Laser Stark Spectroscopy and Isotopic Separation

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ABSTRACT

A potentially useful scheme for photoselective isotope enrichment is presented. The selective laser excitation step is accomplished by utilizing the Stark effect to shift molecular transitions into resonance with laser frequencies. The method is demonstrated for isotope separation of ^{13}C, ^{15}N and ^{2}H. Laser Stark spectroscopy can sensitively detect as few as 10^9 molecules in the optical path, thus the isotopic separation can be achieved from industrial sample mixtures containing natural abundances. A comparison of the isotopic enrichment efficiency using the present method of "exact" resonance and the previously used method of "near" resonance excitation is also given.

I. INTRODUCTION

Four principal methods: photoionization of atoms[1], photodissociation or photopredissociation of molecules[2], photo-deflection of atomic or molecular beams[3], and photoacceleration of chemical reactions[4], have been proposed and demonstrated for utilizing selective laser excitation to separate isotopes. All of these methods require a coincidence in frequency between a laser line and suitable resonant molecular absorption line, which allows one to excite exclusively one isotope species. Very often the laser frequency is only in near-resonance with molecular isotopes, thus the degree of isotopic enrichment is generally governed by the relative absorption cross-section of isotopes at that laser frequency.

The present stage of art in "laser technology" has initiated many laser lines and the advanced high resolution spectroscopic studies have accurately assigned many molecular transitions. However, only a few molecular energy levels coincide with the present laser frequencies in operation. Clearly, this limits the potential for laser isotope separation. To overcome this barrier, one can try to establish more laser frequencies (e. g., improving the laser tunability) or on the other hand one can also shift the energy level of the molecule by various chemical or physical means. The commonly used methods for shifting the molecular energy level are the substitutional effect, the solvent effect, the Zeeman effect and the Stark effect.

In this paper, we illustrate the selectivity of Stark tuning-laser excitation of $^{12}CH_3F$ and $^{13}CH_3F$ using the 9.4μ CO_2 laser lines, of $^{14}NH_3$ and $^{15}NH_3$ using 10μ CO_2 and N_2O lasers, and

of H_2CO and D_2CO using a 5.8μ CO laser. Then, we indicate the
possible second step of photoexcitation which could lead to the
isotope separation. Finally, we compare the separation effi-
ciency with and without the laser Stark excitation.

II. METHODS

A. Apparatus

A block diagram of the experimental set up is shown in
Figure 1. The CO laser, the CO_2 laser, and the N_2O and CO_2
lasers are used for separating the isotopes ^2H, ^{13}C and ^{15}N, re-
spectively. A Lansing piezoelectric stabilizer is employed to
lock the laser on the maximum of the gain profile. The laser
wavelength can be selected by tuning the angle of the plane grat-
ing. The desired laser frequency is then fitted into the spectrum
analyzer for calibration.

The Stark cell contains two Stark electrodes made of
optically flat stainless steel bars, each carrying the dimension
of 40x5x2.5cm. The electrodes are separated by a number of pol-
ished quartz spacers of 1-2 mm thickness and clamped by an alumi-
num cradle. This assembly is then suspended in the middle of the
absorption cell, and oriented so that the Stark field is either
parallel or perpendicular to the optical field direction corres-
ponding to the selection rules $\Delta M = 0$ or $\Delta M = \pm 1$.

