Vibrational Band Origins of the Fundamentals ν_{12} and ν_5 of Furazan from Laser/Microwave Double Resonance

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Information from rotational spectroscopy has been utilised for the interpretation of experimental results from laser/microwave double resonance (LMDR) experiments on furazan. The band origins ν^0 for the fundamental vibrations ν_{12} and ν_5 have been deduced from these experiments as $\nu_{12}^0 = 952.611(2)\ \mathrm{cm}^{-1}$ and $\nu_5^0 = 1005.353(2)\ \mathrm{cm}^{-1}$.

General implications of the approach and of the LMDR technique are considered.

I. Introduction

In recent years we have carried out a fairly thorough investigation of the pure rotational spectrum of the heterocyclic compound furazan, $C_2H_2N_2O$, by the microwave/microwave double resonance modulation (DRM) technique [1]. Besides the molecular structure [2a] and the principal quadrupole coupling constants of the nitrogen atoms [2b] of this compound, this research has also yielded the spectroscopic parameters of molecules in twelve of the 15 fundamental vibrational levels of furazan [2c, d]. That work could not reveal, however, the associated vibrational frequencies in more than a qualitative manner, yet sufficiently accurate for the correlation of the various observed rotational spectra of vibrationally excited states with data from infrared (IR) spectroscopy of the 1970s [3].

It was probably only natural in those circumstances that the large body of relatively precise molecular information, which had been accumulated by microwave spectroscopy alone, made us desirous to complement the existing data through equally precise information on the vibrational frequencies of that molecule. In persuit of that goal we carried out work at the University of Ulm (FRG) where the modes ν_{12} (at $\sim 952\ \mathrm{cm}^{-1}$) and ν_5 (at $\sim 1005\ \mathrm{cm}^{-1}$) of furazan were successfully studied with the CO_2-laser/microwave double resonance (LMDR) apparatus of Dr. H. Jones.

It is the purpose of the present paper to report the results of that work in a formal way.

II. Principles of Laser/Microwave Double Resonance

The LMDR technique has been described in a number of papers which have been summarized by Jones [4]. For readers unfamiliar with that method, a block diagramme of the experimental set-up is shown in Fig. 1 and a brief account of the technique will be given:

The laser used for the present work is the fixed-frequency CO_2 gas laser with some 70 accurately known [5] laser frequencies for each isotopomer of CO_2. The microwave absorption cell, filled with the substance under investigation, is placed *inside* the cavity of the laser (see Figure 1). Under these experimental conditions, the gain of a particular laser line which oscillates at or very near the frequency of a rovibrational transition of the sample gas in the microwave cell depends on the amount of laser radiation which is absorbed in the sample gas, i.e. on the strength of IR absorption in the sample at or very near the laser frequency. That strength depends however on the molecular populations in both the lower and the upper level of the rovibrational transition of the sample. Usually, but by no means necessarily, the lower of these levels belongs to the rotational manifold of the vibrational ground state (G.S.), and the upper level is one of the rotational levels within a vibrationally excited state $\boldsymbol{v}$ (see Figs. 2 or 3). The populations of these levels can readily be affected if pure rotational transitions to or from these levels are induced ("pumped") by microwave radiation of appropriate frequency and intensity since such "resonant pumping" is known to alter the equilibrium populations of the pumped levels. In this way the strength of the rovibrational transition in the sample gas can be varied, and with it the amount of laser

