# Photon echo measurements in $SF_6$ and $SiF_4$

W. M. Gutman and C. V. Heer

Department of Physics, The Ohio State University, Columbus, Ohio 43210

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The polarization of photon echoes stimulated by linear-linear, circular-linear, and linear-circular excitation sequences has been studied in SF<sub>6</sub> with the P(12) through P(26) laser lines of CO<sub>2</sub> near 10.6  $\mu$ m and in SiF<sub>4</sub> with the P(28) through P(34) lines near 9.6  $\mu$ m. A linear-linear pulse sequence with angle  $\beta$  between the linear polarizations produces an echo at angle  $\varphi$  with respect to the second pulse.  $\varphi$  rotates in the same sense as  $\beta$  with P(16) in SF<sub>6</sub> and in the opposite sense as  $\beta$  with the other lines in SF<sub>6</sub>, and with the lines in  $SiF_4$ . A left-circular-linear sequence produces a right-elliptic echo with P(16) in  $SF_6$ , and a left-elliptic echo in the other cases. A linear-left-circular sequence produces a left-circular echo in all cases. These results are in accord with the large-J polarization theory of Heer and Nordstrom. For a linear-linear excitation sequence, this theory predicts an unnormalized echo electric field  $\vec{E} \cong \pm \hat{X}(1/2\sin\beta) + \hat{Z}\cos\beta$ , where the negative sign applies to a P- or R-branch transition, and the plus sign to a Q-branch transition. For a left-circular-linear sequence, the theory predicts an unnormalized echo electric field  $\vec{E} \simeq \pm 1/2i\hat{X} + \hat{Z}$ , where the plus sign refers to a P- or R-branch transition, and the negative sign to a Q-branch transition. Echo decay rates determined from relaxation measurements are used to calculate molecular cross sections, and these cross sections are compared with calculations based on the refractive indices and the Slater-Kirkwood equation. Experimental cross sections are in general smaller than those found from the Slater-Kirkwood equation.

#### I. INTRODUCTION

In a recent paper Heer and Nordstrom<sup>1</sup> developed the theory for the polarization of the photon echo from molecules in high total angular momentum states, that is, J > 10. Small values of J are treated in other papers.<sup>2-4</sup> They were able to reduce the complex problem for large J values to quite simple results for the echo polarization. The experimental data of Heer and Nordstrom indicated that SF<sub>6</sub> stimulated by the P(16) laser line of CO<sub>2</sub> was in good agreement with their theory for a Qbranch transition. No  $\hat{X}$  component of polarization was observed by them for excitation by other laser lines. In a subsequent letter Gutman and Heer<sup>5</sup> reported that the photon echo stimulated by the P(14) laser line of  $CO_2$  was in good agreement with the theory for an R-branch transition, but that no  $\hat{X}$  component of polarization was observed for other laser lines and was in agreement with the earlier data.<sup>1,2</sup> This paper reports on subsequent measurements of photon echoes stimulated in SF<sub>e</sub> by the  $P(12)-P(26) \operatorname{CO}_2$  laser lines near 10.6  $\mu$ m, and in SiF<sub>4</sub> by the P(28)-P(34) CO<sub>2</sub> laser lines near 9.6  $\mu$ m.

Since this paper is concerned primarily with the experimentally observed echo polarization from the spherical top molecules  $SF_6$  and  $SiF_4$  for large values of total angular momentum, the results of the large-J theory<sup>1</sup> are summarized. Let the stimulating laser radiation propagate along the  $\hat{Y}$  axis and let the second pulse be linearly polarized along the  $\hat{Z}$  axis as shown in Fig. 1. Let the first pulse

be linearly polarized along  $\hat{z}$  at angle  $\beta$  with  $\hat{Z}$ . The echo is linearly polarized with an unnormalized electric field vector of

$$\vec{\mathbf{E}} \cong \mp \hat{X}(\frac{1}{2}\sin\beta) + \hat{Z}\cos\beta, \qquad (1)$$

where the plus sign refers to a  $J_a = J_b$  or to the Qbranch transition and the negative sign to the  $J_a$  $= J_b \pm 1$  or to the *P*- and *R*-branch transitions. Thus the photon echo is linearly polarized at an angle  $\varphi$ from the  $\hat{Z}$  axis with  $\tan \varphi = \pm \frac{1}{2} \tan \beta$ . For *P*- and *R*-branch transitions or  $J_a = J_b \pm 1$  the echo polar-



