

Infrared-microwave double resonance spectroscopy of GeH₄

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The highly sensitive method of infrared-microwave double resonance in a laser cavity has been used to observe the distortion-induced rotational spectrum for the ground vibrational state of GeH₄. Coincidences between the (ν_2 , ν_4) fundamental vibration-rotation bands and infrared laser lines (CO₂, isotopic CO₂, and N₂O) were used for detection of the very weak rotational transitions. Four resonances with $J = 18$ and one resonance with $J = 11$ were assigned. The frequencies of these resonances give accurate information on the quartic, sextic, and octic tensor distortion coefficients of GeH₄.

I. INTRODUCTION

Recent infrared-radiofrequency double resonance experiments on CH₄^{1,2} and SiH₄³ have demonstrated that this method has sufficient sensitivity for observing the weak distortion-induced pure rotational transitions between components of centrifugal distortion multiplets in the ground state of tetrahedral molecules.⁴⁻⁷ Although the double resonance method does not allow us to observe transitions systematically (because we have to rely on coincidences between the laser lines and the molecular transitions), the constants determined from these experiments have aided the more extensive studies using conventional microwave spectroscopic methods.⁸⁻¹⁰ In this paper we report an observation of the "forbidden" rotational Q -branch transition of GeH₄ by using the double resonance method. The R -branch transitions in the far infrared region have already been reported by Ozier and Rosenberg.¹¹

The double resonance experiments of GeH₄ have two difficulties which did not exist in those of CH₄^{1,2} and SiH₄³: (i) The infrared active ν_4 -band at 821 cm⁻¹ is much lower than the frequencies of 10 μ m lasers and the ν_2 -band at 931 cm⁻¹ is infrared inactive.¹² Therefore we had to rely on the coincidence (with the laser) of either at the tail of the ν_4 -band or ν_2 -band which is induced by the Coriolis interaction between ν_2 and ν_4 (see Ref. 13 and references therein for infrared spectrum of GeH₄). In either case we had to work in high J region. This necessitated a more time consuming search in the microwave region rather than in the radiofrequency region as in CH₄^{1,2} and SiH₄³. (ii) The Ge atom has five isotopes, all of which are naturally abundant (36.4~7.7%). A small mass dependence of the vibration-rotation transition frequencies makes individual signals weaker. Also, since we do not know the mass dependence of the centrifugal constants, we can be sure of assignments of only those double resonance signals which are related with each other through a common level pumped by the infrared laser. In deriving constants, we neglected the isotropic dependence based on the observation¹⁴ that the ¹³CH₄ spectrum appeared close to the CH₄ spectrum, and on the theoretical prediction which supports the small isotopic dependence.¹⁵ It may be noted that the reduced mass $4m_{\text{H}}m_x/(m_x + 4m_{\text{H}})$ differs by 1.98% between ¹²CH₄ and ¹³CH₄ but by only 0.43% between the lightest (⁷⁰GeH₄) and the heaviest (⁷⁶GeH₄) isotopic modifications of GeH₄.

II. DOUBLE RESONANCE EXPERIMENT

A. Operation

Infrared-microwave double resonance experiments are conducted by inserting into a CO₂-N₂O laser cavity a coaxial microwave cell containing low pressure (15~20 mtorr) GeH₄ gas and applying high microwave power (1~20 W). The high electric field ($E \approx 50$ V/cm) of the microwave radiation compensates for the very small distortion-induced dipole moment ($\mu \approx 10^{-4} \sim 10^{-2}$ D) of the molecule so that the transition moment $\mu E/h$ is sufficiently large to saturate rotational transitions. The microwave frequency is swept, and the laser output power is monitored. The laser pumps molecules with a certain velocity component and thus bleaches holes in the Maxwellian velocity profile of the molecules. When the microwave frequency is tuned to resonance, the hole is filled, causing the load characteristics of the gas and hence the laser power to change sharply.¹⁶

The apparatus used is similar to that used for earlier infrared-radiofrequency double resonance experiments¹⁻³ and two-photon experiments,¹⁷ except that the impedance matching of the coaxial cell is extended to 10 GHz in order to cover high J lines. A microwave sweeper and traveling wavetube amplifiers were used as the high power microwave source. More details of the apparatus will be discussed elsewhere.¹⁸

B. Assigned resonances

The initial search for double resonance signals was attempted for laser lines which showed passive Q -switching for in-cavity GeH₄.¹⁹ Several radiofrequency resonances were found, but the attempt to assign their frequencies to the spherical top multiplet pattern²⁰ was not successful even in the light of a recently measured infrared spectrum of GeH₄.²¹ Definite assignments of resonances were possible only after the measurement was extended to the microwave region.