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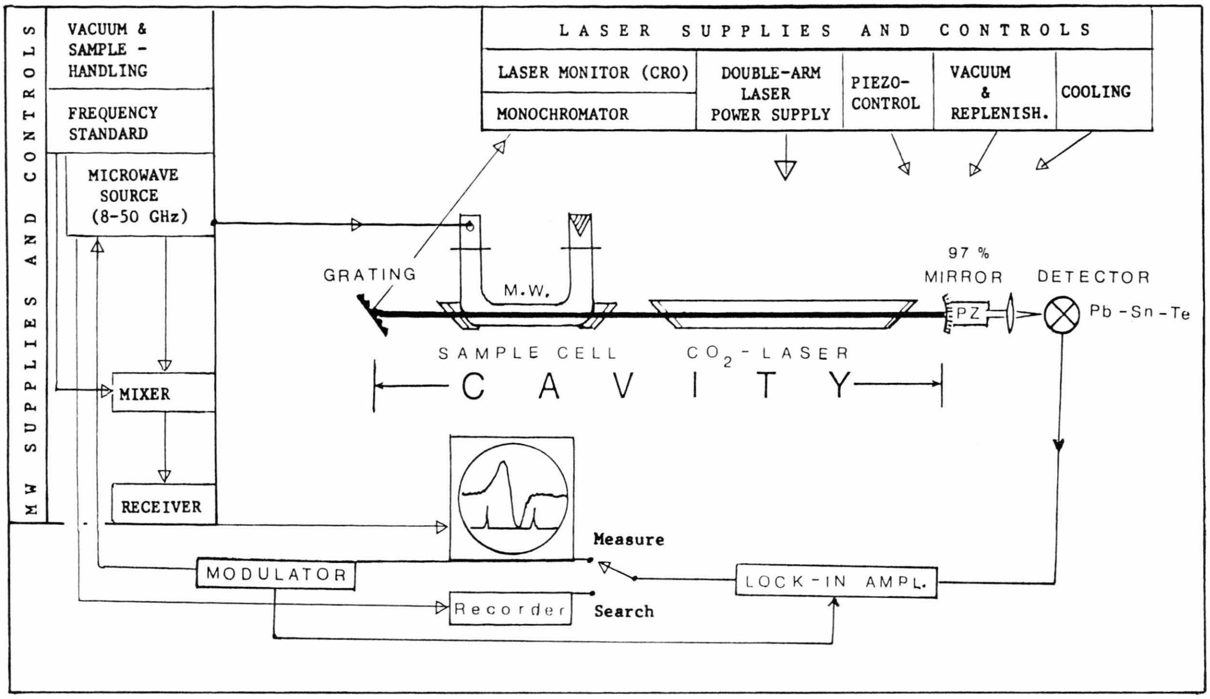


Fig. 1. Laser/microwave double resonance instrument.

radiation lost in the sample gas. Thus, the gain of the CO_2 laser may be varied through microwave irradiation of suitable rotational transitions of the sample gas contained within the laser cavity. The detection of variations in the gain of a fixed-frequency IR laser in dependence of microwave frequencies applied to an intra-cavity sample gas is, therefore, the essential feature or laser/microwave double resonance.

The outlined modification of the laser gain will, of course, only occur if the frequency of the IR laser accidentally coincides very closely with that of a rovibrational transition of the sample gas. Hence, all or nearly all frequencies of the CO_2-laser may have to be examined before such an accidental coincidence with a rovibrational transition of the sample is detected. – Prior knowledge about the disposition of rotational energy levels (and the allowed MW transitions between them) within the vibrational G.S. and within the vibrationally excited state $\boldsymbol{v}$ is therefore an essential ingredient for the correct interpretation of observed LMDR effects: If, as in the present case, rotational levels and transition frequencies are known beforehand for the vibration state $\boldsymbol{v}$ as well as for the G.S., the observation of a single coincidence between a known laser frequency and a rovibrational transition of the sample may well suffice for the determination of the band origin ν^0 of the vibration $\boldsymbol{v}$ of the sample. If however, as is mostly the case, the rotational energy levels are known for the vibrational G.S. only, several LMDR signals will have to be found before the rotational parameters of the $\boldsymbol{v}$-state can be deduced to allow the subsequent determination of ν^0.

III. Application and Results

It is apparent from previous work (Figs. 2 and 3 of [2c]) that three fundamentals of furazan fall into the 10 µm wavelength range of the CO_2 gas laser and may therefore be studied by the LMDR technique. These are the fundamentals $\nu_{12} \sim 952\ \text{cm}^{-1}$ (B_1, A-type), $\nu_5 \sim 1005\ \text{cm}^{-1}$ (A_1, B-type) and the rather weak vibration $\nu_4 \sim 1036\ \text{cm}^{-1}$ (A_1, B-type). Under inclusion of the isotopomers $^{13}C^{16}O_2$, $^{12}C^{18}O_2$, and $^{13}C^{18}O_2$ as the laser gases, some 250 individual laser frequencies were available in this range and at least a few of those were expected to coincide accidentally and sufficiently closely with rovibrational transitions of the above-mentioned three modes of furazan. The range of microwave radiation (covered by Marconi