FIG. 1. Laser radiation is propagating along the  $\hat{Y}$  axis. The first pulse is linearly polarized along the  $\hat{z}$  axis at angle  $\beta$  with the linear polarization of the second pulse which is along the  $\hat{z}$  axis. The linear polarization of the echo makes an angle  $\varphi$  with the  $\hat{z}$  axis.

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ization rotates in the opposite sense of  $\beta$ , and for the *Q*-branch transition the echo polarization rotates in the same sense as  $\beta$ . An intensity ratio between the first and second pulse of 1:4 should yield the best echoes.

If the laser radiation which stimulates the photon echo is along the  $\hat{Y}$  axis, the first pulse is leftcircularly polarized, and the second pulse is linearly polarized along the  $\hat{Z}$  axis, then the elliptical polarization of the photon echo electric field is given by the coefficient of  $e^{-i\omega t}$ . This unnormalized echo polarization is

$$\vec{\mathbf{E}} \cong \pm \frac{1}{2} i \hat{X} + \hat{Z}.$$
 (2)

The positive sign refers to the  $J_a = J_b \pm 1$  or P- and R-branch transitions, and the echo has left-elliptic polarization. The negative sign refers to the  $J_a = J_b$  or Q branch, and the echo has right-elliptic polarization. An intensity ratio of 1:2 for the Q branch and 1:8 for the P and R branches was suggested for better echoes.

If the first pulse is linear and the second pulse is left circular, then the echo is left circular. An intensity ratio of 1:2 for the P and R branches and 1:8 for the Q branch should give the best echoes.

It has been suggested that the decay of the photon echo amplitude with the interval T between the first and second pulse can be used to measure the total elastic cross section.<sup>6</sup> Experimental decay rates reported in this paper on SF<sub>6</sub> and SiF<sub>4</sub>, and earlier data on SF<sub>6</sub> and other molecules,<sup>4,7</sup> are compared with the calculated cross sections and the experimental molecular-beam data.

#### II. EXPERIMENTAL PROCEDURE

The experimental apparatus used to investigate photon echoes from  $SF_6$  and  $SiF_4$  is similar to that used earlier.<sup>1</sup> For the present investigation the rotating mirror Q switch has been replaced, and the new Q switch allows higher rotation rates and shorter pulses. The pulse repetition rate used with  $SF_6$  is typically 240 Hz, and the full width at half-maximum is 160-200 nsec. For SiF, the repetition rate is typically 140 Hz and the pulse duration is 300 nsec. Pressure measurements are made with an oil McLeod gauge with Dow-Corning 704 vacuum pump fluid. In the mTorr pressure range this gauge is not subject to the vapor pressure error which is inherent in the mercury Mc-Leod gauge. A compression ratio of about 1000:1 provides a measurable oil column height when operating in the mTorr range. Before each experiment, the gauge and the oil were baked for several hours to ensure that there was no dissolved gas in the oil. The pressure scale calculated from the geometry of the gauge was checked against the

vapor pressure of  ${}^8$  SF<sub>6</sub> at several liquid-oxygen temperatures.

