

Information from Two-Dimensional Fifth-Order Raman Spectroscopy: Anharmonicity, Nonlinearity, Mode Coupling, and Molecular Structure

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Abstract. In recent years, we have tried to clarify new information inherent in two-dimensional (2D) Raman spectroscopy. In this paper, we review such our theoretical attempts, highlighting key concepts that we have presented in this developing field. Especially, our latest work concerning a new paradigm — 2D Raman spectroscopy as a tool for molecular structure analysis — shall be emphasized.

INTRODUCTION

The molecular vibrational spectrum in the condensed phase is usually broad and featureless in which much information is buried. One possible direction to extract the hidden information takes advantage of the state of the art technology of the high-power short-pulsed optical laser. Irradiation of a pair of such pulse can cause vibrational excitation of molecules, and another delayed probing pulse enables the time-resolved monitoring of the relaxation process of the Raman excitation. This third-order Raman spectroscopy, which is one-dimensional because it contains one delay time (between the first pair pulses and the probe pulse), is related to the conventional spontaneous Raman scattering. In 2D Raman spectroscopy, one more pair of pulse is irradiated before the probe pulse; we use five pulses in total and thus have two delay times (between the first and the second pairs and between the second

pair and the probe pulse). 2D Raman spectroscopy is two-dimensional fifth-order spectroscopy and is an optical counterpart of 2D NMR. This spectroscopy was originally proposed to distinguish homogeneous and inhomogeneous broadening (1) and stimulated experimentalists to challenge the measurements (2,3,4).

ANHARMONICITY VS NONLINEARITY

In the initial paper (1), the origin of the signal is understood as the *nonlinear* dependence of the polarizability on the nuclear coordinate. On the contrary, we showed the possibility that the *anharmonicity* inherent in the electronic ground-state potential surface contributes to the signal (5). We demonstrated that the fifth-order signal is formed as a competition between the *nonlinearity* and the *anharmonicity* (6,7). Further theoretical and experimental developments have exploited this general concept regarding with the origin of the signal.

MODE COUPLING

The heterodyne detection of the signal (8) enables to use weaker but shorter pulse to detect the signal from well-defined intramolecular modes. For such modes, the analysis in the frequency domain is useful by the double-Fourier transformation with respect to the two delay times. We derived equations that show that the mode coupling manifests as cross peaks in the 2D frequency space, offering significant information on nonlinearity and anharmonicity (9). We also proposed a direct frequency-domain experiment (10).

STRUCTURAL TOOL

Recently, we demonstrated a new possibility of 2D Raman spectroscopy as a tool for molecular structure analysis (11). We have shown that the two-dimensional map in the frequency domain changes according to the structural change of molecules. The possibility of the quantitative estimation of the molecular structure change has been pointed out. The structure analysis had been successfully realized by 2D NMR. A possible advantage of this optical counterpart is shorter time resolution; 2D Raman can have a timescale that is one thousands to one millions of that of 2D NMR, i.e., submicrosecond to subpicosecond.