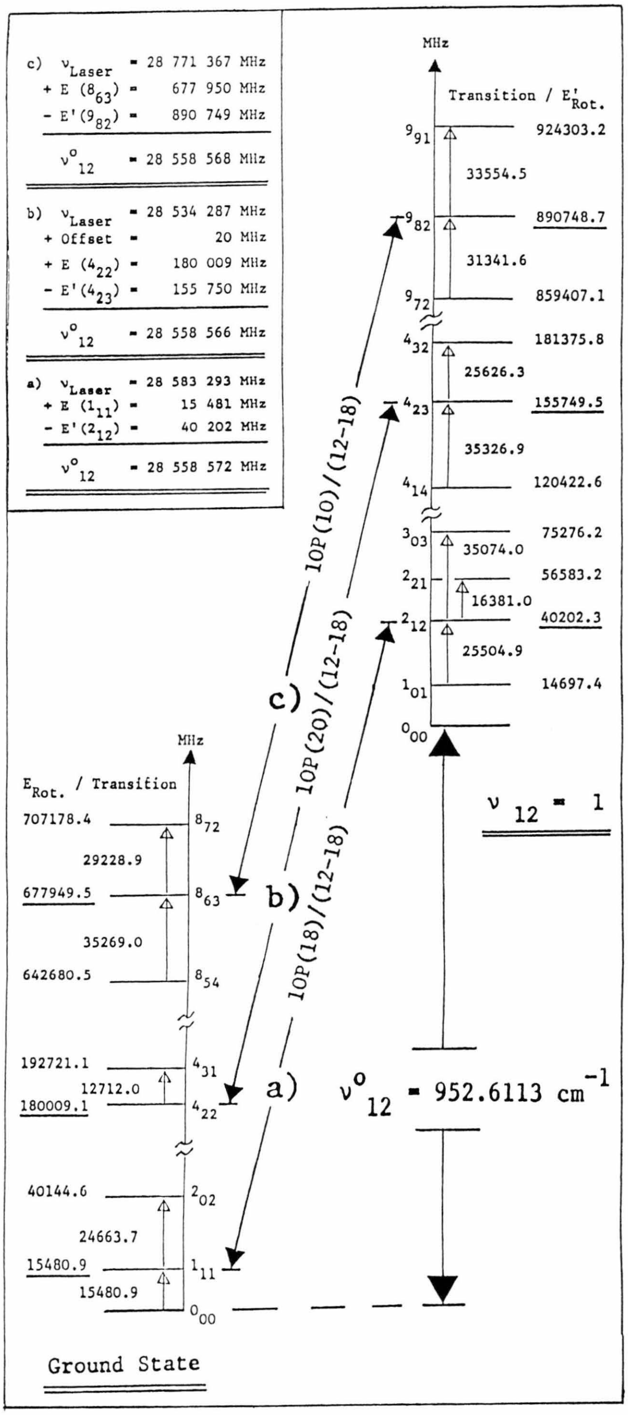


Fig. 2. Identified coincidences of CO_2 laser lines with rovibrational transitions of the ν_{12}-band of furazan.

sweeper sources) reached from 8 GHz to 50 GHz and was thus wider than the frequency range (12 GHz to 40 GHz) in which previous DRM work [2c] had been conducted. The justified concern that furazan was too large and too asymmetric a substance to permit easy and definite interpretations of the hoped-for LMDR signals seemed counterbalanced by the fact that the position of its rotational energy levels and the frequencies of transitions between those were known beforehand not only for the G.S., but also for the three excited states under consideration. Against this background, interpretability of observed LMDR signals was expected to be possible.

a) The B_1 Mode at 952 cm^{-1}

Searches over the microwave range for coincidences of rovibrational transitions of furazan with laser lines of the normal and the ^{13}C-species of CO_2 in the vicinity of 950 cm^{-1} at first confirmed the above concern by yielding a considerable number of LMDR signals for which one level of the rovibrational transitions could be tentatively identified with the help of previous information [2c], but not the other one. The upper levels in these cases are believed to belong to vibrational overtone or combination states in the energy range from 1500 cm^{-1} to 2200 cm^{-1}, for which little or no microwave information is available. These LMDR signals had therefore to remain essentially uninterpretable.