#### **III. EXPERIMENTAL RESULTS**

Photon echoes were stimulated from  $SF_e$  by the P(12)-P(26) laser lines of the (00°1)-(10°0) vibrational band of CO<sub>2</sub> near 10.6  $\mu$ m, and from SiF<sub>4</sub> by the P(28)-P(34) lines of the  $(00^{\circ}1)-(02^{\circ}0)$  band of CO<sub>2</sub> near 9.6  $\mu$ m. The polarization theory<sup>1</sup> developed simple expressions for the echo electric field in the special cases of linear-linear, circular-linear, and linear-circular excitation sequences. These cases were therefore chosen for detailed experimental investigation of the echo polarization. In accordance with the theory, the laser radiation was incident along the  $\hat{Y}$  axis, and the transverse electric fields were in the  $\hat{X}$ - $\hat{Z}$  plane. It is the echo intensity which is measured experimentally, and for a linear-linear sequence, Eq. (1) yields  $I_z = I_0 \cos^2 \beta$  and  $I_x = \frac{1}{4}I_0 \sin^2 \beta$ , where  $I_z$ is the transmitted intensity through the polarization analyzer whose transmission axis is parallel to  $\hat{Z}$ , and  $I_x$  is the transmitted intensity when the transmission axis is perpendicular to  $\hat{Z}$ . For a leftcircular-linear sequence, the echo is either leftor right-elliptically polarized, and Eq. (2) gives  $I = I_0(\frac{1}{4}\sin^2\alpha + \cos^2\alpha)$ , where  $\alpha$  is the angle between the transmission axis of the analyzer and  $\hat{Z}$ .

The results of the echo polarization studies for each type of excitation sequence are described below for each of the laser lines with which echoes are observed.

### A. SF<sub>6</sub> linear-linear

## 1. P(16)

The echoes stimulated by P(16) exhibit a  $\hat{Z}$  component which is given by  $I_Z/I_0 = \cos^2 \beta$  and an  $\hat{X}$  component which is given by  $I_X/I_0 = 0.27 \sin^2 \beta$ , and the experimental points are shown in Fig. 2. The value 0.27 compares favorably with 0.25 predicted by the theory. The angle  $\varphi$  is plotted as a function of  $\beta$  in Fig. 3, and the echo rotates in the same sense as  $\beta$ . An intensity ratio of 1:4 gives the best echoes. The theory can be used to infer that P(16) is absorbed by a Q-branch transition and is in accord with other spectroscopic assignments.<sup>9,10</sup>

### 2. P(12), P(14)

Echoes stimulated by P(12) and P(14) exhibit  $\hat{Z}$  components with  $I_Z/I_0 = \cos^2\beta$ , and  $\hat{X}$  components  $I_X/I_0 = 0.25 \sin^2\beta$  for P(14) and  $I_X/I_0 = 0.24 \sin^2\beta$  for P(12). Experimental data for P(12) and P(14) are shown in Figs. 2 and 3, and the echo polarization rotates in the opposite sense as  $\beta$ . An intensity ratio of 1:4 gives the best echoes. The theory indi-



FIG. 2. Relative echo intensity as a function of angle  $\beta$  is shown for SF<sub>6</sub> stimulated by the P(12), P(14), P(16), and P(20) lines of CO<sub>2</sub>. The solid curves are  $I_Z/I_0 = \cos^2\beta$  and  $I_X/I_0 = 0.25 \sin^2\beta$ .

cates that P(12) and P(14) are absorbed by either P- or R-branch transitions. Conventional spectroscopic techniques<sup>11</sup> and other assignments<sup>9,10</sup> indicate an R branch.

### 3. P(18), P(20), P(22), P(24), P(26)

 $\hat{Z}$  components of echoes stimulated by these lines are well represented by  $I_Z/I_0 = \cos^2\beta$ .  $\hat{X}$  components follow  $I_X/I_0 = A \sin^2\beta$ , where A = 0.06 for P(18), 0.10 for P(20), 0.13 for P(22), and 0.16 for P(24). The  $\hat{X}$  component stimulated by P(26) is too small to analyze. P(26) echoes have not been previously reported. For each line, best echoes are obtained with a 1:4 intensity ratio. Data for P(20) are included in Fig. 2. For each of these lines, the Xcomponent of the echo is considerably smaller than predicted. The echo polarization rotates in the opposite sense as  $\beta$ . Data for P(20) are included in Fig. 3. These points fall some distance from the  $tan\varphi = -\frac{1}{2}tan\beta$  curve and this reflects the fact that the maximum size of  $I_x$  is considerably less than 0.25  $I_0$ . These results and spectroscopic data<sup>9-11</sup> imply that these lines are absorbed by P-branch transitions.