The Stark pulse is generated by connecting a fixed D.C.
voltage to one electrode and an "operational" power supply to the
other. The variable voltage is switched on and off by the first
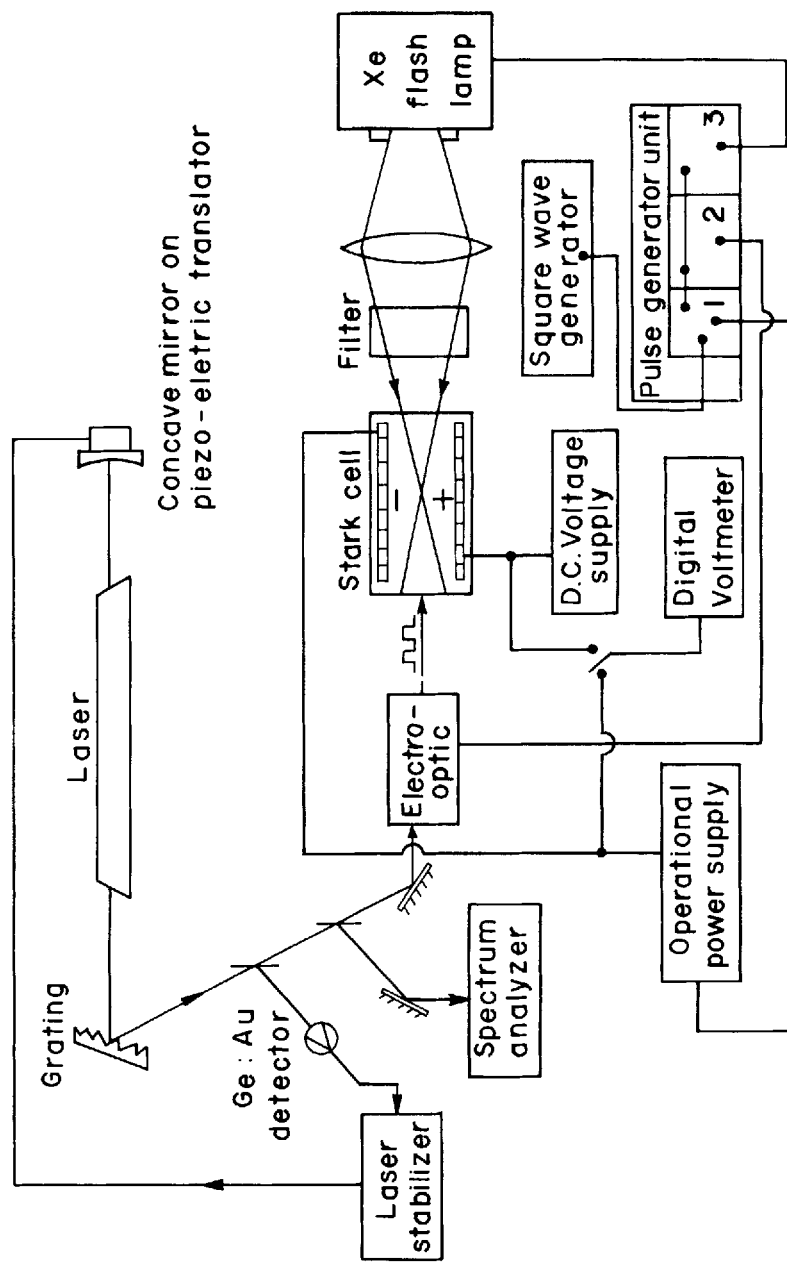unit of a pulse generator which is modulated by a square-wave

Figure 1. A schematic representation of the experimental arrangement for laser Stark spectroscopy and isotopic separation.

generator. A digital voltmeter is used to measure the voltage across the Stark electrodes.

The laser pulse is produced by using an eletro-optic device which is driven by the second unit of the pulse generator. The third unit of the same generator is used to trigger the Xe flash lamp. It is important to note that the pulses from units 1,2 and 3 of the pulse generator can be tuned to occur simultaneously or sequentially. Moreover, the pulse width and pulse interval are also adjustable.

B. Selective excitation and isotopic separation

1. H_2CO and D_2CO

The C=O stretching (ν_2) vibration-rotation bands of H_2CO and D_2CO near 5.8μ have been studied by Johns and McKellar[5] using the technique of laser Stark spectroscopy. They were able to detect Stark resonances between the H_2CO ν_2 band and thirteen CO laser lines in the range from 1708 to 1765 cm^{-1} and between the D_2CO ν_2 band and twelve CO laser lines in the range from 1693 to 1712 cm^{-1}. For the present purpose of laser Stark selective excitation, the most interesting and useful CO laser lines are the 14-13 (V'↔V") P (16) line at 1746.307 cm^{-1} and the 17↔16 P(8) line at 1701.149 cm^{-1}. Figure 2 shows the ν_2 band origin of H_2CO (bottom) and of D_2CO (top) and the Stark field required for the selective excitation. One should note that the 14↔13 P(16) CO laser line occurs just 0.3 cm^{-1} above the H_2CO ν_2 band origin, on the other hand the 17↔16 P(8) CO laser line is located just 0.47 cm^{-1} below the D_2CO ν_2 band origin. Clearly, the Q branch transition of relatively low J and K values, such as the $q_{Q_1}(1)$,

$^qQ_2(2)$, $^qQ_3(3)$ and $^qQ_4(4)$ transitions, can be successively swept into resonance with the laser line by the indicated Stark field. The negative Stark field means the molecular transition has lower wavelength than the corresponding laser line. Thus, if one chooses the laser line and the Stark field given in Figure 2, one could excite exclusively either the D_2CO molecules or the H_2CO molecules in a natural abundance mixture of formaldehyde.

