Retrieval of Interatomic Separation from High-Order Harmonic Spectra Using the Electron Interference Effect

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A new method of extracting interatomic separation of CO2 is proposed based on using the dipole moment extracted from high-order harmonic generation (HHG) spectra. For this method, we show that the Bragg’s equations related to the electron interference effect can be obtained from the zero-points of the dipole moment. Using not only HHG with parallel polarization but also HHG with perpendicular one we discover an error-compensation effect which means that the errors of interatomic separation extracted from the two components of dipole moment are always opposite in the sign. Therefore, the final result of the interatomic separation obtained by the proposed method has a very high accuracy with the systematic error less than 1%. [doi:10.2320/matertrans.MA201504]

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1. Introduction

High-order harmonic generation (HHG) has become a powerful tool to observe molecular dynamics for the last decade1-3 since the publication in Nature,4 in which the highest occupied molecular orbital (HOMO) of N2 is claimed to be retrieved from HHG spectra by the tomography method using ultra-short intense laser pulses with duration of 30 fs. Today, the use of different physical effects appearing in HHG to extract molecular structural information is of great interest.

In the present work, we study the electron interference effect5-7 in the HHG spectra of CO2 and analyze the possibility of using this effect to extract interatomic separation. The simulation method is applied to our investigation. The HHG spectra of CO2 are calculated using the three-step model of Lewenstein8 and are used as ‘experimental’ data for analysis. First, we show how to use the Bragg’s equations obtained from the minima of HHG intensity to retrieve the distance O–O and calculate their systematic errors. Then, we propose a new method based on the use of the dipole moment which can be extracted from HHG spectra. We will report the main result – the error-compensation effect which leads to a highly accurate distance obtained by this method.

2. Theoretical Basis and Calculation Method

2.1 Calculation of high-order harmonic generation

We apply the Lewenstein model to calculation of HHG spectra from CO2 in gas phase exposed to the ultrashort laser pulses of wavelength 1300 nm, intense of $2 \times 10^{14}$ W/cm$^2$, and duration of 30 fs. According to the model, the high-order harmonics are emitted through three steps. First, the HOMO electrons are ionized to the continuum region of energy by tunneling. Second, ionized electrons are accelerated by the electric field of laser and gain energy. In the final step, when the polarization direction of the field is reversed, electrons are driven back to recombine with the parent molecular ions.

![Image of HHG spectra](Fig. 1 HHG spectra with parallel polarization (with respect to the laser polarization direction) (a) and with perpendicular polarization (b) from CO2 aligned at two different angles 10° and 30°. A laser wavelength of 1300 nm, intensity peak of $2 \times 10^{14}$ W/cm$^2$, and duration of 30 fs. The minima of HHG intensity are clearly identified.)

The high-order harmonics are emitted at the moment of recombination. This three-step model provides an analytical method for calculation of HHG. Some formulae to calculate HHG intensity can be found in the original work9 and in our previous publications.9,10

Figure 1 shows the HHG spectra of CO2 for two different alignment angles as an example. For our analysis in the present work, we calculated HHG spectra for all alignment angles from 0° to 90° with the step $\Delta \theta = 5°$. All calculations are well compared with the other works.11,12

2.2 Electron interference effect

In Fig. 1 the minima of HHG intensity are clearly identified. Lein discovered these minima for $H_2^+$ in 20029 and has explained by the electron interference effect. We will provide here some formulae for later use. 

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The energy of emitted photon \( \omega = N \omega_0 \), where \( N \) is harmonics order and \( \omega_0 \) is the laser frequency, is kinetic energy electron gained through the acceleration process in laser field. Therefore, we have the equation for kinetic energy of electron \( E_e = N \omega_0 - I_p \), where \( I_p \) is the ionization potential of CO\(_2\): \( I_p = 13.78 \) eV. The wavelength of the electron emitting the photon with harmonics order \( N \) then is calculated as:

\[
\lambda = \frac{2\pi}{\sqrt{2(N \omega_0 - I_p)}}. \tag{1}
\]

We calculate the wavelength of the electron at the harmonics orders where the HHG intensity is minimum. Calculations are performed for different alignment angles and the results are shown in Fig. 2(a) for HHG with the parallel polarization and in Fig. 2(b) for HHG with the perpendicular one. In Fig. 2 we also plot the Bragg’s lines:

\[
R \cos \theta = (2n + 1)\lambda/2 \quad (a); \quad R \cos \theta = n\lambda \quad (b) \tag{2}
\]

for the case \( n = 1 \) where the input O–O distance is \( R = 4.41 \) a.u. The alignment angle \( \theta \) is the angle between the molecular axis and the polarization direction of laser (the main moving direction of electrons); hence, eqs. (2) are typical for the interference of electron waves.

