INTRODUCTION

The coupling of charge and spin degrees of freedom (hereinafter called charge–spin coupling) sometimes creates characteristic physical properties in correlated electron materials. The colossal magnetoresistance caused by the double-exchange mechanism in perovskite manganites and the superconductivity originating from spin fluctuations in high-$T_c$ cuprates are typical examples (1). The charge-spin coupling is also considered to substantially affect the optical properties (1–3). The electronic structure of undoped cuprates is sometimes discussed using a single-band Hubbard model (4). The previous theoretical studies based on a single-band Hubbard model predicted that an electron and a hole or, equivalently, a doublon and a holon photogenerated on a background of antiferromagnetically interacting spins in a Mott insulator attract each other not only via the Coulomb interaction but also via charge-spin coupling, leading to the formation of an excitonic bound state (5, 6). In addition, femtosecond pump-probe spectroscopy revealed that photoexcited doublon-holon pairs decay on the subpicosecond time scale (7), and a rapid energy transfer to spin excitations or magnons is suggested to be a plausible mechanism for such an ultrafast decay dynamics of photogenerated charge carriers (8–14).

Figure 1 shows the schematics of the theoretically predicted spin-related excitonic effect in two-dimensional (2D) Mott insulators (5, 6); the ground state and an excited doublon-holon pair are illustrated in Fig. 1A and Fig. 1, B and C, respectively. In the case where the doublon and holon are apart from each other (Fig. 1B), the energy of a doublon-holon pair is expressed as $\Delta + 8J$. Here, $\Delta$ is the energy of the charge excitation, and $J$ is the antiferromagnetic exchange interaction. We define $8J$ as the increase of the energy in the spin sector from the ground state. In the case where a doublon and a holon are located at the neighboring sites, the increase of the energy is $\Delta + 7J$ (Fig. 1C). Thus, there should be a binding energy in the order of $J$ between a doublon and a holon due to the antiferromagnetic exchange interaction. This picture suggests the spin-related excitonic effect, which is very analogous to the attractive interaction of a Cooper pair in doped cuprates. Presently, however, the influence of charge-spin coupling on the excitonic effect in undoped 2D Mott insulators has not been demonstrated experimentally. In this study, we investigate the origin of the excitonic effect in undoped cuprates by using terahertz (THz) pulse-pump optical reflectivity probe spectroscopy on three typical compounds, Nd$_2$CuO$_4$, La$_2$CuO$_4$, and Sr$_2$CuO$_2$Cl$_2$, having different magnitudes of $J$ of 155, 133, and 125 meV, respectively (15, 16).

Figure 2A shows the crystal structures of three compounds (17–19). In La$_2$CuO$_4$, each CuO$_2$ plane is composed of CuO$_4$ tetrahedrons, while no apical oxygens exist in the CuO$_2$ planes of Nd$_2$CuO$_4$. In Sr$_2$CuO$_2$Cl$_2$, the apical oxygens of the CuO$_4$ tetrahedrons are replaced with chlorines. The 2D electron systems of these compounds consist of O 2p and Cu 3d orbitals. As shown in Fig. 2B, the Mott-Hubbard gap opens in the 3d band of Cu because of the large on-site Coulomb repulsion energy $U$. The Cu 3d band is located between the Cu 3d upper-Hubbard (UH) band and the lower-Hubbard (LH) band. Thus, the optical gap corresponds to the charge transfer (CT) transition from the O 2p valence band to the Cu 3d UH band. Figure 2C presents the imaginary part of the dielectric constant, $\varepsilon_2$ spectra with the electric fields of lights $E$ parallel to the $a$ axis ($E//a$) in the three compounds (see Results). The energies ($E_{CT}$) of the CT transitions (the peak energies of the $\varepsilon_2$ spectra) are ~1.6, ~2.2, and ~1.9 eV in Nd$_2$CuO$_4$, La$_2$CuO$_4$, and Sr$_2$CuO$_2$Cl$_2$, respectively.