High resolution spectroscopic studies on the excited singlet and triplet electronic states for both D_2CO and H_2CO were reported by several authors[6]. For H_2CO, the 0,0 band of the $\tilde{A}\ ^1A_2 \leftarrow \tilde{X}\ ^1A_1$ is located at 28,188 cm^{-1}, whereas that of the $\tilde{a}\ ^3A_2 \leftarrow \tilde{X}\ ^1A_1$ transition is appeared at 25,194 cm^{-1}. The isotope shift was found to be $(\nu_{0,0})_{D_2CO} - (\nu_{0,0})_{H_2CO} = 113$ cm^{-1}. Recently, the single vibronic photochemistry of formaldehyde has also been investigated extensively by Yeung and Moore[7]. They found a considerable shortening of the observed lifetimes at higher vibronic states, which was ascribed to the effect of predissociation. Using this fact, a "direct" photopredissociation method has been proposed and demonstrated[2-a,d,e] for isotopic enrichment. However, we believe that the highest selectivity for ^2H separation is available by Stark tuning one isotope of formaldehyde into resonance with an intense and monochromatic CO laser field, followed by exciting that isotopic into its photopredissociative vibronic state using a filtered UV flash lamp (~27,000 cm^{-1} for the singlet excitation and ~24,000 cm^{-1} for the triplet excitation).

$D_2 CO$

$^qQ_1(1)$ $^qQ_2(2)$ $^qQ_3(3)$ $^qQ_4(4)$
+27.88   +35.213   +46.98   +58.930 KV/cm

band origin ν_2
(1701·620 cm^{-1})

1696   1704 cm^{-1}

17-16 P(8) CO Laser
(1701.149 cm^{-1})

$H_2 CO$

$^qQ_1(1)$ $^qQ_2(2)$ $^qQ_3(3)$ $^qQ_4(4)$
-19.161   -25.892   -38.185   -53.927 KV/cm

ν_2 band origin
(1746.011 cm^{-1})

1742   1750 cm^{-1}

14-13 P(16) CO Laser
(1746.307 cm^{-1})
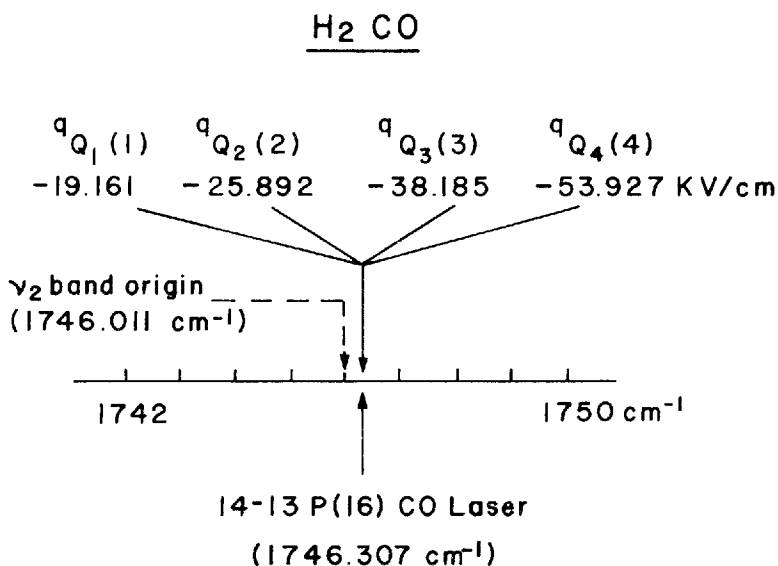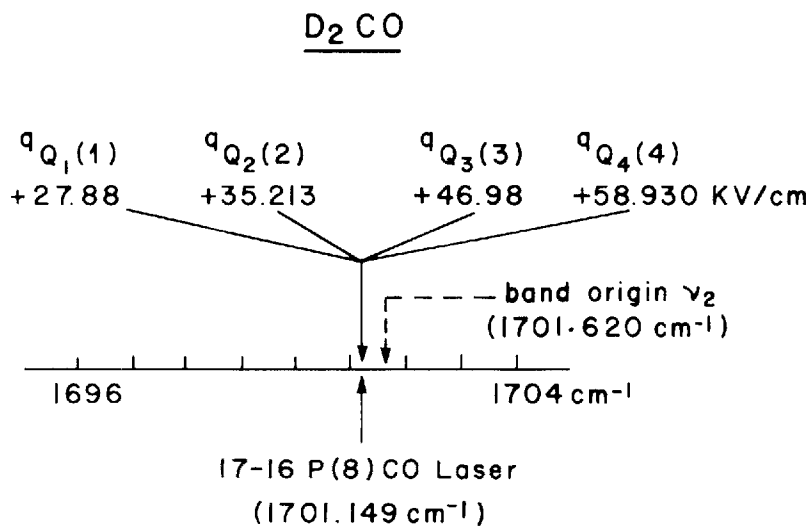
Figure 2. ν_2 band origin and Stark energy level diagram of
D_2CO(top) and of H_2CO(bottom).

