High-resolution spectroscopy of buffer-gas-cooled phthalocyanine

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For over five decades, studies in the field of chemical physics and physical chemistry have primarily aimed to understand the quantum properties of molecules. However, high-resolution rovibronic spectroscopy has been limited to relatively small and simple systems because translationally and rotationally cold samples have not been prepared in sufficiently large quantities for large and complex systems. In this study, we present high-resolution rovibronic spectroscopy results for large gas-phase molecules, namely, free-base phthalocyanine (FBPc). The findings suggest that buffer-gas cooling may be effective for large molecules introduced via laser ablation. High-resolution electronic spectroscopy, combined with other experimental and theoretical studies, will be useful in understanding the quantum properties of molecules. These findings also serve as a guide for quantum chemical calculations of large molecules.
High-resolution molecular spectroscopy is one of the most important techniques for studying molecules in both basic and applied sciences because the quantum nature governing the properties of molecules is embedded in their spectra. A more detailed discussion requires a higher resolution evaluation of the quantum states. For example, rotational resolution is necessary to accurately determine the structure of a molecule. However, high-resolution rovibronic spectroscopy is limited to relatively small and simple systems owing to some fundamental limitations. Large molecules have large moments of inertia, resulting in small energy separations in the rotational state such that there is one order of magnitude narrower than that in the visible region. Therefore, the rotational structure of fullerenes could be consistent with previously reported rotational constants $\lambda = 0.00298$ and $B = 0.00297 \text{ cm}^{-1}$ based on theoretical calculation. The experimental and theoretical considerations (e.g., signal reproducibility, possibility of experimental error, and numerical simulations) suggest that this structure can be attributed to the rotational structure. This periodicity can be understood to some extent by approximating FBPc as a rigid, oblate symmetric top molecule ($A = B$). Because FBPc is considered to be planar, the other rotation constant, $C$, is half the values of $A$ and $B$, such that $A = B = 2C$ (the simulation in Fig. 2 does not use these approximations). The energy level of an oblate symmetric top is given by

$$E = (C - B)K_z^2 + B(J + 1) = -\frac{B}{2}K_z^2 + B(J + 1)$$

where $J$ is a rotational quantum number, and $K_z$ is a projection of $J$ onto the molecular axis ($z$ axis in Fig. 1). As discussed below, the shape of the observed spectra strongly suggests that the transition is a b-type transition. The selection rule for a b-type transition is $\Delta K_z = \pm 1$. Assuming the rotational constants in the excited state are the same as those in the ground state, the transition energy of the P-branch ($\Delta J = -1$) can be written as

$$\Delta E = \nu_0 - B\left(2J'' + K''_z + \frac{1}{2}\right)$$

where $\nu_0$ is the band origin and double primes indicates quantum numbers in the ground state. The plus–minus sign corresponds to the selection rule for $\Delta K_z = \pm 1$. Therefore, transitions with $J'' = J - n$ and $K''_z = J - 2n$ ($n = 0, 1, 2, \ldots$) have the same transition energy, $\nu_0 - B(J + \frac{1}{2})$, for the $\Delta K_z = -1$ transitions and make a bunch of transitions. Because the energy difference between neighboring bunches ($J'' - J$) is $B$, these bunches create the observed oscillation-like structure. The same argument is true in the R branch ($\Delta J = +1$). The bunch structure becomes less visible as $J$ increases because of the small difference in the rotation constants between the ground and excited states and higher-order terms, such as centrifugal distortion terms, which are observed near the edges of the observed spectrum.

**Comparison with simulations.** We found that the observed spectral structure could be simulated well by theoretical calculations although the rotational constants will be determined more accurately through cooperation with high-level ab initio calculations. There are three important findings here in addition to the spectral constants: (1) the rotational temperature is below 10 K, (2) the translational temperature is also below 10 K, and (3) the
S$_1$–S$_0$ transition seems to be b-type (the transition dipole is parallel to the y-axis in Fig. 1) rather than a-type (parallel to the x-axis). The rotational temperature is estimated based on the overall band shape. The band shape agrees with the simulation results at a rotational temperature of 5 K. Even if a conservative estimate was made, a rotational temperature of less than 10 K is considered certain. The approximate Doppler width of the rotational line, which corresponds to the translational temperature, can be estimated by reproducing an oscillation-like rotational structure. The simulation results with a linewidth of 0.0011 cm$^{-1}$ (5 K) showed good agreement with the observed spectrum. The visibility of the rotational structure is considerably lower at translational temperatures higher than 10 K, indicating that the translational temperature is also below 10 K. Whether the transition is a- or b-type can be distinguished by the shape of the spectrum near the Q-branch. There was only a deep dip in the center of the band, and no strong peaks were observed. This shape strongly suggests that the transition is a b-type transition, unlike the previous prediction of an a-type transition (see Supplementary Fig. 1$^{30}$). This suggests that high-resolution spectra can provide the energy of the quantum states and their symmetry species that determine the type of transitions. This information is.

