowed ones at large momentum transfer. Low-energy electron scattering can even excite the spin-forbidden transitions. Loosening the restrictions of the electric dipole selection rule makes the scattering experiment an important experimental method for detecting the dipole-forbidden excitations of atoms and molecules. Therefore, in our previous work,[7] we analyzed and summarized the selection rules for electric multipole transitions of diatomic molecules in scattering experiments. This work extends the selection rules for diatomic molecules to those for the electric multipole transitions of triatomic molecules.

Nowadays the fast electron or x-ray scattering experiments cannot resolve the rotational states of triatomic molecules, so we do not consider the rotational transitions in this work. Furthermore, the selection rules for the vibrational transitions should be considered for the polyatomic molecules due to their multiple vibration modes, even for a dipole-allowed electronic transition. Another factor that needs to be considered is the variation of the molecular geometry in an electronic transition. For example, the ground state of water molecule is bent (belonging to C_{2v} point group), while its 2^1A_1 state near 9.7 eV may be linear (belonging to $D_{\infty h}$ point group).[8] In addition, some dipole-forbidden transitions under the Born–Oppenheimer (BO) approximation may be allowed under the first or higher order approximation when the vibronic coupling, i.e., the interaction between the electronic motion and the nuclear vibration, is taken into account. However, its density is often very weak.[9–11] In this work, we mainly study the selection rules for electric multipole transitions of triatomic molecules under the BO approximation.

2. Theoretical method

This work mainly studies the selection rules of the electric multipole transitions in the fast electron or x-ray scatter-

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ing experiments, in which the first-order Born approximation (FBA) is valid and the transition probability is proportional to the squared transition matrix:

$$\zeta(q,E_n) = \left|\int \Psi_{\rm f}^* \sum_{j=1}^{N} {\rm e}^{{\rm i}\boldsymbol{q}\cdot\boldsymbol{r}_j}\Psi_{\rm i}{\rm d}\tau\right|^2 = \left|\varepsilon(q;f,v',J',M'\leftarrow i,v,J,M)\right|^2, \quad (1)$$

where $\zeta(q,E_n)$ is the inelastic squared form factor, i.e., the square of the transition matrix $\varepsilon(q;f,v',J',M'\leftarrow i,v,J,M)$. $\boldsymbol{q}$ is the momentum transfer, and E_n is the energy loss of the incident particle which corresponds to the excitation energy of molecule. $\Psi_{\rm i}$ and $\Psi_{\rm f}$ are the total wave functions of the initial and final states of the molecule, respectively. $\sum_{j=1}^{N} {\rm e}^{{\rm i}\boldsymbol{q}\cdot\boldsymbol{r}_j}$ is the transition operator in the scattering process, and N is the number of electrons of the molecule. $\boldsymbol{r}_j$ is the position vector of the j-th electron, and ${\rm d}\tau$ represents the integration to the position vectors and spins of all electrons.

According to the BO approximation, the total wave function of a molecule can be written as:

$$\Psi = \psi_{\rm e}(\boldsymbol{r},\boldsymbol{Q})\psi_v(\boldsymbol{Q})\psi_{JM}(\Theta,\Phi). \quad (2)$$

Here $\psi_{\rm e}(\boldsymbol{r},\boldsymbol{Q})$, $\psi_v(\boldsymbol{Q})$, and $\psi_{JM}(\Theta,\Phi)$ are the electronic, vibrational, and rotational wave functions, respectively. $\boldsymbol{r}$ represents the set of all electronic coordinates whose coordinate system is fixed on the molecule, and $\boldsymbol{Q}$ is the normal coordinates. Θ and Φ describe the direction of the molecular rotation principal axis in the laboratory coordinate system.