The energy level diagrams of double resonance for which the rotational levels in the ground state are definitely assigned are shown in Fig. 1. In the energy level scheme shown in Fig. 1(a), the $P(36)$ line of the C ¹⁸O₂ laser in 10.3 μ m band is coincident with an infrared transition starting from the F₂⁽⁴⁾ level with $J = 18$ (*ortho*-GeH₄ with $I = 1$ and negative parity). We do not know the assignment of this infrared transition; neither ν_2 nor allowed ν_4 transitions are predicted at this frequency, and

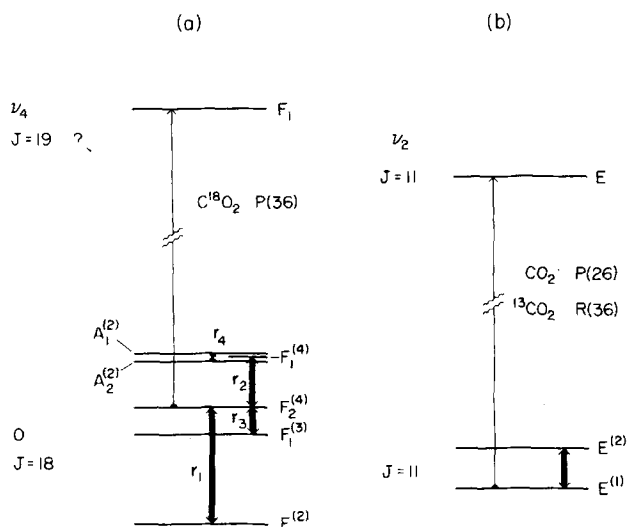


FIG. 1. Energy level schemes for the double resonance experiment in GeH₄. In (a) the P(36) C¹⁸O₂ laser line at 937.765 cm⁻¹ pumps molecules in the F₂⁽⁴⁾ level of the J=18 centrifugal distortion multiplet. The microwave transitions r_1 , r_2 , and r_3 of *ortho*(F)-GeH₄ related to these pumped levels are observed. The signal r_4 for *meta*(A)-GeH₄ was observed using the P(30) CO₂ line. In (b) the P(26) CO₂ laser line at 938.688 cm⁻¹ and the R(36) ¹³CO₂ laser line at 938.778 cm⁻¹ pumps [*para*(E)-GeH₄] in the E⁽¹⁾ level of J=11 and microwave transition E⁽²⁾ → E⁽¹⁾ is observed. In both, many other levels of the multiplets are omitted for clarity.

we think it is most likely the forbidden ($\Delta R = \pm 1$) R(18) transition for the ν_4 fundamental. However from the frequency relation of the observed resonances [shown in Fig. 1(a) with bold arrows r_1 , r_2 , and r_3], we are certain of their rotational assignments. Since these three rotational transitions share a common level, they must belong to the same Ge isotopic species but we do not know which isotope.