2. $^{14}NH_3$ and $^{15}NH_3$

Shimizu recorded and analyzed[8] the Stark spectra for
the out-of-plane bending mode (ν_2) of $^{14}NH_3$ and of $^{15}NH_3$ by 10μ
lasers. He tuned the Stark field and observe ~100 coincidences
between the N_2O and CO_2 laser lines and the ν_2 band lines (J ≤ 7)
of $^{15}NH_3$ as well as those of $^{14}NH_3$. Especially, two Q-branch
bands were found to be covered by 17 N_2O lines (R30 to R37 and
P14 to P6) and 8 CO_2 lines (R8 to R2 and P38 to P32). An example
of the Stark tuning "exact" resonance excitation for $^{15}NH_3$ (top)
and $^{14}NH_3$ (bottom) molecules is summarized in Figure 3. One
should note that the Stark shift of ammonia is due mainly to the
repulsion between the inversion doublet pairs in its ground
state, and the s and a correspond individually to the symmetric
and asymmetric levels of the double well potential surface.

The electronically excited states of ammonia have been
examined by Douglas[9]. The molecule in its lowest electroni-
cally excited state was shown to have a planar geometry and an
N-H bond length greater than in the ground state. The (0,0)
band of the lowest electronic transition $\tilde{A}\ ^1A_2''$ (D_{3h}) ← $\tilde{X}\ ^1A_1(C_{3v})$
was assigned at 46,136 cm^{-1}. All vibronic bands associated with
this transition appear to be very diffuse, indicating a disso-
ciative state for $\tilde{A}\ ^1A_2''$ (D_{3h}). Taking advantage of this, a
"near" resonance selective two step photodissociation method was
demonstrated for separating the nitrogen isotopes by Ambartsumyan
et al[2-b]. They used a pulsed P(16) CO_2 laser of frequency
$\nu_1 = 947.74\ cm^{-1}$ to selectively excite the molecules and an UV
pulse of frequency $\nu_2 = 45,351\ cm^{-1}$ to dissociate the excited
molecules and lead to the separation of isotopes. What empha-

size here is an "exact" resonance two step photodissociation
scheme which is simply replacing the pulsed P(16) CO_2 laser in
the Ambartsumyan's process by a "Stark tuning" excitation scheme
as shown in Figure 3.   The high isotopic separation efficiency
of our "exact" resonance method, in comparison with that of the
previously mentioned "near" resonance excitation process, will
be discussed in a later section.

3. $\underline{^{12}CH_3F \text{ and } ^{13}CH_3F}$

        Methyl fluoride has been employed for various laser
spectroscopic experiments because of its "near" coincidences
with laser lines and the large intensity of absorption.   Herle-
mont et al[10], and Freund and his coworkers[11] were the first
to carry out laser Stark spectroscopy in the 10u region for the
ν_3 bands of $^{12}CH_3F$ and $^{13}CH_3F$ using CO_2 laser lines, where the
ν_3 vibration is due to totally symmetric A_1 species correspond-
ing to the C-F stretching vibration.   About 350 Stark resonances
were measured and reported for the ν_3 fundamental bands of the
methyl fluoride molecule.   In particular, the P(18) and P(40)
lines of the CO_2 laser were observed to be close to the low J,
Q-branch lines of $^{12}CH_3F$ and $^{13}CH_3F$, respectively.   Figure 4
gives the Stark fields and Stark resonances for the transitions
of $^qQ_1(1)$, $^qQ_2(2)$, $^qQ_3(3)$ and $^qQ_4(4)$.   Due to the fact that the
observed Stark resonance signals of methyl fluoride show large
signal to noise ratios, Freund et al[11] were able to calculate
that the number of molecules in the path of the laser radiation
is less than 10^9.   This sensitivity has already reached Shimoda's
estimation[12] which states that minimum detectable number of
molecules by laser spectroscopy is 10^6 -10^2.