**Fig. 1** Schematic of absorption spectroscopy of buffer-gas-cooled free-base phthalocyanine (FBPc). An FBPc tablet fixed on the wall of a buffer gas cell is laser ablated with nanosecond pulses at 532 nm to obtain gas-phase molecules in the cell. The ablated hot molecules are rapidly cooled by collisions with helium atoms, which are nearly in equilibrium with the cell at 5 K. Helium and FBPc molecules flow into the vacuum vessel through an aperture (5 mm diameter). The helium atoms are then adsorbed by charcoal cooled to approximately 5 K to maintain vacuum. A narrow-linewidth continuous-wave laser at 660 nm passes through the cell via an optical port and is measured by a photodetector. The observed absorption increases rapidly after ablation ($t = 0$) and reaches the maximum value 1 ms after ablation. Thereafter, the absorption gradually decays over a period of several milliseconds. Absorption spectra were obtained by recording the absorbance at $t \sim 1$ ms.

**Fig. 2** Observed and simulated spectra of the O–O band of the S$_1$–S$_0$ transition of FBPc. Panel a shows the wide overview spectra. The red line is the observed spectrum and others are tentative simulation results from PGOPHER$^{28}$ assuming the same rotational and translational temperatures. Panel b shows enlarged views of the spectra. Regular spectral oscillation due to rotational motion can be clearly seen.
Fig. 3 Comparison of spectra at high temperatures. The red line is the spectrum of FBPc cooled with helium buffer gas at 5 K, similar to that in Fig. 1. The green line is the spectrum of FBPc cooled with neon buffer gas at 15 K. The black line shows simulation results at 20 K. Absorption intensities are normalized for clarity. Measurements at higher temperature gave broader spectra with wider rotational distribution.

**Neon buffer-gas experiments.** To demonstrate the importance of cooling to cryogenic temperatures, the absorption spectrum was measured at a cell temperature of 15 K. In this experiment, we used neon as a buffer gas because helium cannot be adsorbed by cooled charcoal at this temperature. The observed spectrum was compared to that obtained at 5 K (Fig. 3). Although the signal-to-noise ratio is not sufficient to discuss details of the spectral structures, the spectrum is broader and shows no rotational structure; this was expected, because of the broader rotational distribution and wider Doppler linewidth. This behavior is consistent with the simulation results at 20 K, which is slightly higher than the experimental cell temperature. Further, Fig. 3 suggests that there is no pronounced shift of the transition frequency. There is some debate as to whether the molecules in the cell form clusters with buffer-gas atoms. In particular, large molecules are more likely to cluster because of their large size and intermolecular forces. However, the fact that there was no frequency shift when changing the gas species of the buffer gas suggests that the molecules visible in this band are at least single molecules that do not form clusters with the buffer gas atoms because clustering with a single atom result in a GHz-order shift. Further careful experiments are expected to provide deeper insights into the presence or absence of clusters and their properties.

**Vibrational bands.** We also measured another vibrational band centered at 15258.9 cm⁻¹. Only the 0–0 band showed strong absorption owing to the rigid structure of FBPc due to the Franck-Condon effect. The intensity of the band observed at 15258.9 cm⁻¹ was approximately two orders of magnitude lower than the 0–0 band. Even at this low intensity, the vibrational energy can be determined more accurately than that determined previously because of the high resolution obtained in this study. The frequency of this band was previously reported to be 15258.7 cm⁻¹. A deviation of 0.2 cm⁻¹ = 6 GHz may be negligible for low-resolution spectroscopy with pulsed lasers but significant for narrow-linewidth lasers. Our experiments provided the electronic, vibrational, and rotational energies of large molecules with at least one order of magnitude better uncertainty than those achieved previously.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon request.

**Code availability**

The code used in this study are available from the corresponding author upon reasonable request. We used PGOPHER 10.1.182.

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Author contributions
Y.M., K.I., S.K., and K.E. designed the experiments. Y.M., R.T., Y.T. constructed apparatus. Y.M., K.I., S.K., and K.E. performed the simulation. Y.M., R.T., Y.T. wrote the original manuscript. K.I., S.K, and K.E. reviewed and edited the manuscript.

Competing interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Additional information
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