Figure 1(a) shows also a rotational transition (r_4) for *meta*(A)-GeH₄ (with $I=2$). This radiofrequency transition was observed by using the P(10) CO₂ laser line in

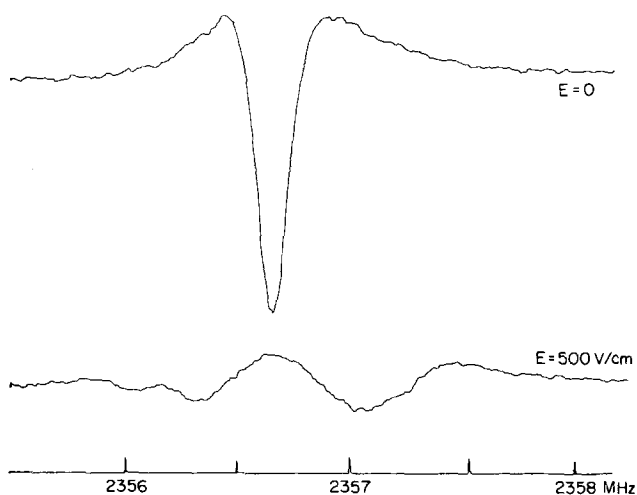


FIG. 2. The J=11 E⁽²⁾ - E⁽¹⁾ double resonance signal at 2356.68 MHz with and without applied inhomogeneous dc electric field. The pressure of the gas is 15 mtorr, and the time constant of detection is 0.3 sec.

TABLE I. Double resonance signals with definite rotational assignments.

Rotational transition	Frequency (MHz) ^a	Laser lines ^b	Infrared transition
J=18	$F_1^{(4)} - F_2^{(4)}$	C ¹⁸ O ₂ P(36)	$\nu_4 - R(18)^c$
	$F_2^{(4)} - F_1^{(2)}$	C ¹⁸ O ₂ P(36)	
	$F_2^{(4)} - F_1^{(3)}$	C ¹⁸ O ₂ P(36)	
	$A_1^{(2)} - A_2^{(2)}$	CO ₂ P(10)	
J=11	$E^{(2)} - E^{(1)}$	CO ₂ P(26)	$\nu_2 - Q(11)$
	$E^{(2)} - E^{(1)}$	¹³ CO ₂ R(36)	

^aThe uncertainty of the frequency is ± 0.1 MHz.

^bThe laser lines are all in the 10 μ m band.

^cThis is most likely the secondly allowed line but is not conclusive.

10.4 μ m band. Its frequency agrees with the calculated value using r_1 , r_2 , and r_3 to within our experimental uncertainty of 0.1 MHz. Many other fine structure levels which are not related to the observed double resonance signals are omitted in Fig. 1(a) for clarity.

Figure 1(b) shows an energy level diagram in which the *para*(E)-GeH₄ takes part. The P(26) line of the CO₂ laser and the R(36) line of the ¹³CO₂ laser in 10.4 μ m are coincident with Q-branch transitions starting in the E⁽¹⁾ level. We are certain of this rotational assignment because of the observed first order Stark effect of the resonance and from the high resolution infrared spectrum.²¹ The observed double resonance signals with and without a dc electric field are shown in Fig. 2. The dc electric field was applied to the coaxial cell and the inhomogeneity of the field smeared out the expected M structure, but the magnitude of the shift confirms the assignment. More detailed analysis of the Stark shift using a parallel plate rf cell will be published later. The relation between the two infrared transitions coincident with the P(26) line of the CO₂ laser and with the R(36) line of the ¹³CO₂ laser is not established. The two laser lines are separated by 0.10939 cm⁻¹, and we believe these GeH₄ transitions correspond to different isotopic species. Then the fact that the measured difference of 0.08 MHz between the two double resonance frequencies is within our experimental error gives support to the assumption used later that the isotope dependence of the distortion constants is very small. These two laser lines may be useful for isotope separation of Ge.

The frequencies of rotationally assigned double resonance signals are summarized in Table I.

C. Unassigned resonances

Many signals were left unassigned. They are summarized in Table II. The first two lines in Table II fit very well to the calculated frequencies, and the suggested assignments are most likely right. However our attempts to confirm their assignments by observing related double resonance signals were unsuccessful. Other signals in Table II could not be fitted to the tetrahedral pattern up to J=30. They must correspond either

to higher J lines or to lines in an excited vibrational state. In particular, the four relatively strong signals observed by the C¹⁸O₂ $P(36)$ line are likely to be the excited state lines in view of the three assigned ground state lines listed in Table I. We have not yet devised a method to discriminate between a microwave transition in the excited state and one in the ground state.