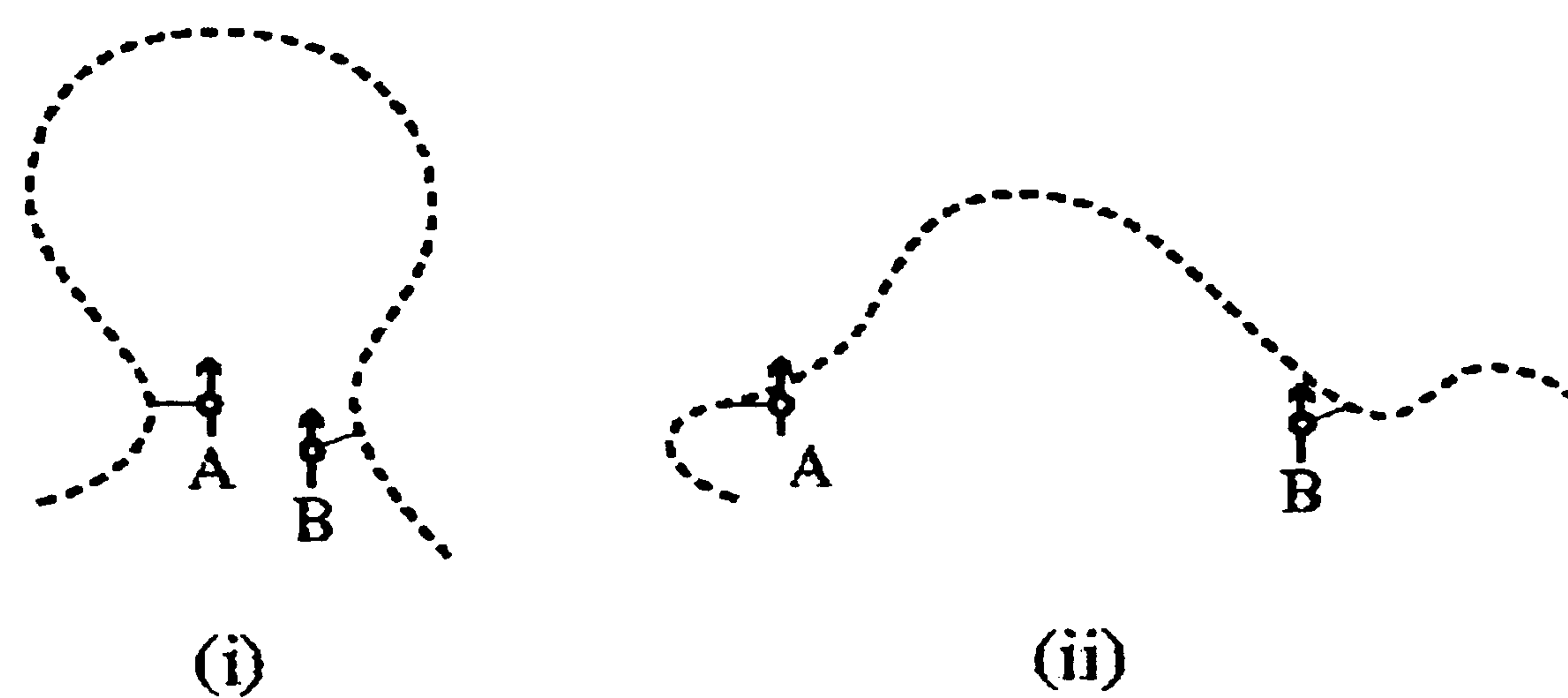


FIGURE 1. A macromolecule that has two induced-dipoles A and B, which are Raman active. The distance between the two modes A and B are different in the structure (i) and (ii).