#### B. SF<sub>6</sub> circular-linear

1. P(16)

For a left-circular-linear excitation sequence, optimum echoes are obtained with a pulse-intensity ratio of 1:2 where the second pulse has the same absolute intensity as for linear-linear. The echo intensity as a function of analyzer angle  $\alpha$  is



FIG. 3. Linear polarization of the photon echo at angle  $\varphi$  is shown as a function of  $\beta$  for SF<sub>6</sub> stimulated by P(12), P(14), P(16), and P(20). The curve shown is tan  $\varphi = \pm \frac{1}{2} \tan \beta$ .

shown in Fig. 4, and since  $I/I_0 = 0.27 \sin^2 \alpha + \cos^2 \alpha$ , indicates elliptic polarization. The sense of the polarization is found to be right elliptic. These results are consistent with theory for absorption by a *Q*-branch transition.

## 2. P(12), P(14)

A pulse intensity ratio of 1:8 yields the best echoes with these lines for a left-circular-linear se-



FIG. 4. Relative exho intensity for a circular-linear excitation sequence is shown for SF<sub>6</sub> stimulated by P(12), P(14), P(16), and P(20) as a function of analyzer angle  $\alpha$ . The curve shown is  $I/I_0 = 0.25 \sin^2 \alpha + \cos^2 \alpha$ .

quence, but 1:2 and 1:4 ratios also give good echoes. For P(12),  $I/I_0 = 0.24 \sin^2 \alpha + \cos^2 \alpha$ , and for P(14),  $I/I_0 = 0.25 \sin^2 \alpha + \cos^2 \alpha$ . Results are included in Fig. 4. The sense of the polarization is left elliptic, and is consistent with predictions for absorption by an *R*-branch transition.

#### 3. P(18), P(20), P(22), P(24), P(26)

For a left-circular-linear excitation sequence, best echoes are obtained with a 1:8 intensity ratio. The data are well represented by  $I/I_0 = B \sin^2 \alpha + \cos^2 \alpha$ , where B = 0.08 for P(18), 0.23 for P(20), 0.17 for P(22), and 0.17 for P(24). The value of B cannot be determined for P(26) due to the small size of the echo. P(20) results are shown in Fig. 4. For P(20), the echoes are left elliptically polarized, but for the other lines, the echoes are too small to allow determination of the sense of the polarization.

#### C. SF<sub>6</sub> linear-circular

A linear-left-circular excitation sequence yields echoes which, within the limits of experimental error, are circularly polarized for the lines P(12)-P(24). Only for P(26) are the echoes too small to analyze. Further, for the lines P(12)-P(20), the sense of the polarization is found to be left circular. For the other lines, the echo size is insufficient to determine the sense of the polarization. For P(16), a 1:8 intensity ratio gives best echoes, while for the other lines, 1:2 is best, but good echoes are obtained with 1:4 and 1:8 ratios.

# D. SiF<sub>4</sub> linear-linear, circular-linear, and linear-circular

Echoes obtained with P(30), P(32), and P(34) exhibit  $\hat{Z}$  components with  $I_Z/I_0 = \cos^2\beta$ , and  $\hat{X}$  components with  $I_X/I_0 = 0.25 \sin^2\beta$ . The echo polarization rotates in the opposite sense as  $\beta$ . This is consistent with absorption by P- or R-branch transitions. The results of Jones *et al.*<sup>12</sup> can be used to infer that they are R branch. For P(28), the  $\hat{X}$  component is below the limit of detectability. Echoes stimulated by P(28) and P(34) had not been previously reported.

With a left-circular-linear excitation sequence, optimum echoes are obtained when the pulse intensity ratio is 1:8. With P(30), P(32), and P(34), the relative echo intensity as a function of analyzer angle is well represented by  $I/I_0 = 0.25 \sin^2 \alpha$  $+\cos^2 \alpha$ . This indicates elliptic polarization, and the sense is found to be left elliptic, which is appropriate for absorption by an *R*-branch transition. With P(28), the echo transmission through the analyzer is too small for measurements.

