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ISOTOPE SHIFTS AND THE ROLE OF FERMI RESONANCE IN THE CO₂ INFRARED MASER*

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It is well known that isotope shifts for electronic energy levels in atoms and molecules are relatively small (typically less than 1 part in 10⁴) while shifts of vibrational levels in molecules can be quite large (on the order of several parts in 100) because of the direct dependence of vibrational and rotational constants on the masses of the individual atoms which form the molecule. In this Letter we wish to report the observation of laser action in several *P* transitions of the 00⁰1 – 10⁰0 and 00⁰1 – 02⁰0 bands of C¹²O₂¹⁸. We also wish to point out the contribution of Fermi resonance to the large observed isotope shift and the importance of Fermi resonance to the kinetics of the laser.

The experiments were performed in a 1-meter Pyrex discharge tube with internal electrodes and gold-coated cavity mirrors in a hemispherical configuration. C¹²O₂¹⁸ was formed by combustion of C₂H₂ in 94% enriched O₂¹⁸ and the resultant gas mixture of H₂O¹⁸ and C¹²O₂¹⁸ was found to give laser action readily under the discharge and pressure conditions previously reported^{1,2} for C¹²O₂¹⁶. The output radiation passed through the flat (silicon) mirror and was detected with a cooled gold-doped germanium detector. Frequency measurements were made with a grating monochromator using a 64-mm × 64-mm grating with 75 lines per mm.

The results of our measurements on the dominant laser transition of C¹²O₂¹⁸ are compared with the results of Patel² on C¹²O₂¹⁶ in Table I.

The weaker 00⁰1 – 02⁰0 laser band we have

observed in a single *P* transition at 956.5 cm⁻¹ for C¹²O₂¹⁸ and at 1046.0 cm⁻¹ for C¹²O₂¹⁶. It is interesting to note that we observe isotope shifts of about +11% for the 00⁰1 – 10⁰0 band while a much smaller effect would be expected if the levels 10⁰0 and 02⁰0 were not in Fermi resonance.

The positions of the vibrational levels for C¹²O₂¹⁸ have been calculated and observed (in some cases) by Eggers and co-workers.^{3,4} Table II is a summary of these data for levels pertinent to the CO₂ infrared maser. Note that the isotope effect is greater for the unperturbed 10⁰0 level than for the unperturbed 02⁰0 level with the net result that the relative positions of the two unperturbed levels are reversed,

Table I. Comparison of observed frequencies of *P* transitions in C¹²O₂¹⁶ and C¹²O₂¹⁸ for the 00⁰1 → 10⁰0 band.

C ¹² O ₂ ¹⁸		C ¹² O ₂ ¹⁶ a	
Identification	ν (cm ⁻¹ , vac)	Identification	ν (cm ⁻¹ , vac)
<i>P</i> (18)	1070.6	<i>P</i> (14)	949.5
<i>P</i> (20)	1069.0	<i>P</i> (16)	947.7
<i>P</i> (22)	1067.4	<i>P</i> (18)	945.9
<i>P</i> (24)	1065.8	<i>P</i> (20)	944.2
<i>P</i> (26)	1064.2	<i>P</i> (22)	942.3
		<i>P</i> (24)	940.5
		<i>P</i> (26)	938.6

^aValues taken from Ref. 2 and rounded to four figures.

Table II. Frequencies in cm^{-1} of the band centers of pertinent transitions in $\text{C}^{12}\text{O}_2^{16}$ and $\text{C}^{12}\text{O}_2^{18}$.

	$\text{C}^{12}\text{O}_2^{16}$	$\text{C}^{12}\text{O}_2^{18}$
ν_3	2349.3 ^b	2314.0 ^d
$2\nu_2(\text{unp})^a$	1328.6 ^c	1311.7 ^e
$\nu_1(\text{unp})^a$	1345.3 ^c	1265.1 ^e
$2\nu_2$	1285.5 ^b	1346.6 ^d
ν_1	1388.3 ^b	1230.2 ^f
$\nu_3-\nu_1$	961.0	1083.8
$\nu_3-2\nu_2$	1063.8	967.4

^aCalculated values for these levels unperturbed by Fermi resonance.

^bSee G. Herzberg, Molecular Spectra and Molecular Structure (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), Vol. II.

^cCalculated from values for Fermi interaction given by D. M. Dennison, *Phys. Rev.* **41**, 304 (1932).

^dFrom observations in Ref. 4.

^eCalculated from constants in Refs. 3 and 4.

^fCalculated from observed Fermi shift in Refs. 3 and 4.

and the Fermi resonance then repels the levels further apart to their observed positions.

The problem of two closely spaced levels in resonance was first solved by Fermi⁵ and refined by Dennison.⁶ The solution can be written

$$E_{1,2} = \bar{E}_{12} \pm \frac{1}{2}(4|W_{12}|^2 + \delta^2)^{1/2}, \quad (1)$$

where \bar{E}_{12} is the averaged position of the unperturbed levels, W_{12} is the matrix element of the perturbation function for the two levels, and δ is the separation of the two levels. For $\text{C}^{12}\text{O}_2^{16}$, Dennison⁷ has found $W_{10^0, 02^0} = 50.4 \text{ cm}^{-1}$ and $\delta = 16.7 \text{ cm}^{-1}$. Using these values one obtains values for the unperturbed 10^0 and 02^0 levels in $\text{C}^{12}\text{O}_2^{16}$. For $\text{C}^{12}\text{O}_2^{18}$ we were able to use observed⁴ values to obtain 02^0 and calculated^{3,4} constants to obtain the unperturbed 10^0 and 02^0 levels for $\text{C}^{12}\text{O}_2^{18}$. By subtracting the calculated value of the unperturbed 02^0 level from the observed value, we established the Fermi shift to be $+34.9 \text{ cm}^{-1}$ for 02^0 and then subtracted 34.9 cm^{-1} from the unperturbed value of 10^0 to obtain its final position.