That the points in Fig. 2 are much closed to the Bragg’s lines means the physics of the HHG intensity minima is related to the electron interference effect. For our case, while using laser with the wavelength 1300 nm, only the first minima corresponding to the case of \( n = 1 \) are detected. Supposing that the Bragg’s eqs. (2) are correct, we can calculate interatomic separations with the data from the HHG intensity at minima as follows:

\[
R^*_p = \frac{3\lambda}{2 \cos \theta} \quad (a), \quad R^*_\perp = \frac{\lambda}{\cos \theta} \quad (b). \tag{3}
\]

Here, formula (3a) is for the HHG with parallel polarization while the formula (3b) is for the HHG with the perpendicular one.

### 2.3 Extracting dipole moment from HHG spectra

Instead of using formula (1), we can use another method to calculate the electron wavelength with different alignment angles. The new method is based on the use of the dipole moment of molecule which can be extracted from the HHG spectra by the method proposed in Ref. 4) (see also Refs. 9, 10) for more details) through the empirical formulation:

\[
|\mathbf{d}(\omega, \theta)| = N^{-1/2}(\theta)|\mathbf{d}_{\text{ref}}(\omega)|\sqrt{S(\omega, \theta)/S_{\text{ref}}(\omega)}. \tag{4}
\]

Here, \( \mathbf{d}(\omega, \theta), \mathbf{d}_{\text{ref}}(\omega) \) are the dipole moment of molecule CO\(_2\) and that of the reference atom, respectively; \( S(\omega, \theta), S_{\text{ref}}(\omega) \) are HHG intensity of CO\(_2\) and that of reference atom; \( N(\theta) \) is ionization rate of CO\(_2\). The dispersion relation \( k = \sqrt{2(\omega - I_p)} \) is applied and the reference atom is chosen to be Kr whose ionization potential (13.99 eV) is much closed to that of CO\(_2\). More details of the method for calculation of dipole moment from HHG spectra are reported.\(^9\)

The dipole moment of CO\(_2\) given\(^9\) is defined as \( \mathbf{d}(k, \theta) = |\psi(\mathbf{r})\rangle \langle \psi(\mathbf{r})| \) where \( |\psi(\mathbf{r})\rangle \) is the wave function of HOMO electron of CO\(_2\). The plane wave \( \exp(i\mathbf{k}.\mathbf{r}) \) is the approximate electron wave in the continuum region of energy. In the molecular frame, we have \( \mathbf{k} \cdot \mathbf{r} = kx \cos \theta + ky \sin \theta \), where \( \theta \) is the alignment angle; \( k \) is the electron wavenumber. Here, the molecular alignment is performed in such a way that the propagation direction of laser is perpendicular to the molecular plane. Thus, we have only two components of dipole moment such as \( d_x(k, \theta) \) and \( d_y(k, \theta) \).

For the molecule CO\(_2\), the HOMO electron wave function is in the form \( |\psi(\mathbf{r})\rangle = \varphi(\mathbf{r} - \mathbf{R}/2) - \varphi(\mathbf{r} + \mathbf{R}/2) \). The explicit form of this wave function constructed within the frame of LCAO theory can be found in Ref. 13). Here, for our calculations we need only the general form of the wave function. Substituting this general form in the formula of the dipole moment, we can prove that the two following equations

\[
d_x(k, \theta) = 0 \quad (a); \quad d_y(k, \theta) = 0 \quad (b) \tag{5}
\]

to lead to the Bragg’s eqs. (2) characterizing for the relation between the electron wavelength \( \lambda \) and the alignment angle (remember the relation \( \lambda = 2\pi/k \)). Thus, instead of using the minima of HHG intensity, we solve the eqs. (5) for each fixed alignment angle to obtain the electron wavelength \( \lambda \), and then extract the interatomic separation by the equations:

\[
R^*_p = \frac{3\lambda}{2 \cos \theta} \quad (a), \quad R^*_\perp = \frac{\lambda}{\cos \theta} \quad (b). \tag{3}
\]
Table 1 Interatomic separation O–O extracted from the minima of HHG intensity for different aligned angles. Input distance $R = 4.41$ a.u.; $R_x^*$ and $R_y^*$ are extracted interatomic separations from HHG of parallel polarization and of perpendicular polarization, respectively.