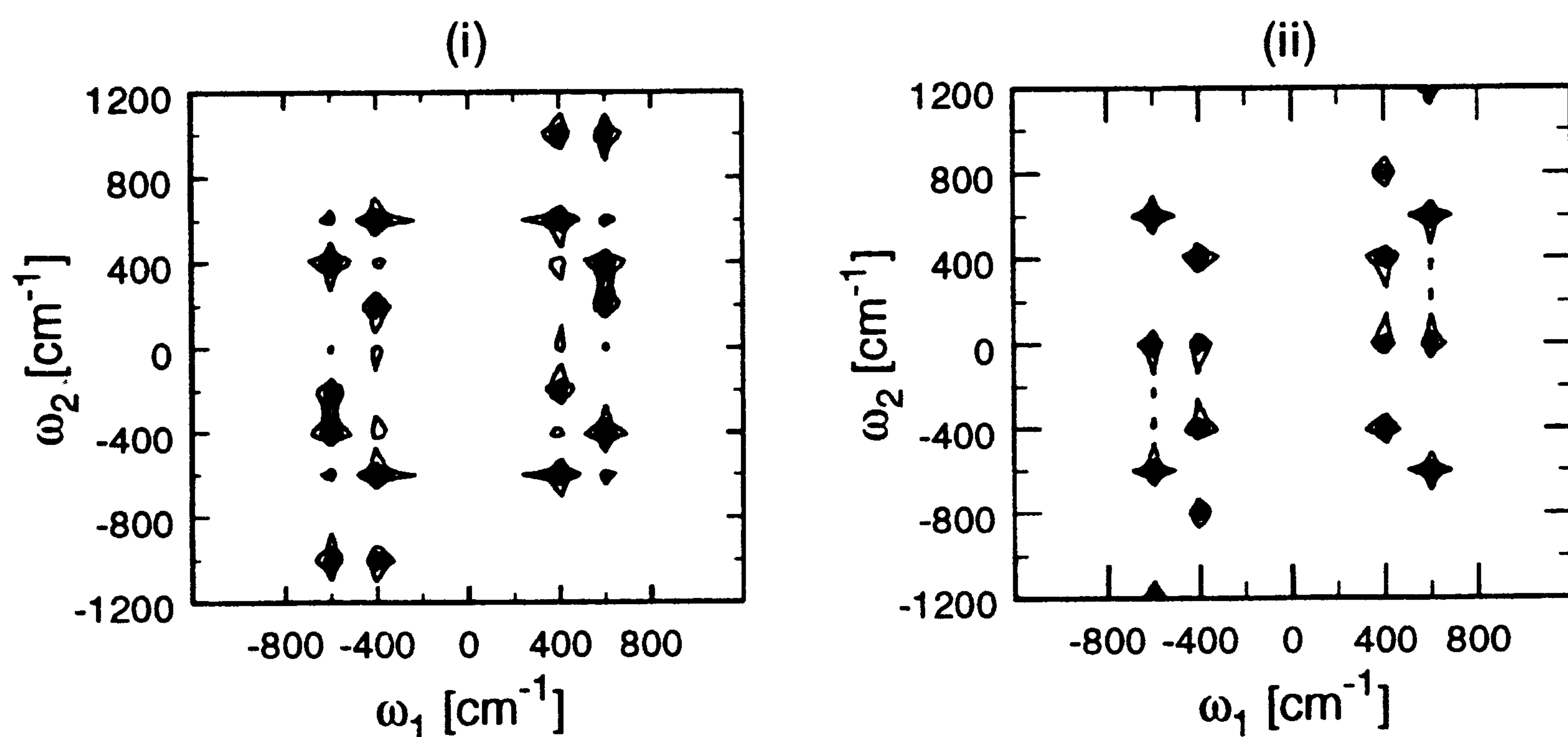


FIGURE 2. The 2D Raman signal in the frequency domain. (i) and (ii) correspond to the structure (i) and (ii) in Fig. 1.

When a macromolecule changes its structure from (i) to (ii) of Fig. 1, the 2D Raman signal changes from (i) to (ii) of Fig. 2, while the third-order signal at the structures (i) and (ii) are the same as in Fig. 3; the cross peaks originating from the coupling between A and B modes are strong at the structure (i) where the spatial distance A-B is short. In addition to the visible distinction on the 2D contour map, quantitative information on the distance can be obtained by use of the scaling law. The peak intensity of the cross peaks scales as the distance cubed and the distance to the sixth in anisotropic and isotropic systems, respectively.