Electroreflectance (ER), which measures the electric field–induced change of the optical reflectivity, is one of the most effective method to investigate these excitonic effects not only in usual semiconductors (20–22) but also in correlated electron materials (23, 24). Using this method, we can determine the energies of one-photon–forbidden even-parity states, which cannot be detected by linear optical spectroscopy. In low-dimensional semiconductors such as π-conjugated polymers and silicon polymers, the splitting energy $E_s$ between the lowest excitonic state with odd parity and the second-lowest excitonic state with even parity can sometimes be a measure of the exciton binding energy in the lowest excitonic state (21, 22) because the second-lowest excitonic state is close to the edge of the electron hole continuum. In a typical ER spectroscopy, optical reflectivity changes are measured by
placing two electrodes on both sides (edges) of a crystal (a film) and applying a quasi-static voltage between them. However, with this method, it is difficult to apply strong electric fields on undoped cuprates because they are good semiconductors. Note that a strong electric field generates a large current flow, which leads to the sample degradations. This makes it impossible to measure the reflectivity changes induced by the electric field. To overcome this problem, we use a nearly monochromatic THz pulse (25) as an external electric field, in which the duration of the electric field is only ~1 ps. Because of the short pulse duration, this method enables us to apply electric fields far stronger than 100 kV/cm with a negligible current flow. Using such a THz pulse, we can measure the electric field–induced reflectivity changes, which are equivalent to those obtained by the conventional ER spectroscopy.

We report the results of the ER spectroscopy measurement on 2D Mott insulators of three undoped cuprates, Nd$_2$CuO$_4$, La$_2$CuO$_4$, and Sr$_2$CuO$_2$Cl$_2$, using a THz pulse as an electric field source. We can consider an electric field–induced reflectivity change as a kind of third-order nonlinear optical responses and derive the spectrum of the third-order nonlinear susceptibility $\chi^{(3)}$ from the results. The analyses of the $\chi^{(3)}$ spectra reveal that the even-parity exciton is located at the energy lower than the odd-parity exciton and that the energy difference between them, which is a measure of the exciton binding energy of the former, increases with an increase of $J$. This trend is reproduced by the $t$-$J$–type model calculations, which provides an unambiguous evidence of spin-related excitonic effects. The agreement of the calculations with the experimental results supports the s-wave symmetry of the excitonic doublon-holon pair in contrast to the d-wave symmetry of a Cooper pair in doped cuprates.

**RESULTS**

**Transient reflectivity changes by a THz electric field in Nd$_2$CuO$_4$**

First, we show the results in Nd$_2$CuO$_4$. Figure 3A shows the schematic setup of the THz pulse-pump optical reflectivity probe measurement. The polarizations of the THz pump pulse and the optical probe pulse are parallel, and both of them are along the $a$ axis. Figure 3B shows a typical electric field waveform, $E_{THz}(t_d)$, of the THz pump pulses. The maximum of $|E_{THz}(t_d)|$ is ~400 kV/cm. The Fourier power spectrum of this pulse is shown by the red line in Fig. 3C. It has a central frequency of 0.8 THz and ranges up to 2.7 THz. The polarized absorption spectrum of a Nd$_2$CuO$_4$ single crystal in the THz region with $E//a$ is also shown by the blue line in the same figure. An absorption peak at ~4 THz is ascribed to an infrared-active phonon mode associated with the displacements of Cu and O ions in the CuO$_2$ plane against Nd and O ions in the Nd$_2$O$_2$ plane (26, 27). In the lower-frequency region below this absorption, no absorption exists. This result is consistent with the polarized reflectivity spectrum in the THz region.

![Diagram](image1.png)

**Fig. 1.** Attractive interaction between a doublon and a holon due to antiferromagnetic exchange interactions in half-filled 2D Mott insulators. (A) Ground state. (B) A pair of a doublon (D) and a holon (H) apart from each other. The energy increase of the spin sector is +8$J$. (C) A pair of a doublon and a holon located at two neighboring sites. The energy increase of the spin sector is +7$J$, which is smaller than that in (B).

**Fig. 2.** Crystal and electronic structures in undoped cuprates of Nd$_2$CuO$_4$, La$_2$CuO$_4$, and Sr$_2$CuO$_2$Cl$_2$. (A) Crystal structures. (B) Schematic electronic structure in CuO$_2$ planes. $U$ is the on-site Coulomb repulsion, and $E_{CT}$ is the energy of the CT transition (see main text). (C) Spectra of the imaginary part of the dielectric constant $\varepsilon_2$ obtained from the polarized reflectivity spectra along the $a$ axis.

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previously reported (26). Thus, we can consider that the THz pulse does not excite any phonons or electronic transitions in Nd$_2$CuO$_4$.