Substituting Eq. (2) into Eq. (1) and neglecting the weak dependence of the transition matrix on the rotational quantum number j, the squared transition matrix can be written as:[1,7]

$$\zeta(q,E_n) = \frac{1}{4\pi}\iint \sin\Theta{\rm d}\Theta{\rm d}\Phi \times \left|\int \psi_{v'}^*(\boldsymbol{Q})\varepsilon_{\rm e}(\boldsymbol{q};\boldsymbol{Q},\Theta,\Phi)\psi_v(\boldsymbol{Q}){\rm d}\boldsymbol{Q}\right|^2, \quad (3)$$

where $\varepsilon_{\rm e}(\boldsymbol{q};\boldsymbol{Q},\Theta,\Phi)$ is the electronic transition matrix. $\psi_v(\boldsymbol{Q})$ and $\psi_{v'}(\boldsymbol{Q})$ are the initial and final vibrational wave functions, respectively. The integration to Θ and Φ means an average to the random orientation of the molecule.

In the formula (3), the electronic transition matrix $\varepsilon_{\rm e}(\boldsymbol{q};\boldsymbol{Q},\Theta,\Phi)$ has a form of[7]

$$\begin{aligned}&\varepsilon_{\rm e}(\boldsymbol{q};\boldsymbol{Q},\Theta,\Phi)\\ &= \sum_{l=0}^{\infty}(2l+1){\rm i}^l\sum_{m=-l}^{l}{\rm Y}_{lm}(\theta',\varphi')\\ &\times\int\psi_f^*(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N,\boldsymbol{Q})\sum_{j=1}^{N}{\rm j}_l(qr_j)\\ &\times{\rm Y}_{lm}(\theta_j,\varphi_j)\psi_i(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N,\boldsymbol{Q}){\rm d}\boldsymbol{r}_1{\rm d}\boldsymbol{r}_2\ldots{\rm d}\boldsymbol{r}_N. \quad (4)\end{aligned}$$

Herein (θ',φ') and (θ_j,φ_j) are the directions of $\boldsymbol{q}$ and $\boldsymbol{r}_j$ in the coordinate system fixed on the molecule and (θ',φ') can be written as a function of (Θ,Φ). In formula (4), the terms corresponding to $l=0,1,2$, and 3 are the electric monopole, dipole, quadrupole, and octupole transitions, respectively.

The electronic transition matrix $\varepsilon_{\rm e}(\boldsymbol{q};\boldsymbol{Q},\Theta,\Phi)$ is in general a more slowly varying function of $\boldsymbol{Q}$ than the vibrational wave functions.[1] So the $\boldsymbol{Q}$ in $\varepsilon_{\rm e}(\boldsymbol{q};\boldsymbol{Q},\Theta,\Phi)$ may be replaced by $\overline{\boldsymbol{Q}}$ which is the equilibrium nuclear position. Then the formula (3) can be written as:

$$\zeta(q,E_n) = \frac{1}{4\pi}\iint\sin\Theta{\rm d}\Theta{\rm d}\Phi \times\left|\varepsilon_{\rm e}(\boldsymbol{q};\overline{\boldsymbol{Q}},\Theta,\Phi)\int\psi_{v'}^*(\boldsymbol{Q})\psi_v(\boldsymbol{Q}){\rm d}\boldsymbol{Q}\right|^2, \quad (5)$$

according to the well-known Franck–Condon approximation. For a polyatomic molecule, only when both the electronic transition matrix $\varepsilon_{\rm e}(\boldsymbol{q};\overline{\boldsymbol{Q}},\Theta,\Phi)$ and the overlap integral of the vibrational wave functions $\int\psi_{v'}^*(\boldsymbol{Q})\psi_v(\boldsymbol{Q}){\rm d}\boldsymbol{Q}$ are not zero, can a vibronic transition take place.

