High frequency ESR measurement on molecular oxygen using pulsed high magnetic field

Shojiro Kimura [a,1], Koichi Kindo [a]

[a] *KYOKUGEN, Osaka University, Machikaneyama 1-3, Toyonaka, Osaka 560-8531, Japan*

Abstract

High field/high frequency ESR measurement on molecular oxygen has been performed in its gas phase at the frequencies 730.5GHz and 1017.6GHz using pulsed high magnetic field. The observed ESR spectrum is analyzed by the theory of Tinkham and Strandberg which was used to interpret the spectrum observed in the previous X-band ESR measurement.

Key words: molecular oxygen; electron spin resonance; high magnetic field

The electronic ground state of the molecular oxygen is $^3\Sigma$ state with $S = 1$. A large amount of work for the molecular oxygen has been done so far because of its magnetic properties. The ESR studies on the molecular oxygen in its gas phase date back to the 1950s [1-3]. From the X-band ESR measurements, complicated ESR spectrum accompanied with a number of sharp structures was observed. The detailed descriptions of the theoretical treatments for the ESR spectrum of the molecular oxygen in the gas phase, including the effective coupling between the spin and the rotational angular momenta, were given by Tinkham and Strandberg [2, 3]. According to the theory, the rotational energy level of the molecule, characterized by the quantum number K, is divided into three sub-levels with the total angular momentum $J = K-1, K, K+1$, due to the rotation-spin coupling and the magnetic anisotropy of the molecule. Under an external magnetic field, each sub-level is further divided into $2J + 1$ levels depending on the magnetic quantum number J_z, which represents the projection of the total angular momentum in the direction of the magnetic field. The observed ESR absorption lines were well explained by the transitions between the energy levels, of which difference ΔJ_z of the magnetic quantum numbers is ΔJ_z=$\pm$1 within the same rotational state. However, since rather large magnetic anisotropy term gives energy gaps more than 50GHz between the states of $J = K$ and $J = K \pm 1$ at zero magnetic field, the transitions between these states occur outside of the usual magnetic field used in the X-band ESR system. Therefore, to observe the whole ESR spectrum of the molecular oxygen in the gas phase, it is necessary to perform the measurement using high frequency and high magnetic field. In this study, the high frequency/high field ESR measurement on the molecular oxygen has been performed at the frequencies 730.5GHz and 1017.6GHz using pulsed high magnetic field. O_2 gas is filled in the sample cell, which consists of a stainless steel pipe and a window made of STYCAST^{TM}1266, under the ambient pressure. The length of the sample cell is 38mm and the difference of the magnetic fields between the center and the edge of the sample cell is a few percent of the center field.

Figure 1 shows the ESR spectrum of the molecular oxygen in the gas phase observed at 730.5GHz at 120K. The ESR spectrum, accompanied with several peak structures, is observed. These structures are distributed in wide magnetic field region from 24T to 28.5T. Figure 2 shows the frequency-field relations of the observed peak structures. The extrapolations of the

[1] Corresponding author. KYOKUGEN, Osaka University, Machikaneyama 1-3, Toyonaka, Osaka 560-8531, Japan E-mail: kimura@hmf.mag.rcem.osaka-u.ac.jp

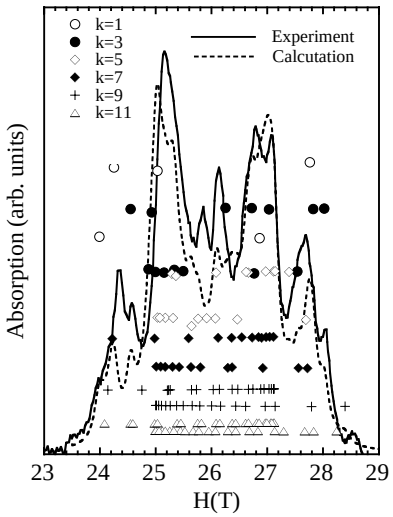

Fig. 1. The ESR spectrum of the molecular oxygen observed at 730.5GHz at 120K. The dashed line shows the theoretical curve. The open and the closed circles, the open and the closed diamonds, the crosses and the triangles show the relations between the resonance field and the signal amplitude calculated for the rotational states of K=1, 3, 5, 7, 9 and 11, respectively. See the text for the details