The reflectivity change $\Delta R(t_d)/R$ at 1.55 eV near the CT transition peak is shown by the open circles in the middle part of Fig. 3D. The reflectivity sharply decreases by the THz electric field around the time origin. The time characteristic of $\Delta R(t_d)/R$ shows exactly the same as that of $-[E_{THz}(t_d)]^2$ (the blue solid line). This relation $\Delta R(t_d)/R \propto |E_{THz}(t_d)|^2$ indicates that the observed response does not originate from a Zener tunneling (28) or a Franz-Keldysh effect (29, 30) but is caused by the third-order optical nonlinearity (31). At the lower (0.95 eV) and higher (1.70 eV) energies, $\Delta R(t)/R$ shows the similar instantaneous changes following $|E_{THz}(t_d)|^2$, although the $\Delta R(t)/R$ signals are positive.

In the ER spectroscopy using THz electric fields, the photon energy of the THz pulse (4 meV) was negligibly small compared with the optical gap. In the case that the intervals of the energy levels in the excited states are larger than ~4 meV, THz electric fields can be regarded as static electric fields (25). This condition applies to our case, as shown later. Thus, the observed nonlinear optical responses are expressed as follows

$$P^{(3)}(\omega) = 3\varepsilon_0 \chi^{(3)}(-\omega; 0, 0, \omega) E_{THz}(0) E_{THz}(0) E(\omega)$$

(1)

Here, $P^{(3)}(\omega)$ is the third-order nonlinear polarization. $E_{THz}(0)$ and $E(\omega)$ represent the electric fields of the THz pump pulse and the optical probe pulse, respectively. $\varepsilon_0$ and $\chi^{(3)}(-\omega; 0, 0, \omega)$ are the permittivity of vacuum and the third-order nonlinear susceptibility, respectively.

To obtain information about energy-level structures of the photoexcited state, we measured the probe energy dependence of $\Delta R(t_d)/R$ and plotted the values, $\Delta R(0)/R$, at the time origin, which are shown in Fig. 3E (open circles), together with the original reflectivity (R) spectrum. A characteristic plus-minus-plus structure is observed. Using the Kramers-Kronig (KK) transformation, we obtained the dielectric constant $\varepsilon = \varepsilon_1 + i\varepsilon_2$ and its change $\Delta \varepsilon = \Delta \varepsilon_1 + i\Delta \varepsilon_2$ from the $R$ and $\Delta R(0)/R$ spectra, respectively (see the Supplementary Materials). We also calculated the Im$\chi^{(3)}(-\omega; 0, 0, \omega)$ spectrum from the $\Delta \varepsilon_2$ spectrum using the relationship $\Delta \varepsilon_2 = 3|E_{THz}(0)|^2 \text{Im} \chi^{(3)}(-\omega; 0, 0, \omega)$. The obtained $\varepsilon_2$ and $\text{Im} \chi^{(3)}(-\omega; 0, 0, \omega)$ spectra are shown in Fig. 4A.

The $\text{Im} \chi^{(3)}(-\omega; 0, 0, \omega)$ spectrum also shows a plus-minus-plus structure around the CT transition peak. This spectrum cannot be reproduced by a simple narrowing or broadening of the original $\varepsilon_2$ spectrum (see the Supplementary Materials). $\text{Im} \chi^{(3)}(-\omega; 0, 0, \omega)$ or $\Delta \varepsilon_2$ spectra in 1D semiconductors previously obtained by conventional ER spectroscopy revealed that a one-photon–forbidden even-parity state |2) was located above a one-photon–allowed odd-parity state |1) and that the field-induced mixing of those two states caused a plus-minus-plus structure (20–22). In this case, the $\varepsilon_2$ and $\text{Im} \chi^{(3)}(-\omega; 0, 0, \omega)$ or $\Delta \varepsilon_2$ spectra can be analyzed using the three-level model, in which the ground state |0) and two excited states |1) and |2) are considered. In our study, we also adopt a similar three-level model.