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$R_x^*$ (a.u.)</th>
<th>$R_y^*$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5°</td>
<td>4.64</td>
<td>4.12</td>
</tr>
<tr>
<td>10°</td>
<td>4.63</td>
<td>4.02</td>
</tr>
<tr>
<td>15°</td>
<td>4.61</td>
<td>3.80</td>
</tr>
<tr>
<td>20°</td>
<td>4.58</td>
<td>3.59</td>
</tr>
<tr>
<td>25°</td>
<td>4.65</td>
<td>3.38</td>
</tr>
<tr>
<td>30°</td>
<td>4.60</td>
<td>3.20</td>
</tr>
<tr>
<td>35°</td>
<td>4.62</td>
<td>3.10</td>
</tr>
<tr>
<td>40°</td>
<td>4.62</td>
<td>3.03</td>
</tr>
<tr>
<td>Average</td>
<td>4.62</td>
<td>3.53</td>
</tr>
<tr>
<td>Variance</td>
<td>0.02</td>
<td>0.39</td>
</tr>
<tr>
<td>Accuracy</td>
<td>4.8%</td>
<td>20.0%</td>
</tr>
</tbody>
</table>

with perpendicular polarization, the result is bad: $\tilde{R}_y = 3.53$ a.u. with the big variance $\sigma = 0.39$ a.u. and the big systematic error of nearly 20%.

Table 2 Interatomic separation O–O extracted from the zero-points of the dipole moment for different alignment angles. Input distance $R = 4.41$ a.u.; $R_x^*$ and $R_y^*$ are extracted interatomic separations from x-component and y-component of the dipole moment, respectively.

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$R_x^*$ (a.u.)</th>
<th>$R_y^*$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5°</td>
<td>4.76</td>
<td>4.07</td>
</tr>
<tr>
<td>10°</td>
<td>4.71</td>
<td>3.99</td>
</tr>
<tr>
<td>15°</td>
<td>4.72</td>
<td>4.04</td>
</tr>
<tr>
<td>20°</td>
<td>4.71</td>
<td>4.07</td>
</tr>
<tr>
<td>25°</td>
<td>4.68</td>
<td>4.08</td>
</tr>
<tr>
<td>30°</td>
<td>4.66</td>
<td>3.98</td>
</tr>
<tr>
<td>35°</td>
<td>4.60</td>
<td>3.71</td>
</tr>
<tr>
<td>40°</td>
<td>4.60</td>
<td>4.53</td>
</tr>
<tr>
<td>Average</td>
<td>4.68</td>
<td>4.06</td>
</tr>
<tr>
<td>Variance</td>
<td>0.05</td>
<td>0.21</td>
</tr>
<tr>
<td>Accuracy</td>
<td>6.1%</td>
<td>7.9%</td>
</tr>
</tbody>
</table>

$R_{dx}^* = \frac{3\lambda}{2 \cos \theta}$ (a); $R_{dy}^* = \frac{\lambda}{\cos \theta}$ (b). (6)

Figures 3(a), (b) show the points of the calculated $\lambda$ by eq. (5a) and by eq. (5b) respectively for different alignment angles. These points are much more closed to the Bragg’s lines than the points calculated by eq. (1) using the minima of HHG intensity (Fig. 2).

3. Results and Discussions

Table 1 shows the interatomic separation O–O extracted from the minima of HHG intensity using the Bragg’s equations for the alignment angles from 5° to 40° with an angle step $\Delta \theta = 5°$. For other angles, it does not exist minima of HHG intensity in the plateau region. Thus, there are only eight cases to calculate. From the HHG spectra with parallel polarization, we have the average distance $\bar{R}_y = 4.62$ a.u. with the standard variance $\sigma = 0.02$ a.u. This value has a systematic error about 4.8% in comparing with the input distance $R$. It is quite good result. However, for the HHG

4. Conclusion

The electron interference effect can be effectively applied to retrieval of interatomic separation of CO$_2$ with a systematic error less than 5%. The new method proposed in this
work bases on the use of zero-points of the dipole moment and gives a better result for extracted distance. For the both components of the dipole moment, the extracted distances have a systematic errors less than 8%. Moreover, that the errors are opposite in the sign, which is called an error-compensation effect, results in the average interatomic distance much closed to the input data with the systematic error less than 1%.

The error-compensation effect is very important and needed to be checked by ab initio calculations. The method proposed in the work can be applied to other molecules with two centers of emitting electrons.

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REFERENCES