Echoes stimulated by a linear-left-circular se-

quence with P(30), P(32), and P(34) are found to be circularly polarized, although there is insufficient signal for the sense of the polarization to be determined. A 1:2 intensity ratio yields best echoes. P(28) echoes are too small for analysis.

#### E. Pressure dependence of echo decay for SF<sub>6</sub> and SiF<sub>4</sub>

The decay in echo intensity  $I/I_0 = e^{-4\gamma T}$  with the interval T between pulses can be used to measure the decay rate  $\gamma = T_2^{-1}$  or the relaxation time  $T_2$ . No difference in decay rate was evident between different molecular lines, nor was any difference observed for the decay rate of the  $\hat{X}$  and  $\hat{Z}$  components. The data for SF<sub>6</sub> are well represented by  $PT_2 = 22 \times 10^{-9}$  sec Torr and is in agreement with the results of Patel and Slusher<sup>7</sup> and with the results of Alimpiev and Karlov.<sup>4</sup> This corrects an error in earlier measurements<sup>1,13</sup> which was due to the mercury vapor pressure of the McLeod guage, erroneous SF<sub>6</sub> vapor-pressure data, and some confusion in reported cross sections.<sup>7</sup>

For SiF<sub>4</sub> good data were obtained for stimulation by P(30) in the pressure range from 5 to 48 mTorr. These data are fairly well represented by  $PT_2 =$  $(19+520P) \times 10^{-9}$  sec Torr where P is in Torr and  $T_2$  is pressure dependent. The pressure-dependent term may be due to absorption of the echo in the long cell. A reliable low-pressure value of  $PT_2$  is  $19 \times 10^{-9}$  sec Torr.

#### F. Temperature dependence

A cooling jacket was constructed for the sample cell, which allowed the absorbing gas temperature to be adjusted from room temperature to 180 °K. The jacket allowed the temperature to be maintained constant to within a few degrees along the cell for an hour or more. With P(12), P(14), and P(16) at temperatures of 220 °K or less, echoes are observed which are larger than those at room temperature. The polarization properties of these echoes are in excellent agreement with the theory for Q- and R-branch transitions as determined from room-temperature results. P(16) echoes are particularly interesting. A linear-linear sequence of pulses with  $\beta = 0^{\circ}$  and separated by time T stimulates a very large primary echo, and in addition, a second and a third echo are observed. The second echo is as large as 10% of the intensity of the primary echo, and follows it by a time of approximately T. The third echo follows the second also by approximately T and is still smaller. At a temperature of 203 °K and a pressure of 4 mTorr, the second echo is observed only if the exciting pulses are separated by less than 3  $\mu$  sec. For the third echo to be formed, the exciting pulses must be

even closer. A second echo often is observed with P(14), although it is smaller than with P(16) and observed only when the exciting pulses are quite close. Multiple echoes have been observed by Bölger and Diels in Cs vapor.<sup>14</sup>

P(18) echoes at reduced temperatures are similar in size to those at room temperature, and their polarization properties are in good agreement with the theory. Echoes stimulated by P(20)-P(26) are smaller at reduced temperatures. Below 204 °K, echoes are no longer observed with P(24) or P(26). For each of the lines P(20)-P(26), the size of the  $\hat{X}$  component expected with a linearlinear sequence is below the level of the noise. Relaxation rates measured from the decay in echo intensity at reduced temperatures give a value for  $PT_2$  smaller than that found at room temperature. At 213 °K,  $PT_2$  is  $20 \times 10^{-9}$  sec Torr. P(20) - P(26)and P(12) are absorbed weakly at reduced temperatures, and this weak absorption may be due to the decreased excitation of the "hot bands."