According to the knowledge of molecular point group, if the direct product of the irreducible representations that the initial and final electronic states and the transition operator belong to contains the totally symmetric irreducible representation, the electronic transition matrix is not zero. The irreducible representations of the initial and final electronic states can be easily found in the character table of the corresponding point group according to the terms of initial and final states. If we write the spherical harmonic function as the real-spherical harmonic function, it is easy to find the irreducible representation that electric multipole transition operator corresponds to.[7,12] The direct product of the irreducible representation and the decomposition of reducible representation are described in detail in the textbook of quantum chemistry or molecular point group.[13] Then we can judge whether the electronic transition matrix is zero or not, which is similar to the procedure to judge the electronic multipolarity of a transition for diatomic molecule.[7]

The geometry of a polyatomic molecule may change in the transition process, so the ground and excited states may belong to different point groups. For example, the ground state of CO_2 is linear, while the excited state may be bent. The point group of the bent geometry is a subgroup of the point group of the linear geometry. In this case, in order to judge whether the transition is allowed or not, it is necessary to find the irreducible representation of the high symmetry in the low symmetry point group. And then we can use the above-mentioned method to judge the transition multipolarity. We will give examples about this case in the section of results and discussion.

Only when the electronic transition is allowed, it is meaningful to discuss the selection rules for the vibrational transitions. If the electronic transition is forbidden, there is no transition intensity naturally between any two vibronic states belonging to the different electronic states. Under the circumstance that the electronic transition is allowed, we can use the

selection rules for the vibrational transitions to judge whether the vibronic transition is allowed or not, and the corresponding selection rules for the vibrational transitions can be found in the textbook.[8]

3. Results and discussion

In this work, we study three kinds typical stable triatomic molecules with the geometries of: (i) a C_{2v} ground state and a C_{2v} or $D_{\infty h}$ excited state, such as SO_2, H_2O, H_2S, O_3 and NO_2; (ii) a $D_{\infty h}$ ground state and a C_{2v} or $D_{\infty h}$ excited state, such as CO_2 and CS_2; (iii) a $C_{\infty v}$ ground state and a $C_{\infty v}$ or C_s excited state, such as N_2O, HCN and OCS.

3.1. The triatomic molecule with a C_{2v} ground state and a C_{2v} or $D_{\infty h}$ excited state

For the molecule with both the ground state and excited state belonging to the C_{2v} point group, the corresponding selection rules for different electric multipolarities are listed in Table 1. The first column represents the initial states, and the first row represents the final states. Furthermore, the spin-exchange transition is forbidden for the fast electron and x-ray scattering experiment throughout this paper.

Table 1. Transition selection rules of the molecule belonging to the C_{2v} point group. The selection rules for the electric monopole, dipole, quadrupole and octupole transitions are shown from left to right. X denotes that the transition is allowed while O represents the transition is forbidden.

C_{2v}	A_1	A_2	B_1	B_2
A_1	X|X|X|X	O|O|X|X	O|X|X|X	O|X|X|X
A_2		X|X|X|X	O|X|X|X	O|X|X|X
B_1			X|X|X|X	O|O|X|X
B_2				X|X|X|X

H_2O is a typical molecule belonging to C_{2v} point group, whose electronic configuration of the ground state is

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2,$$

and the corresponding electronic term is $\widetilde{X}^1A_1$. According to Table 1, the excitation to $^1A_2$ from the ground state $\widetilde{X}^1A_1$ is electric dipole-forbidden. The other states are electric dipole-allowed. Figure 1 shows the electron energy loss spectrum of H_2O measured by Chan *et al.* at an incident electron energy of 3000 eV and a scattering angle of 0°[14] with the excitations assigned according to the suggestions of Itikawa and Mason.[15] In the energy loss region of 6 eV–10.2 eV, the squared momentum transfer is very small, i.e., $q^2 < 0.01$ a.u. (The unit a.u. is the abbreviation for atomic unit), which satisfies the optical approximation. Therefore, according to the transition selection rules listed in Table 1, only the dipole-allowed transitions shown as red terms in Fig. 1 can appear in the spectrum at the scattering angle of 0°, and the contribution from the dipole-forbidden transition of $1^1A_2 \leftarrow \widetilde{X}^1A_1$ can be negligible. Furthermore, the triplet excitations are not observed due to the spin-exchange nature as mentioned above. The theoretical predications are in agreement with the experimental observations.