Experiments with the $^{12}C^{18}O_2$ species as the lasing gas produced easily interpretable results: with the laser oscillating on the 10P(18) line of this isotopomer, a change in laser gain was observed for five microwave frequencies, all of which were coincident with known rotational transition frequencies in furazan. These were:

15 480.9 MHz = $0_{00} \rightarrow 1_{11}$ and
24 663.7 MHz = $1_{11} \rightarrow 2_{02}$ of the G.S. of furazan, and
25 504.9 MHz = $1_{01} \rightarrow 2_{12}$
16 381.0 MHz = $2_{12} \rightarrow 2_{21}$ and
35 074.0 MHz = $2_{12} \rightarrow 3_{03}$

of the first excited state of the mode ν_{12} (state "7" in [2c]). From the position of the energy levels involved in these five transitions, as illustrated in Fig. 2, connection a), it had to be concluded that the 10P(18)/(12–18) laser frequency of 28 583 293 MHz (953.4360 cm^{-1}) was closely coincident with the rovibrational transition from the 1_{11}-level in the G.S. of furazan to the 2_{12}-level of the excited state $\nu_{12} = 1$. Since the

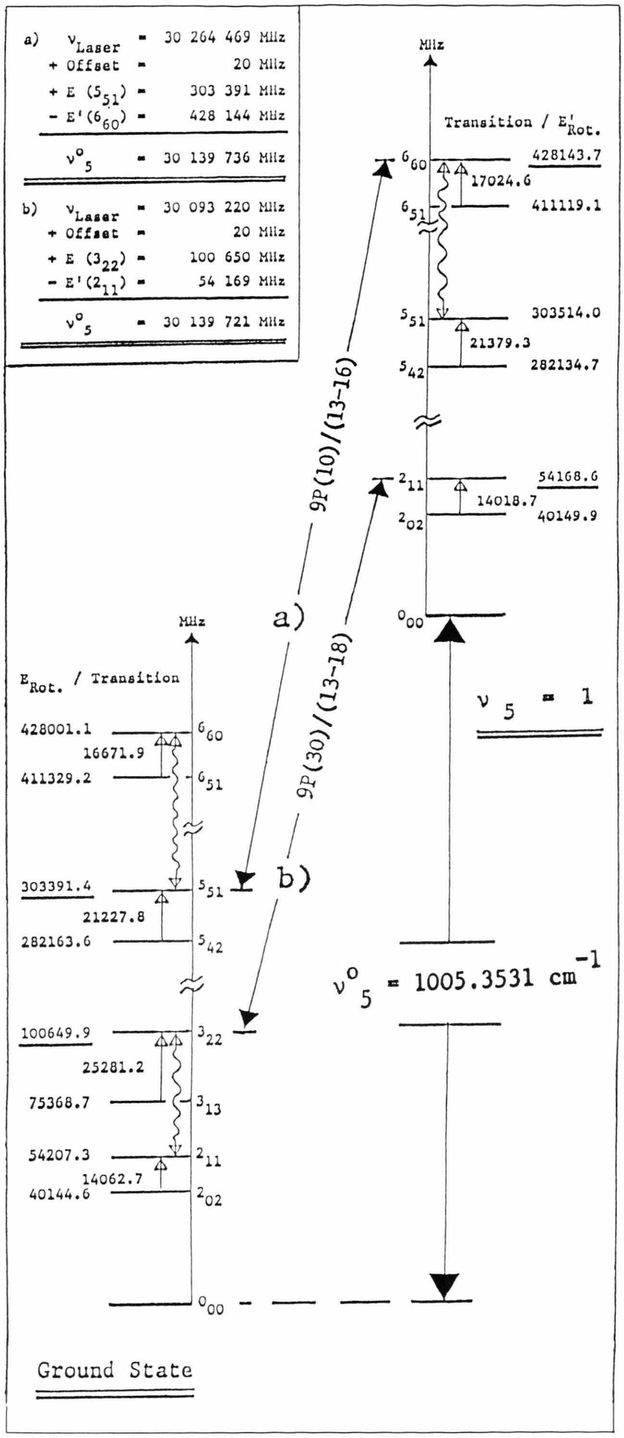


Fig. 3. Identified coincidences of CO_2 laser lines with rovibrational transitions of the ν_5-band of furazan.