#### IV. DISCUSSION OF RESULTS

The recent assignment by McDowell et al.<sup>10</sup> that the CO<sub>2</sub> laser line P(14) excites the SF<sub>6</sub> $R(28)A_2^0$ octahedral symmetry lower level, P(18) excites  $P(33)A_2^1$ , and P(20) excites P(59) or  $P(60)F_2$ , establishes that high J values occur for these echo transitions. It is reasonable to expect that the other echo transitions occur for high values of total angular momentum and that the polarization of photon echoes should follow from the theory<sup>1</sup> for large J. All polarization results for echoes stimulated in SF<sub>6</sub> by P(16) are in good agreement with the theory for a Q-branch transition. Agreement is good for the R-branch echoes stimulated by P(12) and P(14). The agreement is fair to poor for echoes stimulated from the P branch by the lines P(18)-P(26). Apparently, improvement in experimental technique has made observable the  $\hat{X}$  component in the linear-linear and an elliptic

component in the circular-linear pulse sequences for lines other than P(16) and P(14). Further improvement in experimental technique may lead to even better agreement with theory. Polarization results for echoes stimulated in SiF<sub>4</sub> by P(30), P(32), and P(34) are in good agreement with the theory for an *R*-branch transition.

The importance of velocity-changing collisions upon the decay of the photon echo amplitude was emphasized by Schmidt *et al.*<sup>15</sup> One may show<sup>6</sup> that for radiation of wavelength  $\lambda$  in the *Y* direction, the echo amplitude decays as

$$\exp\{(i2\pi/\lambda)[Y(T) - Y(0) - v_{y}(0)T]\}$$

and depends on the displacement of the molecule relative to a constant velocity displacement. A similar quantity was of importance in the discussion of Gyorffy et al.<sup>16</sup> of the broadening of gas laser lines. In the discussion of this average, Heer<sup>6</sup> has emphasized that the measurement of the decay of the photon echo amplitude with pulse interval T should yield the total elastic cross section for molecular collisions. Both the work of Heer<sup>6</sup> and that of Berman et al.<sup>17</sup> indicate that for a large pulse interval T, the echo intensity decays as the probability of no collisions in interval 2T, that is,  $e^{-4\gamma T}$  where  $\gamma$  is the total collision rate  $\gamma = n \langle V \sigma \rangle_c$ . The same small-angle scattering which is of importance in the scattering of molecular beams is of importance in the change of position and is due primarily to the  $C/r^6$  Van der Waals long-range interaction between molecules. The total collision rate and this constant C are related by

$$\gamma = n \left[ 2\pi (3\pi C / 8\hbar \overline{V})^{2/5} \overline{V} \right] = n \overline{V} \sigma.$$
(3)

Model-independent cross sections  $\sigma$  which are determined from experimental values of  $\gamma$  are given in Table I. The Slater-Kirkwood<sup>18,19</sup> equation for the relationship between *C* and the molecular polarizabilities is used to calculate the total cross section, and this data is shown for comparison.

TABLE I. Experimental cross sections are compared with values calculated from Van der Waals coefficients obtained using the Slater-Kirkwood equation.

Molecules	$\sigma_{\text{expt}} (10^{-20} \text{ m}^2)$	$C_{\rm calc} (10^{-79}  {\rm Jm}^6)$	$\sigma_{calc} (10^{-20} \mathrm{m}^2)$	
$SF_6 - SF_6$	480	830	1190	
$SiF_4-SiF_4$	470	430	860	
BCl <sub>3</sub> -BCl <sub>3</sub> <sup>a</sup>	350	1380	1400	
SF <sub>6</sub> -He <sup>b</sup>	87	37	190	
SF <sub>6</sub> -Ne <sup>b</sup>	150	86	360	
SF <sub>6</sub> -H <sub>2</sub> <sup>b</sup>	200	96	240	
CH <sub>3</sub> F-CH <sub>3</sub> F°	380	360	820 <sup>d</sup>	

<sup>a</sup>Reference 4.

<sup>b</sup>Reference 7.

<sup>c</sup>Reference 15.

<sup>d</sup>This term includes the nonresonant permanent electric dipole.