III. ANALYSIS

The splitting of a J manifold of tetrahedral molecules due to tensor centrifugal distortion has been worked out up to sextic terms by Moret-Bailly and his collaborators^{22,23} and by Watson and his collaborators.^{20,24}

Ozier extended Watson's treatment to the octic terms.²⁵ We used the perturbation formula in the Watson-Ozier formalism,

$$E_t = [D_t + H_{4t}J(J+1) + L_{4t}J^2(J+1)^2]f + [H_{6t} + L_{6t}J(J+1)]g + L_{8t}h + (H_{6t}^2/D_t)\bar{g}, \quad (1)$$

where D_t is the quartic, H_{4t} and H_{6t} are the sextic, and L_{4t} , L_{6t} , and L_{8t} are the octic tensor distortion coefficients. Values of the numerical factors f and g were given by Kirschner and Watson,²⁴ and those of h and \bar{g} were given by Ozier²⁵ up to $J=20$.

The three $J=18$ *ortho*(F)-GeH₄ double resonance signals listed in Table I enabled us to determine three linear combinations of distortion constants as listed in Table III. These three combinations give the calculated value for the *meta*(A)-GeH₄ double resonance signal of 895.80 MHz which agrees with the observed values listed in Table I to within 10 kHz. Thus we see the consistency of the four resonances. The $E^{(3)} - E^{(2)}$ and the $E^{(2)} - E^{(1)}$ transition with $J=18$ for *para*-GeH₄ are predicted to be at 9615.29 MHz and 22555.10 MHz, respectively, by using these combinations.

If we add the frequency of the $J=11$ resonance by neglecting the possible isotope dependence, we can separate D_t and H_{4t} as shown in Table III. The number of observed resonances is not sufficiently high to separate octic distortion terms. Their contribution to D_t is of the order of 50 Hz and to H_{4t} and H_{6t} about 0.5 Hz. Therefore for approximate calculation, we can neglect

TABLE II. Unassigned double resonance signals.

Laser lines	Frequency (MHz) ^a	Possible assignment
C ¹⁸ O ₂ $R(16)$	216.17	$J=7 F_1^{(2)} - F_2^{(2)}$
C ¹⁸ O ₂ $R(36)$	543.69	$J=13 F_1^{(4)} - F_2^{(3)}$
	189.08	
C ¹⁸ O ₂ $P(36)$	3666.91	Vibrationally excited state
	2666.83	
	2621.51	
	2541.05	
C ¹⁸ O ₂ $P(26)$	1818.52	
CO ₂ $P(28)$	92.72	
	1634.8 ± 0.5	

^aThe uncertainty of the frequencies is 0.2 MHz unless otherwise noted.

TABLE III. Tensor centrifugal distortion constants of GeH₄.

$J=18$	
$D_t + 342H_{4t} + 116964L_{4t}$	65 980.3 Hz
$H_{6t} + 342L_{6t}$	2.830 Hz
L_{8t}	-6.200×10^{-4} Hz
$J=18$ and $J=11$	
$D_t - 45144L_{4t} - 13201L_{6t}$	67 765.5 Hz
$H_{4t} + 474L_{4t} + 38.6L_{6t}$	-5.220 Hz
$H_{6t} + 342L_{6t}$	2.830 Hz

these octic terms.

The vibration-rotation theory of tetrahedral molecules developed by Hecht²⁶ gives the analytic expression for D_t as

$$D_t = \frac{1}{5} \left(\frac{1}{\nu_2^2} - \frac{\zeta_{23}^2}{\nu_3^2} - \frac{\zeta_{24}^2}{\nu_4^2} \right) B^3. \quad (2)$$

By using molecular constants given by Kattenberg, Gabes, and Oskam¹³ [$\nu_2 = 930.6$ cm⁻¹, $\nu_3 = 2111.46$ cm⁻¹, $\nu_4 = 821.0$ cm⁻¹, $B = 2.6969$ cm⁻¹, $\zeta_{23} = 0.836$, and $\zeta_{24} = 0.548$], we obtain the theoretical value of D_t to be 64.97 kHz, which agrees reasonably well with our value of 67.77 kHz.

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