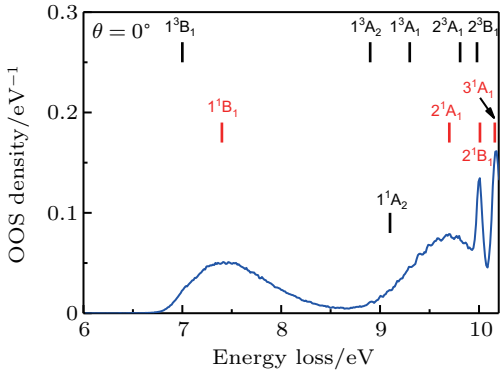


Fig. 1. (color online) The electron energy loss spectrum of H_2O measured by Chan *et al.*[14] at an incident electron energy of 3000 eV and a scattering angles of 0°.

The $1^1A_2 \leftarrow \widetilde{X}^1A_1$ transition of H_2O is electric monopole and dipole forbidden, while electric quadrupole and octupole allowed, which can be observed in the electron energy loss spectrum at a large momentum transfer. Unfortunately, up to now, there are no fast electron energy loss spectra at non-zero scattering angle of H_2O reported to the best of our knowledge. In the low-energy electron scattering experiment of H_2O,[16] there are signs of the existence of the $1^1A_2 \leftarrow \widetilde{X}^1A_1$ transition although it is contaminated by the nearby spin-forbidden transitions. The 2^1A_1 state near 9.7 eV may be linear[8] with a $D_{\infty h}$ symmetry. We should still take the C_{2v} point group to judge its transition multipolarities, and it is allowed. The reduction of the irreducible representations of the $D_{\infty h}$ point group to the C_{2v} is listed in Table 2.

Table 2. The irreducible representations of the $D_{\infty h}$ point group and its reduction to those of the C_{2v} subgroup.

$D_{\infty h}$	Σ_g^+	Σ_g^-	Σ_u^+	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u
C_{2v}	A_1	B_1	B_2	A_2	A_2, B_2	A_1, B_1	A_1, B_1	A_2, B_2

In short, for the triatomic molecule with C_{2v} symmetry, the selection rules for the electric multipole transitions are listed in Table 1. In the case of the excited state with a linear geometry $D_{\infty h}$, the electric multipolarities can be judged by reducing the irreducible representation of the $D_{\infty h}$ to those of the C_{2v} according to Table 2. Then the transition multipolarities of the valence-shell excitations of H_2O have been elucidated.

3.2. The triatomic molecule with a $D_{\infty h}$ ground state and a C_{2v} or $D_{\infty h}$ excited state

For the linear triatomic molecule with a $D_{\infty h}$ ground state, if its excited state is also linear, it follows the selection rules for the electric multipole transition of the $D_{\infty h}$ point group which is listed in Ref. [7]. If its excited state is bent, it follows the selection rules for the electric multipole transition of the C_{2v} point group as shown in Table 1 by reducing the irreducible

representations of the $D_{\infty h}$ to the ones of the C_{2v} as shown in Table 2.

CO_2 is a typical molecule with a $D_{\infty h}$ ground state, while its excited states may belong to the C_{2v} or $D_{\infty h}$ point group. The electron configuration of ground state of CO_2 is

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(3\sigma_g)^2(2\sigma_u)^2(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4,$$

and the corresponding electronic term is $X^1\Sigma_g^+$.