Before the analyses of the $\text{Im} \chi^{(3)}(-\omega; 0, 0, \omega)$ spectra using the three-level model, it is necessary to analyze the original $\varepsilon_2$ spectrum. To express the dispersion of $\varepsilon_2$ originating from the odd-parity state, we adopt the following Lorentzian-type dielectric function

$$\varepsilon_2 = \frac{N e^2}{\hbar \epsilon_0} (0 | x | 1)^2 \text{Im} \left( \frac{1}{\omega_1 - \omega - i\gamma_1} + \frac{1}{\omega_1 + \omega + i\gamma_1} \right)$$

(2)

where $N$ is the density of Cu atoms, $e$ is the elementary charge, and $\hbar$ is the reduced Planck constant. $0 | x | 1$ represents the transition dipole moment between |0) and |1). $\omega_0$, $\omega_1$, and $\gamma_1$ are the energy and the damping constant of the state |1), respectively. We evaluated the magnitudes of $0 | x | 1$, $\omega_0$, and $\gamma_1$ by fitting Eq. 2 to the experimental $\varepsilon_2$ spectrum. The fitting curve (the red dashed line at the top of Fig. 4A) reproduced well the peak structure in the $\varepsilon_2$ spectrum.
The energy positions of the odd-parity and even-parity states are indicated by the dotted lines in Fig. 4A. The successful fitting suggests that the states $|1\rangle$ and $|2\rangle$ have discrete energy levels and are excitonic bound states or equivalently excitons consisting of a doublon-holon pair. The even-parity exciton is located at the lower energy than the odd-parity exciton.

As seen in Fig. 4A, the higher-energy part of the $e_2$ spectrum colored in green cannot be reproduced by the Lorentzian function (Eq. 2). From the spectral shape of this component, it is reasonable to consider that it corresponds to the continuum and that the odd-parity exciton responsible for the peak of the $e_2$ spectrum is located close to the band edge. Thus, the splitting $E_e = h\omega_1 - h\omega_2$ between the odd-parity and even-parity excitons can be a measure of the binding energy of a doublon-holon pair in the lowest even-parity exciton. The origin of the excitonic effect is elucidated in Discussion.

The values of the physical parameters evaluated from the analyses of the linear and nonlinear optical spectra, $h\omega_1$, $h\omega_2$, $h\gamma_1$, $h\gamma_2$, $\langle 0 \mid x \mid 1 \rangle$, and $\langle 1 \mid x \mid 2 \rangle$, the maximum values of $|\text{Im} \chi^{(3)}(-\omega_0, 0, \omega)|$, $\max |\text{Im} \chi^{(3)}(-\omega_0, 0, \omega)|$, and $E_e$ are listed in Table 1, together with the other important parameters, the exchange interaction $J$ and the Cu–O bond length $d_{\text{Cu-O}}$ in the 2D CuO plane.

**Transient reflectivity changes by a THz electric field in La$_2$CuO$_4$ and Sr$_2$CuO$_2$Cl$_2$**

To investigate how the nonlinear response to the THz electric field observed in Nd$_2$CuO$_4$ depends on physical parameters, such as the optical gap energy $E_{\text{CT}}$ ($h\omega_0$), the exchange interaction $J$, and the structure of the CuO planes, we performed similar studies in the other cuprate Mott insulators, La$_2$CuO$_4$ and Sr$_2$CuO$_2$Cl$_2$. The previous polarized reflectivity measurements in the THz region revealed that the lowest infrared-active phonons are located at 145 and 176 cm$^{-1}$ in La$_2$CuO$_4$ and Sr$_2$CuO$_2$Cl$_2$, respectively, and that no absorptions exist below 100 cm$^{-1}$ (27), so that the reflectivity changes generated by a THz pulse in these two compounds can be considered to be the nonlinear electronic responses to the THz electric field, similar to the case of Nd$_2$CuO$_4$.

In La$_2$CuO$_4$ and Sr$_2$CuO$_2$Cl$_2$, we measured the time evolutions of reflectivity changes, $\Delta R(t_d)/R$, by the THz pulse in almost the same experimental condition as in Nd$_2$CuO$_4$. The maximum electric field of the THz pulse is $\sim$400 kV/cm. The detected $\Delta R(t_d)/R$ signals follow the square of the THz electric field, $[E_{\text{THz}}(t_d)]^2$. The spectra of $\Delta R(0)/R$ show a plus-minus-plus structure similar to that of Nd$_2$CuO$_4$ in Fig. 3E. The data in La$_2$CuO$_4$ and Sr$_2$CuO$_2$Cl$_2$ are reported in the Supplementary Materials.

