Rovibronic quantum structure of large molecules

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(Dated: June 17, 2022)

For over five decades, studies in the field of chemical physics and physical chemistry have primarily aimed to understand the structure and dynamics of molecules as quantum objects. However, high-resolution rovibronic spectroscopy has been limited to relatively small and simple systems because translatonally 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 was effective for large molecules introduced via laser ablation. Rotationally resolved electronic spectroscopy revealed the structures of ground and excited states and the dynamics of large molecules, such as molecular clustering. These findings also serve as a guide for quantum chemical calculations of large molecules. We believe that our study will help in the molecular design of various chemical and biochemical systems.

INTRODUCTION

High-resolution molecular spectroscopy is one of the most important techniques for studying molecular structure and dynamics in both basic and applied sciences because the quantum nature governing the properties of molecules is embedded in their spectra [1,2]. 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 their Doppler width hides their structure. To reduce the Doppler width, the molecules must be cooled to extremely low temperatures. Although supersonic jets of noble gases have long been used to prepare low-temperature molecules for high-resolution spectroscopy, it is difficult to inject large molecules in sufficient quantities for high-resolution rovibronic spectroscopy.

Although buffer-gas cooling is a conventional method [3,4], it has recently attracted considerable attention [5,6]. This is because various applications using the quantum control of cryogenic molecules have recently been proposed in fundamental physics, quantum information, and ultracold chemistry [7]. Buffer-gas cooling is a robust method owing to its simple principle of collision with a cryogenic noble gas [8,9]. Therefore, it is widely used as a preparatory method for further cooling, such as laser cooling [9,10]. Buffer-gas cooling has also been widely studied for high-resolution spectroscopy [11,12]; however, the focus has been on relatively small molecules, and the extent to which large molecules can be cooled is not well understood [13,14].

Rotationally resolved vibrational absorption spectra of fullerenes (M = 720) were recently reported and were measured using a sophisticated apparatus combining a buffer-gas cooling method and a frequency comb [15]. The fullerene was cooled to approximately 150 K using an Ar buffer gas. As the Doppler width is proportional to the transition energy, the Doppler width of the vibrational spectrum in the infrared region is one order of magnitude narrower than that in the visible region. Therefore, the rotational structure of fullerenes could be observed even at a relatively high temperature of ~150 K. In contrast, rotational resolution of the rovibronic spectrum in the visible region would require a much lower temperature.

Herein, we report rotationally resolved visible spectra of the rovibronic transition of free-base phthalocyanine (FBPc) cooled by helium buffer gas at cryogenic temperatures. To the best of our knowledge, this is the first successful observation of the resolved rotational structure of a large molecule of this size (M = 514) in electronic spectra. Although precise determination of the molecular structure requires further theoretical studies, including high-level ab initio calculations, a simple simulation can reproduce the overall spectral shape. The comparison between the measurement and simulation results shows that both the rotational and translational temperatures of FBPc are below 10 K. These results suggest that even large molecules can be cooled to cryogenic temperatures...
by buffer-gas cooling, and that they are targets of rotationally resolved quantum measurement and control.

Compared with standard spectroscopy methods, high-resolution rovibrionic spectroscopy provides a deeper understanding of the molecular dynamics, including scattering and clustering processes and chemical reactions. Although many studies have been conducted on molecular dynamics in the gas phase, detailed studies have been limited to relatively small molecules [20]. This is because intermolecular interactions are much weaker than intramolecular interactions, and high-resolution spectroscopy is required to study the former in detail. Detailed information of quantum states provided by high-resolution rovibrionic spectroscopy also serves as a guide for quantum chemical calculations of large molecules. Ab initio calculations of large molecules remain challenging because of the difficulty in constructing both the calculation method and basis functions [27]. High-resolution spectroscopy of large molecules opens a new era of molecular design of large molecules in a variety of chemical and biochemical systems, as it can provide detailed structural information on large molecules comparable to functional molecules, such as porphyrins, chlorophyll, and nucleic acids.

RESULTS AND DISCUSSION

The apparatus used for high-resolution spectroscopy of the FBPc is schematically shown in Fig. 1. The FBPc in the gas phase, produced by laser ablation, is cooled by collisions with helium atoms. Absorption was measured using a continuous-wave dye laser with a linewidth of approximately 1 MHz. After ablation (t = 0), the absorption increased rapidly and reached its maximum value approximately 1 ms after ablation. Thereafter, it gradually decayed over a time scale of several milliseconds. This behavior is similar to that of other smaller molecules prepared by laser ablation in buffer-gas cells reported previously [5]. Owing to the nature of ablation, the absorption intensity fluctuates and decays when the ablation is performed continuously. To reduce this effect, the ablation position was continually changed during the experiment. The observed 0-0 band of the $S_1 \rightarrow S_0$ transition of FBPc is shown in Fig. 2 with the simulation results obtained using PGOPHER [28]. The overall spectrum extends from approximately 15131.0 to 15132.4 cm$^{-1}$, reflecting the population distribution of the rotational states in the ground state. The magnified spectrum in Fig. 2 shows an oscillation-like structure with a period of approximately 0.003 cm$^{-1}$, which is consistent with previously reported rotational constants $A = 0.00298$ and $B = 0.00297$ cm$^{-1}$ [29] based on theoretical calculation [30].