Figure 2 shows the electron energy loss spectra of CO_2 measured at an incident electron energy of 1500 eV and the scattering angles of 1.5° and 6.5°.[17] The excitations are assigned according to Ref. [10], and the terms in red are the experimentally observed transitions. In the energy loss region of 7.5 eV–10.5 eV, there are three electronic states, i.e., $^1\Delta_u$, $^1\Sigma_u^-$, and $^1\Pi_g$, and all of them are electric dipole-forbidden in the linear geometry. $^1\Pi_g \leftarrow X^1\Sigma_g^+$ is an electric monopole, dipole and octupole forbidden, but electric quadrupole allowed transition. $^1\Delta_u \leftarrow X^1\Sigma_g^+$ is an electric monopole, dipole and quadrupole forbidden, but electric octupole allowed transition. $^1\Sigma_u^- \leftarrow X^1\Sigma_g^+$ is forbidden for all the electric multipolarities. The momentum transfer at a scattering angle of 1.5° is small, so the intensity of the broad peak of the $^1\Pi_g$ and $^1\Delta_u$ transitions in 7.5 eV–10.5 eV is very weak. The relative intensity of this peak at 6.5° becomes larger due to the large momentum transfer, which is the typical behavior of the dipole-forbidden transition.

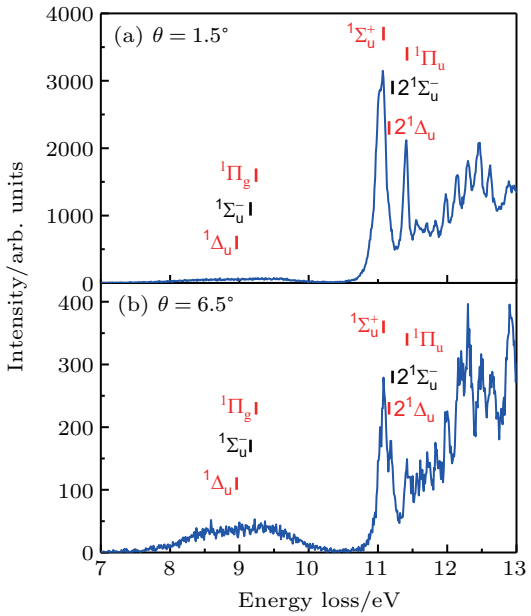


Fig. 2. (color online) The electron energy loss spectra of CO_2 measured at an incident electron energy of 1500 eV and the scattering angles of 1.5° and 6.5°, respectively. The corresponding squared momentum transfers at 1.5° and 6.5° are 0.077 a.u. (the unit a.u. is short for atomic unit) and 1.41 a.u., respectively.

Hertzberg has clearly pointed out that the $^1\Delta_u$ state in 7.5 eV–10.5 eV is bent with a bond angle of $122° \pm 2°$,[8] which is B_2 in the C_{2v} point group, so it is dipole-allowed considering that the ground state of $^1\Sigma_g^+$ in $D_{\infty h}$ is reduced into $^1A_1$ in C_{2v}. This is the reason that the feature in the 7.5 eV–10.5 eV still has a weak intensity in the photoabsorption spectra[18,19] and electron energy loss spectrum at the optical approximation.[20] In the electron or x-ray scattering experiment, the generalized oscillator strength for a typical dipole-allowed transition decreases as the momentum transfer increases. In the recent experiments,[10,17] the generalized oscillator strength of this feature has the behavior that it first increases and then decreases with the momentum transfer increasing. The calculation of Watanabe *et al.*[10] considering the change of molecular geometry agrees well with the experimental results. Similar behavior is revealed for the $^1\Pi_g$ state in 7.5 eV–10.5 eV.[10]

The energy level structures of the excited states of polyatomic molecules are very complicated. In the energy region of 7.5 eV ~ 10.5 eV for CO_2, it is generally accepted that there are three electronic states of $^1\Delta_u$, $^1\Sigma_u^-$, and $^1\Pi_g$ as mentioned above. The calculation by Watanabe *et al.* mark the electronic states at 8.93 eV as the $^1\Pi_g$ and the electronic state near 9.32 eV as the $^1\Delta_u$.[10] However, the assignments are reverse in Ref. [20], which is accord with the Hertzberg's classical textbook.[8] Generally, the intensity of the electric quadrupole transition is stronger than that of the electric octupole transition at small momentum transfer. By analyzing our high-resolution experimental spectra,[17] it is found that at small momentum transfer the intensity of the lower state is weaker than that of the higher state. Therefore, we think that the lower state is the electric octupole-allowed transition of the $^1\Delta_u$, and the higher state is the electric quadrupole-allowed transition of the $^1\Pi_g$. It should be mentioned that the contribution of the $^1\Sigma_u^-$ is small even considering its geometry variation, which is pointed out by Watanabe *et al.*[10]