We performed the KK transformations of the $\Delta R(0)/R$ spectra and obtained the $\text{Im} \chi^{(3)}(-\omega_0, 0, \omega)$ spectra, which are shown in Fig. 4 (B and C), together with the $e_2$ spectra. The $\text{Im} \chi^{(3)}(-\omega_0, 0, \omega)$ spectra of Sr$_2$CuO$_2$Cl$_2$ and La$_2$CuO$_4$ also show a plus-minus-plus structure. We analyzed the $e_2$ and $\text{Im} \chi^{(3)}(-\omega_0, 0, \omega)$ spectra with the same procedures performed on those spectra of Nd$_2$CuO$_4$ mentioned in the previous subsection. The fitting curves (Eq. 2) of the lowest peak structures in the $e_2$ spectra are shown by the red dashed lines at the top of Fig. 4 (B and C). The peaks are attributable to the odd-parity excitons, and the deviations of the data from the fitting curves colored in green are also considered to correspond to the doublon-holon continuum. The $\text{Im} \chi^{(3)}(-\omega_0, 0, \omega)$ spectra are analyzed by the three-level model. The fitting curves are shown by the red dashed lines at the bottom of Fig. 4 (B and C), which almost reproduce the characteristic plus-minus-plus structures of $\text{Im} \chi^{(3)}(-\omega_0, 0, \omega)$. The parameter values evaluated from the analyses of the linear and nonlinear optical spectra in La$_2$CuO$_4$ and Sr$_2$CuO$_2$Cl$_2$ are also listed in Table 1, together with $J$ and $d_{\text{Cu-O}}$ values.
As seen in Fig. 4 (A to C), in all the three compounds, the energy of the even-parity exciton $|2\rangle$ was lower than that of the odd-parity exciton $|1\rangle$, i.e., $E_i = \hbar \omega_1 - \hbar \omega_2 > 0$. The even-parity excitons in 2D cuprate Mott insulators were previously studied by two-photon absorption spectroscopy (32, 33). However, the reported energy positions depend on the experimental conditions. In pump-probe absorption spectroscopy of Sr$_2$CuO$_2$Cl$_2$, the even-parity and odd-parity states are almost degenerate (32), whereas in Z-scan spectroscopy of Nd$_2$CuO$_4$, the even-parity state is located below the odd-parity state (33). The present study supports the latter result. In the 1D Mott insulators such as halogen-bridged nickel-chain compounds, the even-parity exciton is located at the higher energy than the odd-parity exciton ($\hbar \omega_1 - \hbar \omega_2 < 0$) (23). This feature is the same as that in the other 1D semiconductors such as $\pi$-conjugated polymers and silicon polymers. The feature of 1D Mott insulators is that the difference between the optical gap energy is ~1.3 eV (24), that is, the odd-parity and even-parity excitons are almost degenerate in 1D Mott insulators. This is related to the nature of spin-charge separation characteristic of 1D correlated electron systems; the charge sector is separated from the spin sector, and the wave functions of the odd-parity and even-parity excitons are almost the same with each other except for their phases (34).

Therefore, the lower-lying even-parity exciton demonstrated in the present study on the three undoped cuprates is considered to be characteristic of 2D Mott insulators (35). In Fig. 5A, we show the energy-level structure of 2D cuprate Mott insulators. The symmetry of the wave functions of two excitonic states is discussed again later.

**DISCUSSION**

First, we discuss the material dependence of the parameters obtained from the analyses of the linear and nonlinear optical spectra in the three-cuprate Mott insulators. To examine the trends of the physical parameters, we plot in Fig. 5 (B to D) the values of $|J, E_i(= \hbar \omega_1 - \hbar \omega_2)|$, max $|\text{Im}\chi^{(3)}(\omega; 0, 0, \omega)|$, $|0 \cdots x| 2\rangle$, and $|0 \cdots x| 2\rangle^2$ as a function of the lowest odd-parity exciton energy $\hbar \omega_1$. The parameters except for $0 \cdots x| 2\rangle^2$ seem to be closely correlated with each other.