The positions of the actual laser transitions were calculated from the data shown in Table II using rotational constants⁴ for $\text{C}^{12}\text{O}_2^{18}$, corrected for Fermi interaction of the levels 10^0 and 02^0 . These constants are

$$B_{00^0 1} = 0.34392 \text{ cm}^{-1}; \quad B_{02^0 0} = 0.34722 \text{ cm}^{-1};$$

$$B_{10^0 0} = 0.34637 \text{ cm}^{-1}. \quad (2)$$

The calculated values for the laser transitions are in complete agreement with the observed values to the number of significant figures quoted in Table I.

It is interesting to note that the dominant laser band is the $00^0 1 - 10^0 0$ transition in both cases. This is consistent with optical-absorption data⁹ which shows the $10^0 0 - 00^0 1$ transition probability to be roughly twice the $02^0 0 - 00^0 1$ transition probability in $\text{C}^{12}\text{O}_2^{16}$, taking wavelength and population factors into account. Normally one expects the $10^0 0 - 00^0 1$ (binary)¹⁰ band to be much stronger⁵ than the $02^0 0 - 00^0 1$ (ternary)¹⁰ band. That the observed absorptions are comparable stems from the fact that the absorption transitions originate from levels in resonance. Thus the perturbed states can be represented as mixtures of the unperturbed states and the $02^0 0 - 00^0 1$ absorption becomes enhanced by the presence of $10^0 0$ unperturbed wave function in the wave function representing the perturbed $02^0 0$ state. For $\delta > 0$ the mixed wave function representing the perturbed $10^0 0$ state will always contain relatively more of the unperturbed $10^0 0$ wave function with the result that the $10^0 0 - 00^0 1$ band dominates in laser emission.

The question of depopulation mechanisms of the $10^0 0$ level is presently under investigation, and it is evident that the Fermi interaction will have to be taken into account to describe the system completely. There is experimental and theoretical evidence^{11,12} that the ν_2 mode has the fastest collisional relaxation rate of the three vibrational modes and that the ν_1 mode relaxes through interaction with the ν_2 mode. Radiative relaxation to the $01^1 0$ level also depends on the Fermi resonance since the $10^0 0 - 01^1 0$ (binary) transition would normally be weaker than the $02^0 0 - 01^1 0$ transition.⁸

There are many other possible isotopic forms of CO_2 which should give laser action at different frequencies. In addition, the method of isotopic substitution is widely applicable to all known molecular lasers¹³ and should provide numerous additional coherent sources of infrared radiation.

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RELAXATION NARROWING OF MÖSSBAUER GAMMA RAYS*

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Time-delayed coincidence measurements on Mössbauer gamma rays have demonstrated changes in resonance line shapes, including broadening and narrowing to less than natural linewidths.^{1,2} These changes, which were first analyzed in terms of classical radiation theory² and later quantum mechanically,³ are due to the modulation of the normally exponential decay of the resonance emission by electronic gating of the detector circuits. We wish to point out in this Letter that there exists a class of naturally occurring relaxation phenomena which may cause similar effects for Mössbauer gamma rays due to atomic and solid-state effects.

We consider systems in which the emission of the resonance gamma ray is preceded by a relatively energetic nuclear event, such that the local environment is initially disturbed from equilibrium, and subsequently relaxes in a time comparable to the gamma-ray lifetime. The relaxation process causes a modulation of the normally exponential decay analogous to modulations caused by instrumental means. The class of such relaxation phenomena includes the excitation of localized lattice-vibrational modes, temporary changes in atomic force constants, higher charge states, and atomic states which produce appreciably different quadrupole splittings in the excited and equilibrium states. We will here discuss one example, the case of heated localized modes.

Dilute impurities in regular lattices have locally distorted vibrational spectra when the mass or force constant of the impurity atom differs from the host atoms, and for significantly lighter impurities or greater force con-

stants, there is a localized vibrational mode which lies above the vibrational band of the host.⁴ The relaxation time of the localized mode depends upon its separation from the band and its anharmonicity: Relaxation times are estimated to be as much as 10^4 periods of the highest frequencies in the band.⁵⁻⁷ We consider a radiating Mössbauer atom vibrating in a long-lived localized mode of frequency Ω_L , which has been stimulated to a vibrational amplitude greater than the equilibrium value. The mean-squared displacement x^2 of the impurity averaged over a period of the localized mode is assumed to relax with a single relaxation time $1/\gamma$ according to

$$x^2 - \langle x^2 \rangle = [x_0^2 - \langle x^2 \rangle] e^{-\gamma t}, \quad (1)$$

where x_0^2 and $\langle x^2 \rangle$ are the initial and thermally relaxed values. The theory of Lax and Waller⁸ shows that the usual form of the dependence of the recoil-free fraction on the displacement of the atoms in thermal equilibrium,

$$\langle f \rangle = \exp(-\langle x^2 \rangle / \lambda^2),$$

is justified even in the presence of normal mode damping, provided that the relaxation time is sufficiently long, $\hbar\gamma \ll kT$, $\gamma \ll \Omega_L$. Hence, we can calculate the time dependence of the gamma-ray intensity $|E(t)|^2$ and the corresponding line shape $|E(\omega)|^2$ by taking explicit account of the relaxation given by Eq. (1) and the transient $f = \exp(-x^2/\lambda^2)$. Adapting the usual equa-