^{15}NH$_3$

sa^{q}Q$_3$(3) sa^{q}Q$_1$(1)   sa^{q}Q$_4$(4) sa^{q}Q$_2$(2)

−20.52   − 40.62   − 49.38   −46.89 KV/cm

band origin ν_2
(962.897 cm^{-1})

958   966 cm^{-1}

R 29 N$_2$O Laser ⌐   ⌐ R 30 N$_2$O Laser

(962.284 cm^{-1})   (963. 014 cm^{-1})

^{14}NH$_3$

sa^{q}Q$_1$(1)   sa^{q}Q$_4$(4) sa^{q}Q$_2$(2)   sa^{q}Q$_3$(3)

−7.14   −39.48   − 31.95   − 51.63 KV/cm

ν_2 band origin
(968.080 cm^{-1})

964   972 cm^{-1}

R 36 N$_2$O Laser ⌐   ⌐ R 37 N$_2$O Laser
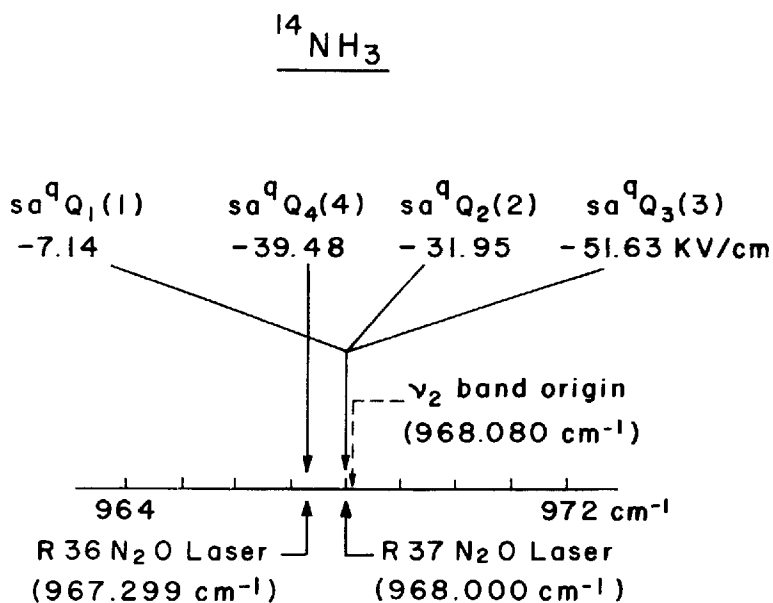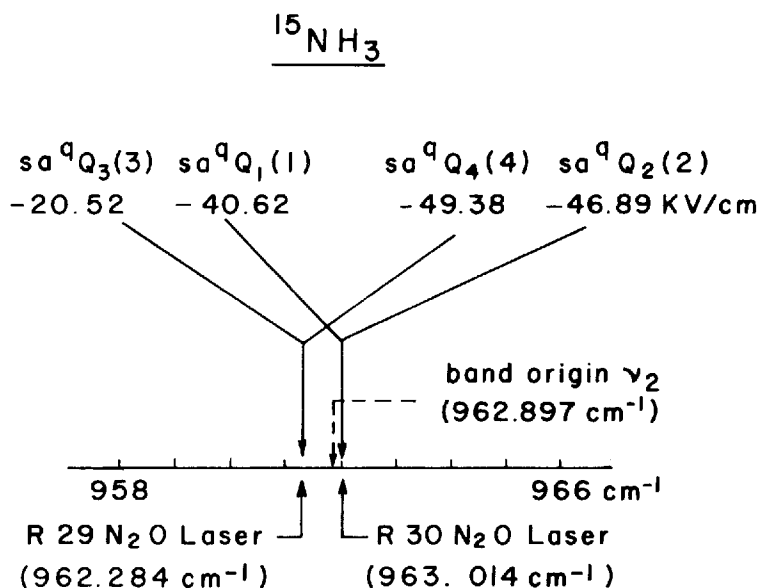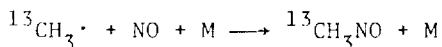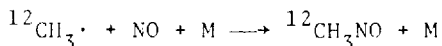
(967.299 cm^{-1})   (968.000 cm^{-1})

Figure 3.   An example of the Stark resonances between the
Q-branch transitions of ^{15}NH$_3$ and ^{14}NH$_3$ and the
N$_2$O laser.