According to the simple perturbation treatment, $|0 \cdots x| 1\rangle$ is proportional to $t_{pd}/E_{CT}$ (36), where $E_{CT} = \hbar \omega_1$ and $t_{pd}$ is the transfer energy between the O 2p and the Cu 3d orbitals. We can consider that $t_{pd}$ is dominated by $d_{Cu-O}$; $t_{pd}$ increases with the decrease of

| Table 1. Parameter values evaluated from the analyses of $\varepsilon_2$ and $\text{Im}\chi^{(3)}(-\omega; 0, 0, \omega)$ spectra and other important parameters in Nd$_2$CuO$_4$, Sr$_2$CuO$_2$Cl$_2$, and La$_2$CuO$_4$. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                  | $\hbar \omega_1$ (eV) | $\hbar \omega_2$ (eV) | $\varepsilon_2$ (eV) | $\varepsilon_2$ (eV) | $\Delta(=\hbar \omega_1 - \hbar \omega_2)$ (eV) | Max $|\text{Im}\chi^{(3)}(\omega; 0, 0, \omega)|$ (esu) | $E_i$ (eV) | $J$ (meV) |
| Nd$_2$CuO$_4$    | 1.57            | 1.34            | 0.182           | 0.196           | 0.465           | 3.03            | 2.0 $\times 10^{-10}$ | 0.23            | 155$^{14}$      | 1.973$^{17}$   |
| Sr$_2$CuO$_2$Cl$_2$ | 1.95   | 1.87            | 0.186           | 0.162           | 0.390           | 5.80            | 6.5 $\times 10^{-10}$ | 0.08            | 125$^{15}$      | 1.986$^{18}$   |
| La$_2$CuO$_4$    | 2.16            | 2.01            | 0.292           | 0.113           | 0.401           | 3.22            | 1.5 $\times 10^{-10}$ | 0.15            | 133$^{14}$      | 1.905$^{16}$   |

**Fig. 5.** Physical parameters associated with odd-parity and even-parity excitons dominating nonlinear optical responses in undoped cuprates. (A) Energy-level structures and schematic wave functions of excitons. (B to D) Physical parameters as a function of the odd-parity exciton energy $\hbar \omega_1$. (E) Exchange interaction $J$. (C) splitting between the odd-parity and even-parity excitons $E_i(= \hbar \omega_1 - \hbar \omega_2)$. (D) max $|\text{Im}\chi^{(3)}(\omega; 0, 0, \omega)|$, and the squares of the transition dipole moments $0 \cdots x| 1\rangle^2$ and $0 \cdots x| 2\rangle^2$. (E and F) Physical parameters as a function of $J$: $E_i(= \hbar \omega_1 - \hbar \omega_2)$. (G) Calculated values of $E_i$ as a function of $J$ with $J/t = 0.4$ for three cases: $V = 0$, $V = 1.5t$, and $V = 3t$. 

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The relatively large (0 | x | 1) in Na2CuO4 is ascribed to the small $\hbar \omega_0$ (Table 1). La2CuO4 has the largest $\hbar \omega_0$, but its (0 | x | 1) is slightly larger than that of Sr2CuO2Cl2. This is attributed to the relatively small $d_{\text{Cu-O}}$ (large $p_{pd}$) in La2CuO4. However, the difference in (0 | x | 1) in the three compounds is not so large (Table 1). The similar perturbation treatment gives a relation $J \propto (p_{pd}/E_{CT})^2$ (36). The subtle balance of $t_{pd}$ and $E_{CT}$ leads to the largest $J$ (155 meV) in Na2CuO4, the smallest $J$ (125 meV) in Sr2CuO2Cl2, and the intermediate $J$ (133 meV) in La2CuO4.

Among the three compounds, Sr2CuO2Cl2 has the largest max $|\text{Im}\chi^{(3)}(-\omega; 0, 0, 0)|$. The important factors that dominate the magnitude of $|\text{Im}\chi^{(3)}(-\omega; 0, 0, 0)|$ are the transition dipole moments, (0 | x | 1) and (1 | x | 2), because $|\text{Im}\chi^{(3)}(-\omega; 0, 0, 0)|$ is proportional to (0 | x | 1)$^2$(1 | x | 2)$^2$. Figure 5D shows that the relative magnitudes of max $|\text{Im}\chi^{(3)}(-\omega; 0, 0, 0)|$ are dominated by those of (1 | x | 2)$^2$; the largest max $|\text{Im}\chi^{(3)}(-\omega; 0, 0, 0)|$ in Sr2CuO2Cl2 is caused by the largest (1 | x | 2)$^2$, which is much larger than that in the other two compounds.