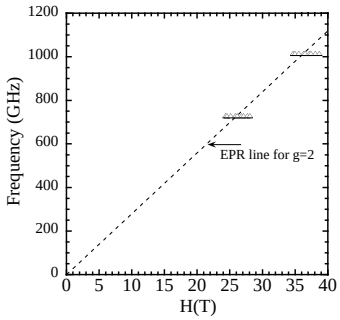

Fig. 2. The frequency-field relations of the peak structures of the ESR spectrum observed at 120K.

ESR branchs of these peak structures do not cross the origin, reflecting the zero field gaps. From the X-band ESR measurement non-linear Zeeman splitting with respect to the external magnetic field are suggested in the low field region [3], whereas the ESR branches, shown in Fig. 2, exhibits the linear dependence with the slopes nearly the same as that of $g = 2$. This behavior suggests that the ESR spectrum, observed in our measurement, occurs in the Paschen-Back region, where the Zeeman energy is large enough compared with the rotation-spin coupling and the magnetic anisotropy. The ESR spectrum, observed at 730.5GHz, is analyzed by the theory of Tinkham and Strandberg [2, 3]. It is interpreted that the observed ESR spectrum results from the overlap of a number of the ESR absorption lines coming from each of the rotational states. The energy levels of the molecular oxygen in $^3\Sigma$ state under an external magnetic field are calculated from eq. (4) and (5) in ref. [3], and the resonance fields for the ΔJ_z=$\pm$1 transitions at 730.5GHz within each of the rotational states are obtained. Small corrections from the electron-orbital and the rotational-induced magnetic moments, treated in ref. [3], are not included in our analysis. The signal amplitude $I(i, j)$ for the ESR transition between i and j states are calculated from the following relation:

$$I(i,j) \propto \langle i|S_{\rm x}|j\rangle \times (\exp(-E_{\rm i}/k_{\rm B}T) - \exp(-E_{\rm j}/k_{\rm B}T))/Z, \qquad (1)$$

where $S_{\rm x}$ is the spin component perpendicular to the external magnetic field. The field dependence of the partition function Z is neglected in our analysis. The matrix element $\langle i|S_{\rm x}|j\rangle$ can be obtained from eq. (37) in ref. [3]. The relations between the resonance field and the signal amplitude calculated with the parameters, used for the analysis of the ESR spectrum observed in the X-band ESR measurement [3], are shown in Fig. 1. Those are obtained for the rotational states from $K = 1$ to $K = 11$. It should be mentioned that only the states with odd K exist due to the homonuclear character of the molecular oxygen [2]. It is difficult to discuss the line shape and the linewidth because of the imhomogeneity of the magnetic field in our measurement, but we assume the Lorentzian line shape with the linewidth of 0.2T for each of the calculated ESR absorption lines. The obtained theoretical curve, shown by the dashed line in Fig. 2, agrees well with the experimental result. Small discrepancies between the experimental and the theoretical results are probably due to the fact that the Zeeman energy is treated as the second order perturbation with respect to the rotational levels in the theory, because the Zeeman splitting of 730.5GHz is comparable with the splitting between the rotational states of K and $K \pm 2$.

Acknowledgements

This work was supported by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists and partially supported by Grant-in-Aid for Science from the Ministry of Education, Science, Sports and Culture.

References

[1] R. Beringer, J. G. Castle, Phys. Rev.**81** (1951) 82.

[2] M. Tinkham, M. W. P. Strandberg, Phys. Rev. **97** (1955) 951.

[3] M. Tinkham, M. W. P. Strandberg, Phys. Rev. **97** (1955) 973.