It was shown[13] that the observed electronic transitions of methyl fluoride in the vaccum ultraviolet (VUV) range are atomic like and could be described as Rydberg states. Experimentally, it is complicated to employ the second photon of VUV to excite or to dissociate the CH_3F molecules. Thus, a new photophysical or photochemical process, which is different from those of the sections II-B-1 and II-B-2, is needed for the isotopic separation of $^{12}CH_3F$ from $^{13}CH_3F$ or vice versa.
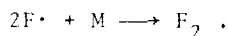
It was suggested[4-c] that a multiple photon absorption of CO_2 laser radiation at high power density by a polyatomic molecule could lead to a high state of molecular excitation, or dissociation. Using this fact, when a sample mixture of methyl fluoride and NO is Stark tuned into resonance with the CO_2 laser line, (cf. Figure 4), the free radicals of either $^{13}CH_3\cdot$ or $^{12}CH_3\cdot$ and $F\cdot$ are generated. The methyl radicals can then react with NO by the following known chemical reaction[14]

$$^{13}CH_3\cdot + NO + M \longrightarrow {}^{13}CH_3NO + M$$

or

$$^{12}CH_3\cdot + NO + M \longrightarrow {}^{12}CH_3NO + M$$
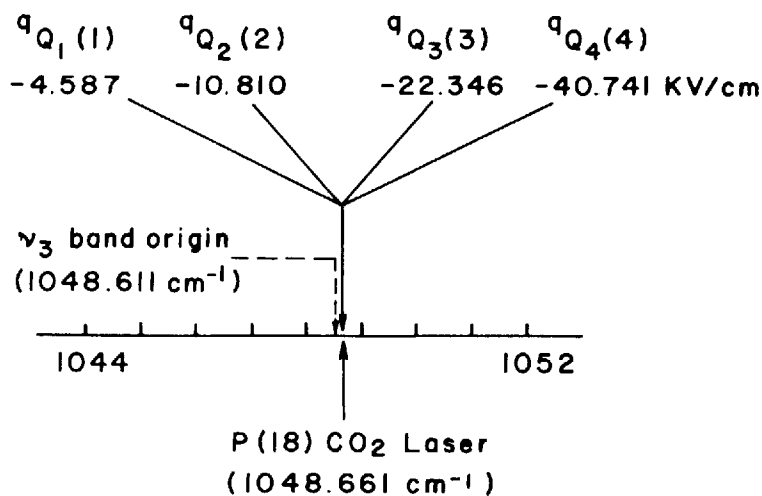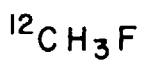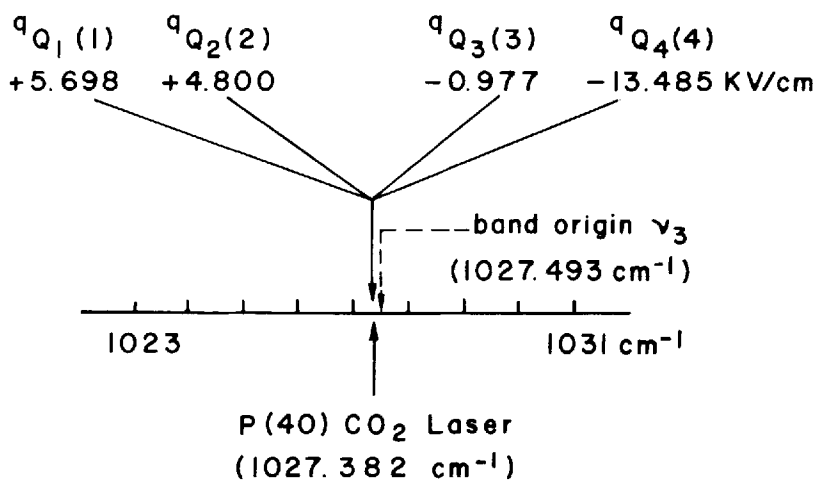
and $2F\cdot + M \longrightarrow F_2$.