In Fig. 5 (C and D), (1 | x | 2)$^2$ seems also related to $E_z$ (1 | x | 2)$^2$ increases from Nd2CuO4 to Sr2CuO2Cl2 and then decreases to La2CuO4, while $E_z$ decreases and then increases, leading to the largest (1 | x | 2)$^2$ and the smallest $E_z$ in Sr2CuO2Cl2. Such an inverse correlation between (1 | x | 2)$^2$ and $E_z$ can be understood if one notices the fact that a small $E_z$ implies similar spatial extensions of the wave functions along the a axis in the states | 1 and | 2), which may lead to a large (1 | x | 2). $E_z$ in Fig. 5C does not depend systematically on the optical gap energy $\hbar \omega_0$ but shows a strong correlation with $J$ in Fig. 5B. By plotting $E_z$ (0 | x | 1)$^2$, (1 | x | 2)$^2$, and max $|\text{Im}\chi^{(3)}(-\omega; 0, 0, 0)|$ as a function of $J$ in Fig. 5 (E and F), we notice that $E_z$ is scaled by $J$ (1 | x | 2)$^2$ is also correlated with $J$.

In Results, we pointed out that the magnitude of $E_z$ can be a measure of the binding energy of the lowest even-parity exciton. The strong correlation between $E_z$ and $J$ makes us expect an important influence of the spin sector on the excitonic effect as we commented on in the introduction referring to Fig. 1. To demonstrate this scenario, we theoretically analyzed the photoexcited states in 2D Mott insulators, where a doublon and a holon are created by an optical pulse and where spins in the background interact with each other by the nearest neighbor exchange interaction $J$. The resulting Hamiltonian for the two particles resembles a t-J-type model with two-hole carriers. More precisely, the Hamiltonian contains the exchange interaction $J$ and hopping terms of the holon and doublon with the nearest neighbor amplitude $t$, the second-nearest neighbor amplitude $t'$, and the third-nearest neighbor amplitude $t''$, together with the nearest neighbor attractive Coulomb interaction (V) between the holon and the doublon (37). The parameters $t'$ and $t''$ are necessary to introduce the electron hole asymmetry.

The parameters are determined as follows. In the cuprates, it is known that $|J/t|$ is almost equal to 0.4 in common (38–40). Therefore, we set $|J/t| = 0.4$. For $t'$ and $t''$, we use typical relations in the cuprates, $t'/t = -0.25$ and $t''/t = 0.12$, respectively (41). Because we want to know the influence of the spin sector on the excitonic effect, we use $J$ as a parameter to control the sector. To clarify the effect of $V$ on the excitonic effect, we investigated $E_z$ for the three cases, $V/t = 0, 1.5$, and 3. By numerically diagonalizing the Hamiltonian for a $\sqrt{20} \times \sqrt{20}$ periodic lattice, we obtain lowest-energy even-parity and odd-parity eigenstates. We find that the eigenenergy of the even-parity state is lower than that of the odd-parity state. The odd-parity (even-parity) eigenstate exhibits the lowest-energy excitonic peak under the one-photon–allowed (two-photon–allowed) excitation (6). Therefore, the eigenenergy of the even-parity state corresponds to $\hbar \omega_0$, whereas that of the odd-parity state corresponds to $\hbar \omega_2$, which is qualitatively consistent with the experimental results (Fig. 5E). This suggests that the attractive force between doublons and holons would be related to the energy change of the spin sector. With the increase of $V$, both $\hbar \omega_0$ and $\hbar \omega_2$ are expected to decrease, while $E_z$ does not depend on $V$ so much (Fig. 5G). This suggests that $J$ increases the stability of the even-parity exciton relative to the odd-parity exciton corresponding to an absorption peak that is close to the edge of the doublon-holon continuum. To reproduce the experimental results more quantitatively, an advanced theoretical analysis, e.g., dynamical mean field theory calculation, will be necessary. Such a study is an important subject in the future.

Encouraged by the possible description of the observed excitonic effects using the t-J-type model with doublon and holon, we discuss the symmetry of the lowest even-parity exciton and the second-lowest odd-parity exciton obtained by the same model. The odd-parity exciton should have a p-wave symmetry (Fig. 5A). The theoretical study also indicates that the lowest even-parity exciton has an s-wave symmetry (Fig. 5A) (6). This disagrees with the d-wave symmetry of a Cooper pair in doped cuprates (42). A Cooper pair is formed by two holons, whereas an exciton is formed by a doublon and a holon. The doublon has a negative charge, in contrast to the positively charged holon. This charge difference induces an additional sign for the nearest neighbor hopping of a doublon. The sign affects the phase of the pair wave function, leading to s-wave symmetry for a pair of a doublon and a holon in contrast to the d-wave symmetry for two holons.