There are three states of the $^1\Sigma_u^+$, $2^1\Delta_u$, and $2^1\Sigma_u^-$ around 11 eV. It is noted that both in the scattering spectra at 1.5° and 6.5°, the strongest transition is the dipole-allowed transition $^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$. Similarly, the transition of $2^1\Sigma_u^- \leftarrow X^1\Sigma_g^+$ is forbidden for all the electric multipolarities in the linear geometry, so its contribution is negligible small in the electron energy loss spectra at both small and large scattering angles.[10] The transition of $2^1\Delta_u \leftarrow X^1\Sigma_g^+$ is electric monopole-, dipole-, and quadrupole-forbidden, but it is electric octupole-allowed. Therefore, the small peak on the right shoulder of the $^1\Sigma_u^+$ near 11 eV in the spectrum at 6.5° is its contribution, and it is absent in the spectrum at 0°.

In this subsection,using the CO_2 as an example, we analyze the transitions for the triatomic molecule with a $D_{\infty h}$ ground state and a C_{2v} or $D_{\infty h}$ excited state. And the the valence-shell excitations of CO_2 are elucidated.

3.3. The triatomic molecule with a $C_{\infty v}$ ground state and a $C_{\infty v}$ or C_s excited state

For a triatomic molecule with a $C_{\infty v}$ ground state, if its excited state is also linear, it follows the selection rules of the $C_{\infty v}$ point group to judge its electric multipolarities as shown

in Ref. [7]. If the excited state is bent, it follows the selection rules of the electric multipole transition of the C_s point group, as listed in Table 3. Similarly, we should reduce the irreducible representations of the $C_{\infty v}$ into the ones of the subgroup C_s, as shown in Table 4. It can be seen from Table 3 that for a molecule belonging to C_s point group, the transition between any two electronic states is electric dipole-allowed.

Table 3. Same as Table 1 but for the molecule belonging to C_s point group.

C_s	A′	A″
A′	X|X|X|X	O|X|X|X
A″		X|X|X|X

Table 4. The irreducible representations of the $C_{\infty v}$ point group and its reduction to those of the C_s subgroup.

$C_{\infty v}$	Σ^+	Σ^-	Δ	Π
C_s	A′	A″	A′, A″	A′, A″

N_2O is a typical molecule with a $C_{\infty v}$ ground state, and its excited states may belong to the $C_{\infty v}$ or C_s point group. Its electron configuration of ground state is

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^4,$$

and the corresponding electronic term is $X^1\Sigma^+$.

Figure 3 shows the electron energy loss spectra of N_2O measured at an incident electron energy of 2500 eV and the scattering angles of 0° and 6.5°.[2] The excitations are assigned according to Ref. [11], and the terms marked in red are the experimentally observed transitions. Herein the transition of $B^1\Delta \leftarrow X^1\Sigma^+$ is electric monopole- and dipole-forbidden, but electric quadrupole- and octupole-allowed. Therefore, it is hard to be observed in the spectrum at 0°. In the spectrum at 6°, the peak in the energy region of 6 eV–8 eV is its contribution. Similar to the $^1\Delta_u$ of CO_2, the $B^1\Delta \leftarrow X^1\Sigma^+$ of N_2O has also been observed in the photoabsorption spectrum[21,22] due to the bend geometry, although it is almost invisible in Fig. 3(a). Furthermore, its generalized oscillator strength also shows the typical behavior of a dipole-forbidden transition.[2,11] According to the calculation of Watanabe *et al.*, the vibronic coupling is important for the $B^1\Delta \leftarrow X^1\Sigma^+$.[11] The transition of $1^1\Sigma^- \leftarrow X^1\Sigma^+$ is forbidden for all the electric multipolarities, so its contribution is negligibly small both at 0° and 6°,[11] which is similar to the $^1\Sigma_u^- \leftarrow X^1\Sigma_g^+$ of CO_2. The transitions of $C^1\Pi \leftarrow X^1\Sigma^+$ and $D^1\Sigma^+ \leftarrow X^1\Sigma^+$ are dipole-allowed, so they dominate the spectra at both 0° and 6°.