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 FBPcs is considered to be planar, the other rotation constant, $C$, is half the values of $A$ and $B$, such that $A = B = 2C$. The energy level of an oblate symmetric top is given by

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

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

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

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 $K''_z = J - 2n (n = 0, 1, 2, ...)$ 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 ($J \rightarrow J \pm 1$) 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.

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 is 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 Information) [50]. This suggests that rotationally resolved spectra can provide the energy of the quantum states and their symmetric species that determine the type of transitions. This information is essential for the development of first-principles calculations for large molecules, which includes construction of the basis sets, testing of functionals in density functional theory, and estimation of the effect beyond the Born-Oppenheimer approximation. A detailed discussion of the spectral constants will be provided in a future report.

To demonstrate the importance of cooling in the Kelvin region, 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. Further careful experiments are expected to provide deeper insights into the presence or absence of clusters and their properties.
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$^{-1}$ [31]. 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 higher precision than those achieved previously.

CONCLUSIONS

The high-resolution rovibronic spectra of buffer-gas-cooled cryogenic FBPc were reported to have an oscillation-like rotational structure. The tentative simulation results show that both the translational and rotational temperatures are below 10 K, indicating that the buffer-gas cooling method is feasible for cooling large and heavy molecules to cryogenic temperatures. The $S_1 - S_0$ transition was found to be a b-type transition, which reveals the symmetric species of the excited electronic state. The spectrum at 15 K with neon buffer gas is broad and has no rotational structure, indicating the importance of cooling samples to the Kelvin regime to unveil the quantum structure of large molecules. The other vibrational band was also observed, which provided information on vibrational energy with higher precision than that reported previously. Thus, with information on all the quantum states of molecules currently available, more precise first-principles calculations of large molecules can be investigated. This research paves the way for high-quality quantum measurements and control of large molecules, including biochemical molecules. The present discussion of the experimental data is limited by the signal-to-noise ratio. Methods with higher sensitivity, such as laser-induced fluorescence (LIF), could greatly increase the signal-to-noise ratio and allow a more detailed discussion of the molecular structure and dynamics. In addition, Doppler-free spectroscopy has the potential to observe finer spectral structures. Doppler-free LIF of the large functional molecules would be an interesting future work to learn more about such molecules.
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 Figure 1. The blue 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.

ACKNOWLEDGMENTS

We would like to thank Prof. Doyle, Prof. Takahashi, Prof. Hutzler, Prof. Uetake, and Prof. Takasu for their kind cooperation. Y. M. would like to thank the members of Core for Quantum Universe (RIIS, Okayama University). Y. T. would like to thank the Masason Foundation for their financial support. This work was supported by JSPS KAKENHI Grant Nos. 18H01229 and 22H01249, and Masason Foundation. We would like to thank Editage (www.editage.com) for English language editing.

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METHODS

The apparatus used for high-resolution spectroscopy of FBPs is shown schematically in Fig. 1. The setup was enclosed in a 40-K shield in a room-temperature vacuum chamber. The output from a 532-nm nanosecond-pulsed Nd:YAG laser (Litron nano, $\sim 2 \text{ mJ}, \sim 10 \text{ ns}$ wide) was focused loosely on an FBPs tablet fixed on the wall of a buffer-gas cell. The cell was cooled to 4.7 K with a pulse tube refrigerator (Sumitomo Heavy Industries, 0.5 W, 4 K). During the experiments, the cell was heated to approximately 5 K via ablation. The helium buffer gas was precooled to approximately 40 K and introduced through the gas inlet into the cell. The He atoms thermalized with the cell collided with the ablated FBPs molecules and cooled them to a low temperature. The helium and FBPs molecules were fed into the vacuum chamber through a 5-mm-diameter aperture. The helium atoms were then adsorbed by charcoal cooled to approximately 5 K to maintain vacuum. Narrow-linewidth laser light from a ring dye laser (Coherent 899, dye: DCM) passed through the optical port into the cell. The laser light used for the absorption measurements was attenuated with filters to prevent the saturation of the silicon photodetector. Half of the laser power was used for iodine subDoppler spectroscopy for frequency calibration. A portion of the laser radiation was sent to a wavemeter (Highfinesse, WS6-200). The frequency uncertainty was approximately 50 MHz after calibration. Absorption spectra were obtained by recording the absorbance $\sim 1 \text{ ms}$ after ablation.
Simulated spectra for a- and b-type transitions

Here, we present the simulation results for the S₁ ← S₀ transition of the free base phthalocyanine in Fig. S1, assuming an a- or b-type transition using PGOPHER [1]. The simulation was performed with D₂h symmetry. The irreducible representation of the ground state is A₉, while those of the excited state are B₃u (a-type) or B₂u (b-type). The rotational and translational temperatures are 10 K. Rotational constants are set as follows: Aₕ = 0.002991, Bₕ = 0.002986, Cₕ = 0.001494, Aₑ = 0.002994, Bₑ = 0.002973, and Cₑ = 0.001497 (cm⁻¹). It should be noted that these values are inconclusive. Although a more detailed discussion of the simulation and rotational constants will be reported in a separate paper, the results suggest that the observed transition is a b-type transition.

Fig. S1 Simulated spectra. (a) a-type transition and (b) b-type transition.

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