The molecular polarizabilities were taken from the data of Rothe and Bernstein.<sup>19</sup> They used the total cross section of an alkali atom with the gas molecule of interest to measure *C*. This value of *C* was then compared with the value which was determined from the Slater-Kirkwood equation, where the molecular polarizabilities were determined from the index of refraction. Although ratios between similar gas molecules yielded reasonable agreement, the absolute error in the cross sections was as large as 50%. A similar error can be expected in the calculated cross sections in Table I. Even for the most reliable  $SF_6$ - $SF_6$  data the cross sections differ by a factor of 2, and since  $C \propto \sigma^{5/2}$ , the deviation in *C* is much larger.

Although the probability of no collision during the interval 2T may seem quite drastic, one may use the cross section proportional to  $e^{-a\theta^2}$  of Mason *et al.*<sup>20</sup> to show that the average displacement which is caused by a collision is approximately  $(\hbar/2\mu)$  $\times (8\hbar \overline{V}/3\pi C)^{1/5}t$  or  $(\hbar/2\mu)(2\pi/\sigma)^{1/2}t$ . The change in phase is  $(\hbar/2\mu\lambda)(2\pi/\sigma)^{1/2}t$  and the change in phase reaches 1 rad in less than  $\frac{1}{2}$  µsec after the collision. An interval between pulses of the order of a few µsec would seem to require no collisions for the formation of the echo. A more detailed expression for the echo decay is the average

 $\langle \exp\{(i2\pi/\lambda)[Y(2T)-Y(T)]\}$ 

 $\times \exp\{(-i2\pi/\lambda)[Y(T)-Y(0)]\}\rangle,$ 

and the two exponentials have been treated as statistically independent. This is not strictly true, but it would seem to be a good approximation. The effect of multiple collisions is different for echoes stimulated by radiation near resonance or excited molecules traveling transverse to the radiation than for echoes stimulated off resonance or excited molecules with a velocity component along the radiation. A consideration of this effect is not simple.

The collision rate  $\gamma(v_r)$  for a stimulated molecule with velocity  $v_r$  equal to the most probable velocity is only 15% greater than that for  $\gamma(0)$  for an  $r^{-6}$  interaction.  $\gamma(0)/\gamma \cong 0.95$  and even if all the excited molecules were traveling transverse to the radiation, the correction would be only 5%. Although the photon echo experiment selects a certain velocity group, this cannot account for cross sections which are smaller than expected. Grossman *et*  $al.^{21}$  have measured the velocity dependence  $\gamma(v_r)/\gamma(0)$  for <sup>13</sup>CH<sub>3</sub>F and found a change of 30% between  $v_r = 0$  and  $v_r$  equal to the most probable velocity. This is somewhat larger than expected for an  $r^{-6}$ interaction. Their theoretical curve is in error.<sup>22</sup>

In an earlier discussion<sup>6</sup> the second virial coefficient and a Lennard-Jones 6-12 potential was used to determine the Van der Waals constant. The value of *C* determined from the data of Hamann and Pearse<sup>23</sup> is in very poor agreement with the value which was determined from the SF<sub>6</sub> and SiF<sub>4</sub> data. One can use a hard-core repulsive potential and obtain much better agreement.

The results of this paper and of other papers<sup>4,7</sup> for the echo decay rate do not yield cross sections as large as expected, and may not provide a new method for measuring the total elastic cross section. It would seem desirable to use Cs as a buffer gas in a photon echo experiment, and then a direct comparison could be made with the molecular-beam experiments.

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<sup>22</sup>For a  $C/r^{s}$  interaction the collision rate for a molecule with velocity  $v_{Y}$ ,  $\xi^{2} = mv_{Y}^{2}/2kT$ , is given by

$$\frac{\gamma(\xi)}{\gamma} = A e^{\xi} \int_{\xi}^{\infty} dx \, e^{-x^2} \int_{0}^{\infty} y \, dy \, e^{-y^2} \, (|y+x|^{2a} - |y-x|^{2a}),$$

where

a = (3s - 5)/2(s - 1) and  $A^{-1} = 2^{a - 1}a \Gamma(a + \frac{1}{2})$ .

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