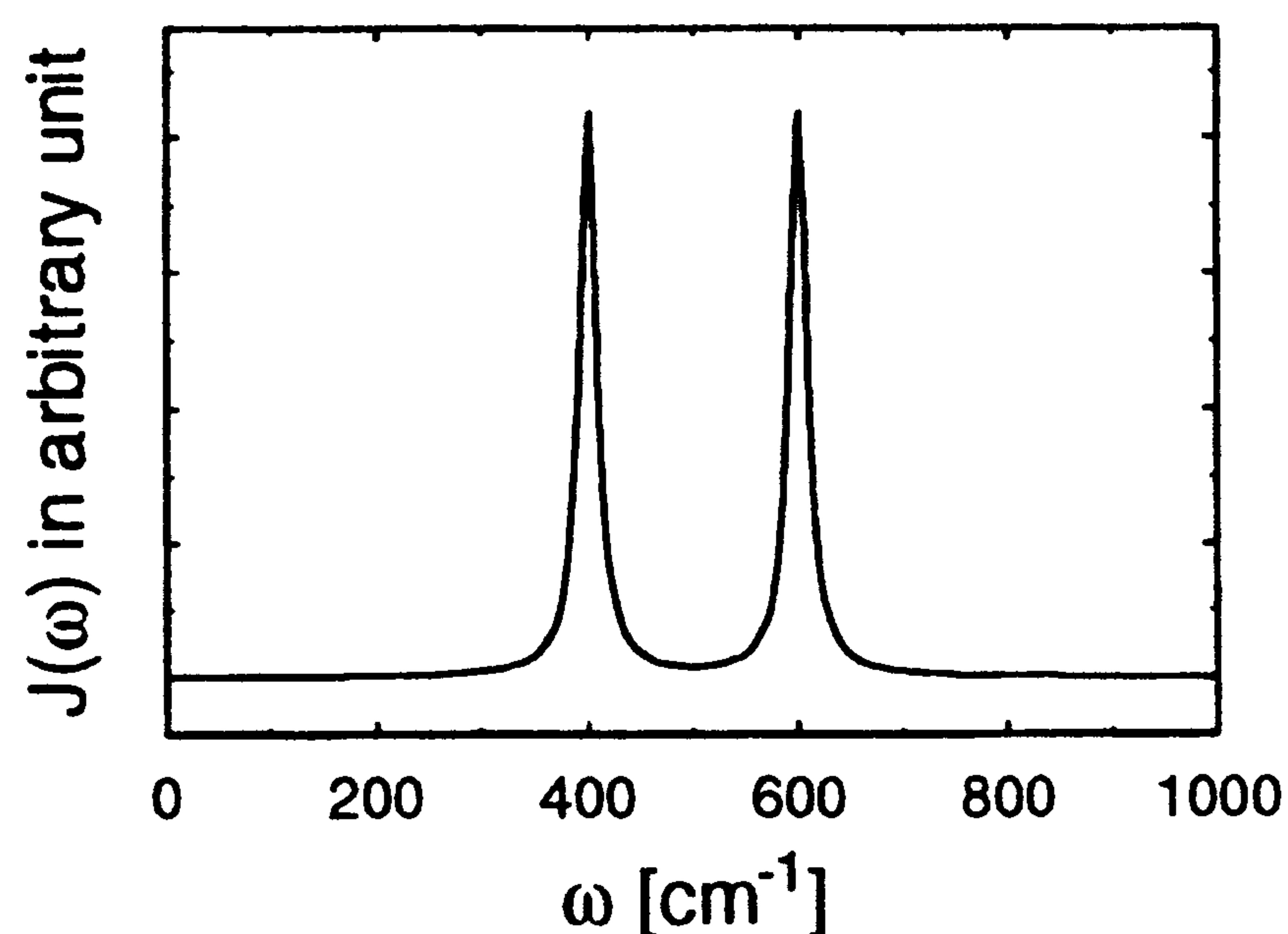


FIGURE 3. The third-order signal of the macromolecule in the frequency domain. The two peaks correspond to the mode frequencies of A and B, respectively. The third-order signal at the structures (i) and (ii) of Fig. 1 are the same; the third-order signal is insensitive to the structure change.

ACKNOWLEDGEMENTS

The present work is supported by a Grant-in-Aid for Encouragement of Young Scientists from the Japanese Ministry of Education, Science, Sports, and Culture.

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