There are three electronic states around 10.5 eV, i.e., $2^1\Delta$, $2^1\Sigma^-$, and $2^1\Pi$. Similarly, the transition of $2^1\Sigma^- \leftarrow X^1\Sigma^+$ is forbidden for all the electric multipolarities, and it is negligible in the measured spectra. The transition of $2^1\Pi \leftarrow X^1\Sigma^+$ is electric dipole-allowed, while the $2^1\Delta \leftarrow X^1\Sigma^+$ is electric quadrupole- and octupole-allowed. Therefore, the peak at 10.5 eV at 0° mainly contains the contribution of the $2^1\Pi \leftarrow X^1\Sigma^+$, while the broadening of this peak at 6.5° is due to the considerable contribution of the $2^1\Delta \leftarrow X^1\Sigma^+$.

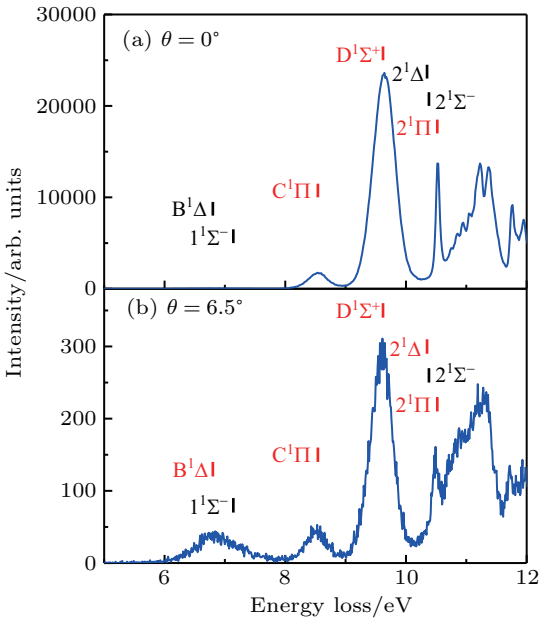


Fig. 3. (color online) The electron energy loss spectra of N_2O measured at an incident electron energy of 2500 eV and the scattering angles of 0° and 6.5°, respectively. The corresponding squared momentum transfers at 0° and 6.5° are < 0.01 a.u. and 2.36 a.u., respectively.

In a word, the selection rules for the triatomic molecule with a $C_{\infty v}$ ground state and a $C_{\infty v}$ or C_s excited state such as N_2O are summarized in Table 3. And the transition multipolarities of the valence-shell excitations of N_2O are elucidated.

4. Conclusion

In this work, we derive and summarize the selection rules for the electric multipolarities of the electronic transitions of triatomic molecule in scattering experiments based on the knowledge of molecular point group, which are listed in Tables 1 and 3. The influence of the molecular geometry variation in the transition process to the electric multipolarities has been considered. The electron energy loss spectra at small and large momentum transfer for the typical bend molecule of H_2O (C_{2v}) and linear molecules of CO_2 ($D_{\infty h}$) and N_2O ($C_{\infty v}$) are elucidated based on the presently obtained selection rules. The weak intensities for the dipole-forbidden transitions of $^1\Delta_u$ and $^1\Pi_g$ of CO_2 and the $B^1\Delta$ of N_2O in the photoabsorption spectra are due to the molecular geometry variation, and they show the typical momentum transition dependence behavior of a dipole-forbidden transition.

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