In summary, we evaluated the $\chi^{(3)}(-\omega; 0, 0, 0)$ spectra for the 2D Mott insulators of undoped cuprates by the ER spectroscopy using THz electric field pulses. Analysis with a three-level model indicated that the even-parity exciton is located below the odd-parity exciton and that their energy difference, which is a measure of the excitonic effect, increases with increase of the antiiferromagnetic exchange interaction $J$. This trend was reproduced by the t-J-type model calculations. Our results demonstrate that a doublon and a holon in a 2D Mott insulator attract each other via the antiiferromagnetic exchange interaction. As reported here, nonlinear optical spectroscopy using a strong THz pulse is a powerful tool to investigate the hidden nature in electronic structures and photoexcited states. We expect that it can be applied not only to correlated electron systems but also to the other various kinds of complex electron materials.

**MATERIALS AND METHODS**

**Sample preparation**

In the present study, we used single crystals of Nd2CuO4, La2CuO4, and Sr2CuO2Cl2, which were grown by the methods previously reported in (43), (44), and (19), respectively. The crystal structures of Nd2CuO4 and Sr2CuO2Cl2 are tetragonal, and their $a$ and $b$ axes are parallel to the Cu–O bonds in the CuO2 planes. On the other hand, the crystal structure of La2CuO4 is orthorhombic in the strict sense (17). Here, the axes of La2CuO4 are taken in the same manner as Nd2CuO4 and Sr2CuO2Cl2, i.e., $a$ and $b$ axes are parallel to the Cu–O bonds in the CuO2 plane as shown in Fig. 2A.

**THz time-domain spectroscopy**

To measure the absorption spectrum of Nd2CuO4 shown in Fig. 3C, we used a THz time-domain spectroscopy (THz-TDS). The thickness
the THz pulses by an electro-optical (EO) sampling. We measured the strength. All the measurements were performed at 294 K. To avoid controlled by changing the path length of the probe pulse. The time induced THz radiation (Terashige et al. 2012). The other was used for the detection of each transmitted THz pulse, \( I_{\text{sample}}(\omega) \) and \( I_{\text{ref}}(\omega) \), was obtained. Using these spectra, we simply calculated the optical density (OD) spectrum by OD = \( -\log(I_{\text{sample}}(\omega)/I_{\text{ref}}(\omega)) \).

**THz pulse-pump optical reflectivity probe spectroscopy**

As the light source of the pump and probe pulses, we used a Titanium:sapphire RA with a pulse duration of 90 fs, a central photon energy of 1.56 eV, a repetition rate of 1 kHz, and an output power of 4.5 W. The output of the RA was divided into two beams. One was used to generate THz pulses via the optical rectification in a LiNbO\(_3\) crystal. To generate intense THz pulses, we used a pulse front–tilting method (46). The THz pump pulses were focused on the sample by parabolic mirrors. To measure the electric field waveforms, we used a ZnTe crystal instead of a sample and applied an EO sampling method. Detailed procedures for creating and detecting THz pulses are reported elsewhere (25). The other output from the RA was used to excite an optical parametric amplifier from which light pulses with 0.4 to 2.8 eV having a temporal width of 90 fs were obtained. The delay time \( \tau_d \) of the probe pulse relative to the pump pulse was controlled by changing the path length of the probe pulse. The time origin was defined at the position of the maximum THZ electric field. All the measurements were performed at 294 K. To avoid sample degradation, we performed the measurements of \( \text{Sr}_2\text{CuO}_2\text{Cl}_2 \) in vacuum.
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Acknowledgments

Funding: This work was partly supported by a Grant-in-Aid (KAKENHI: project number JP25247049) from the Ministry of Education, Science, Culture, and Sports of Japan and by CREST (grant number JPMJCR1661), Japan Science and Technology Agency. T.T.e. was supported by JSPS through the Program for Leading Graduate Schools (MERIT). **Author contributions:** T.T.e., T.O., T.Mo., and H.Y. constructed the THz pump optical probe spectroscopy system. T.T.e., T.O., and N.K. constructed the THz-TDS system. T.T.e. and T.O. performed the measurements. T.T.e., T.Mi., and H.Y. constructed the THz-pulse generation. T.T.e. and T.O. contributed to writing the paper. **Competing interests:** The authors declare that they have no competing financial interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.