In practice, the carbon isotope enrichment is attainable simply by neglecting the UV pulse from the unit 3 of the pulse generator in Figure 1 and by using a high power pulsed CO_2 laser at a focus of $P \geq 10^9$ W/cm^2.

$^{13}CH_3F$

$^qQ_1(1)$ $^qQ_2(2)$ $^qQ_3(3)$ $^qQ_4(4)$

$+5.698$ $+4.800$ -0.977 -13.485 KV/cm

- - - band origin ν_3
$(1027.493 \text{ cm}^{-1})$

1023   1031 cm^{-1}

P(40) CO$_2$ Laser
$(1027.382 \text{ cm}^{-1})$

$^{12}CH_3F$

$^qQ_1(1)$ $^qQ_2(2)$ $^qQ_3(3)$ $^qQ_4(4)$

-4.587 -10.810 -22.346 -40.741 KV/cm

ν_3 band origin
$(1048.611 \text{ cm}^{-1})$

1044   1052

P(18) CO$_2$ Laser
$(1048.661 \text{ cm}^{-1})$
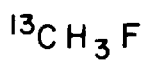
III. DISCUSSION AND REMARKS

In this paper we have illustrated the applicability
of laser Stark spectroscopy to the isotope separation of ^{13}C,
^{15}N and ^{2}H. One needs to emphasize that there are two advan-
tages in using the present process over previously proposed
methods: one advantage is the high sensitivity and the other is
the "exact" resonance excitation.

As we have indicated earlier, laser Stark spectroscopy
can detect as few as 10^9 molecules in the laser optical light
path. If one assumes that the sample pressure in the Stark cell
is 10 torr, the sample cell is 40 cm in length as given in Fig-
ure 1, and the cross section of the laser radiation is 0.02 cm^2,
then the number of molecules existing within the laser radiation
path can be calculated as 2.5×10^{17}. Moreover, as the natural
abundance of the $^{13}CH_3F$ in methyl fluoride, of the D_2CO in for-
maldehyde and of the $^{15}NH_3$ in ammonia is 1.11×10^{-2}, 2.35×10^{-8}
and 3.7×10^{-3}, respectively, under our experimental condition we
would have 2.8×10^{15} molecules of $^{13}CH_3F$, 5.9×10^9 molecules of
D_2CO and 9.3×10^{14} molecules of $^{15}NH_3$ available in the laser
optical path for the isotope separation of ^{13}C, ^{2}H and ^{15}N, re-
spectively. In all cases, the number of isotope molecules that
exist in the laser light path is definitely greater than the
sensitivity limit of laser Stark spectroscopy.

Figure 4.   Stark energy diagrams for the $^{q}Q_1(1)$, $^{q}Q_2(2)$,
$^{q}Q_3(3)$ and $^{q}Q_4(4)$ transitions of $^{13}CH_3F$ and
$^{12}CH_3F$.

From section II-B of this paper, we calculate that the
average frequency difference between the laser line and the mo-
lecular transition line is 0.3 cm^{-1}. Since a typical lifetime
from a vibration-rotation line is -1×10^{-6} sec, the natural line-
width of those transition lines can be evaluated as 1.6×10^{-5}
cm^{-1}. Experimentally, the Doppler linewidth for formaldehyde,
ammonia and methyl fluoride was determined[15] to be 2.4×10^{-3},
3.2×10^{-3} and 1.2×10^{-3} cm^{-1}, at room temperature. Assuming a
Lorentzian shape for all the transition lines, the absorption
0.3 cm^{-1} away is 2.5×10^{-9} of the absorption strength at the cen-
ter. Evidently, if one employs the laser Stark tuning technique
to achieve an "exact" resonance excitation, one would be able to
obtain a 4×10^{8} times larger absorption strength than the absorp-
tion strength obtained without using the Stark technique. Fur-
thermore, one would also have a greater possibility of exciting
the unwanted isotope species within the ± 0.3 cm^{-1} spectral
range.

It is important to mention at this point that the
applicability of Stark tuning-laser photochemistry has been
demonstrated by Lin and Porto[4-a] for isotopic separation of
deuterium and for the production of "heavy water". It was shown
that the cost for producing D_2O using laser Stark spectroscopy
is much lower than the ordinary electrolysis process[16]. The
detailed experimental results on the isotopic separation of ^{13}C,
^{15}N and ^{2}H will be given in the forthcoming papers.

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