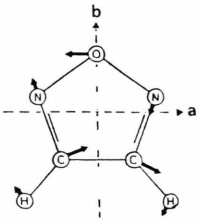
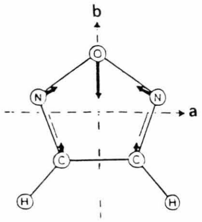
purely rotational energy of both these levels with reference to their respective rotational ground states (0_{00}) was known from previous work [2c], the band origin ν_{12}^0 followed by simple arithmetic (given in the upper left corner of Fig. 2) as 28 558 572 MHz (952.6113 cm^{-1}).

Two further near-coincidences of laser lines of the $^{12}C^{18}O_2$-species with rovibrational transitions of the ν_{12}-band of furazan were found subsequently and their interpretations, which are illustrated in Fig. 2, connections b) and c), were based on considerations analogous to those given above. To achieve optimal coincidence of the 10 P(20)/(12−18) laser frequency (connection b)) with the $4_{23} \leftarrow 4_{22}$ transition of furazan, it was necessary to tune the laser (via the Piezo-control, Fig. 1) towards the upper edge of its gain curve. This deviation from the centre frequency of the laser line was estimated as $+(20 \pm 10)$ MHz, and is taken into account in the calculation of ν_{12}^0 as "offset" in Figure 2.

b) The A_1 Mode at 1005 cm^{-1}

Numerous microwave frequencies which gave LMDR signals could neither be correlated with rotational transitions within the G.S. of furazan nor with known transitions within the excited states $\nu_5 = 1$ or $\nu_4 = 1$. Consequently, these LMDR signals had to remain uninterpreted. However, with the isotopomer $^{13}C^{16}O_2$ as the lasing gas, four pre-assigned microwave frequencies produced LMDR effects with the laser line 9 P(10) at 1009.5140 cm^{-1}. Two of these MW frequencies corresponded with known Q-branch transitions in the G.S. of furazan, and the other two correlated with the same pair of rotational transitions within the state $\nu_5 = 1$. Since neither the two G.S. transitions nor the two excited state transitions share a common energy level (Fig. 3, connection a)), population transfer through collisions [6] ("wavy" arrows in Fig. 3) between the levels $5_{51} \leftrightarrow 6_{60}$ within each vibrational state had to be invoked to explain the occurrence and to rationalise the lower intensity of two of the four observed LMDR signals. From this, the rovibrational transition $6_{60} \leftarrow 5_{51}$ was inferred as the most probable candidate to be in near coincidence with the laser line 9 P(10)/(13−16). As indicated in the top left corner of Fig. 3, this resulted in a value of $\nu_5^0 = 30\,139\,736$ MHz (1005.3532 cm^{-1}) for the band origin. – Critical inspection of Fig. 3 reveals, however,

Table 1. General information and band origins for the vibrations ν_{12} and ν_5 of furazan.

Vibr. Mode, Level	$\nu_{12}=1$	$\nu_5=1$
State index previously [2c]	"7"	"8"
C_{2v} symmetry species	B_1	A_1
Description	antisymmetric in-plane vibration	symmetric in-plane vibration
Dipole selection rule	μ_a	μ_b
IR band contour [2c]	A-type	B-type
Diagrammatic illustration		
Band origin ν^0 (in cm^{-1})	952.611(2)	1005.353(2)

that an alternative interpretation of this experiment, under neglect of the intensity ratios, would be that the 9 P(10)/(13–16) CO_2 laser line is in near coincidence with the transition $6_{51} \leftarrow 5_{42}$ in furazan, with population transfers $5_{42} \leftrightarrow 6_{51}$ in both states. This would result in a value of 30 135 543 MHz (1005.2131 cm^{-1}) for the band origin ν_5^0. Hence, to confirm or revise the interpretation suggested above, LMDR experiments were continued with $^{13}C^{18}O_2$ as the laser gas. A near coincidence between its 9 P(30)/(13–18) laser line and the rovibrational transition $2_{11} \leftarrow 3_{22}$ (alternative: $2_{02} \leftarrow 3_{13}$) of the ν_5-band of furazan (Fig. 3, connection b)) gave $\nu_5^0 = 30\,139\,721$ MHz (1005.3527 cm^{-1}) in good agreement with the preferred interpretation of the first experiment on this band.

c) Summary of LMDR Results

While no LMDR signals attributable to the weak ν_4 mode of furazan were found in the course of these experiments, the vibrational centre frequencies of the fundamentals ν_{12} and ν_5 appear to have been determined with an internal consistency of ± 0.0003 cm^{-1}. However, for the gauging of the true uncertainty of these results it has to be observed that in three cases (Fig. 2, connection b) and both connections in Fig. 3) the laser frequencies were detectably below the centre of the rovibrational transitions of furazan, which themselves are estimated ~120 MHz (0.004 cm^{-1}) wide (full width at half height). It follows therefore that the frequencies of the five laser lines must at least have been within the Doppler width of the rovibrational transitions of furazan, i.e. within ~60 MHz (0.002 cm^{-1}) of the line centres. Since no two-photon transitions [4] were observed in any of the five successful experiments, we arrive at the values given in Table 1 for the band origins, with the uncertainties on the conservative side. More precise values for the band origins are expected to lie in the upper half of the quoted range for both modes.

IV. Discussion

The limitation in accuracy of the LMDR technique in the present case arises from the fact that exact coincidence, or coincidence to within some 10 MHz, of a CO_2 laser frequency with a rovibrational transition of a sample is generally highly unlikely, and the difference between those two frequencies can only be estimated here on the basis of qualitative considerations. This, in turn, prevents the utilisation of the inherent accuracy of the rotational data. For that reason, fractions of a MHz have been ignored in the calculation of the band origins in Figs. 2 and 3. The inability to measure the "off-set" of the laser from its centre frequency to a higher accuracy than ±10 MHz further adds to the overall uncertainty in the derived ν^0-values. The IR-transitions could have only been measured with higher accuracy via the observation of two-photon saturation dips [4]. Unfortunately, in furazan the situation proved too unfavourable to allow the observation of this type of signal under the experimental conditions used.

The limited accuracy of the LMDR results in combination with the sparsity of identified near-coincidences between laser and furazan transition frequencies in the present case rules out a revision, let alone a refinement, of the rotational information from DRM microwave techniques which was inserted into the analysis. Nevertheless, the present study combines with success the results from rotational spectroscopy with an experimental technique (LMDR) which reaches over into vibrational (infrared) spectroscopy. The relative ease with which definite conclusions could be reached from the reported LMDR experiments within a rather short period (two weeks) and despite the occurrence of so many "uninterpretable" LMDR signals in furazan seems to provide clear proof that microwave spectroscopy, when carried out under double resonance modulation, can provide information of much further reaching relevance than when carried out under Stark effect modulation. Thus, the success of the present work rests to a large extent on the fact that the pure rotational spectra of the excited states under examination were known extensively in advance. This made possible the instant distinction between the few LMDR signals which could be interpreted and the great number of "uninterpretable" ones. A discussion of the origin and significance of the latter variety is omitted here.

Rotational and vibrational spectroscopy have of course always been known to be fundamentally interconnected. They are nowadays drawing together with respect to their instrumental capabilities and they complement each other in a highly satisfactory manner. However, this "merger" rests entirely on the absence of contradictions between the separate results achieved by either method. In view of that, the most distinctive feature of the LMDR technique has to be seen in the fact that it alone bridges the gap from rotational to vibrational spectroscopy through actual experiment.

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[1] O. L. Stiefvater, Z. Naturforsch. **30a,** 1742, 1756 (1975), and papers quoted there.

[2] O. L. Stiefvater, Z. Naturforsch. a) **43a,** 597 (1988); b) **43a,** 607 (1988); c) **45a,** 1117 (1990); d) **45a,** 1131 (1990).

[3] D. H. Christensen, P. W. Jensen, J. T. Nielsen, and O. F. Nielsen, Spectrochim. Acta **29 A,** 1393 (1973).

[4] H. Jones, in: Modern Aspects of Microwave Spectroscopy (G. W. Chantry, ed.), Academic Press, London 1979.

[5] C. Freed, A. H. M. Ross, and R. G. O'Donell, J. Mol. Spectroscopy **49,** 439 (1974).

[6] T. Oka, J. Chem. Phys. **45,** 754 (1966).