

Phase Shifts in the Molecular Beam Method of Separated Oscillating Fields*

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The effects of phase differences between the two oscillating fields in the separated oscillating fields method for molecular beam radiofrequency spectroscopy is discussed theoretically. It is shown that measurements in which the relative phase is changed from 0° to 180° effectively double the intensity of the signal and hence increase the sensitivity of the apparatus. Phase shifts of $\pi/2$ radians give resonances in the form of dispersion curves. Consequently, measurements in which the phase is changed from $+\delta$ to $-\delta$, where δ is near 90° , give particularly sensitive means of determining the resonance frequency.

IN Ramsey's¹ original paper on the molecular beam resonance method with separated oscillating fields, the only case considered was that in which the two oscillating fields were in the same phase. However, if the second field leads the first by a phase angle δ the first part of the earlier paper¹ must be modified by the replacement of $\omega(\tau+T)$ by $\omega(\tau+T)+\delta$ in Eqs. (8e) and (8f). As a result, the λT in Eq. (12) is replaced by $\lambda T-\delta$ and the probability for transition from state p to state q is

$${}_s P_{p,q} = 4 \sin^2 \theta \sin^2 \frac{1}{2} a \tau \left[\cos \frac{1}{2} (\lambda T - \delta) \cos \frac{1}{2} a \tau - \cos \theta \sin \frac{1}{2} (\lambda T - \delta) \sin \frac{1}{2} a \tau \right]^2, \quad (1)$$

where τ is the length of time the molecule is in each of the oscillating field regions, T is the length of time in the intermediate regions, $\hbar b e^{i\omega t}$ is the perturbation inducing the transition, and the remaining quantities are defined by

$$a = [(\omega_0 - \omega)^2 + (2b)^2]^{\frac{1}{2}}, \quad \omega_0 = (W_q - W_p)/\hbar, \quad (2)$$

$$\cos \theta = (\omega_0 - \omega)/a, \quad \sin \theta = 2b/a,$$

and

$$\lambda = [(\bar{W}_q - \bar{W}_p)/\hbar] - \omega. \quad (3)$$

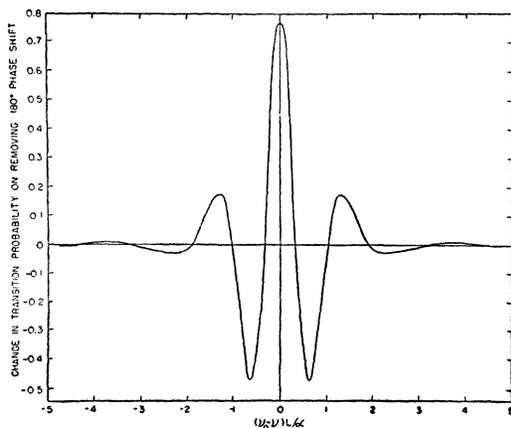


FIG. 1. Theoretical change in transition probability on removing 180° phase shift.

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¹ N. F. Ramsey, Phys. Rev. **78**, 695 (1950).

The interesting limit for (1) is that near resonance where $|\omega_0 - \omega|$ is much less than $2b$, in which case

$${}_s P_{p,q} = \sin^2 2b\tau \cos^2 \frac{1}{2} (\lambda T - \delta). \quad (4)$$

This expression may be averaged over the molecular velocities with the usual molecular beam weighting factor to yield

$$\langle {}_s P_{p,q} \rangle_{av} = 2 \int_0^\infty \exp(-y^2) y^3 \sin^2 \left(\frac{2bl}{\alpha y} \right) \times \cos^2 \left(\frac{\lambda L}{2\alpha y} - \frac{\delta}{2} \right) dy, \quad (5)$$

where y is the molecular velocity divided by the most probable velocity $\alpha = (2kT/m)^{\frac{1}{2}}$ while l is the length of each oscillating field region and L is the length of the intermediate region.

The numerical work of evaluating (5) can be much simplified by the use of trigonometric expansions to reduce it to a sum of terms involving only the two integral functions,

$$I(x) = \int_0^\infty \exp(-y^2) y^3 \cos(x/y) dy, \quad (6)$$

and

$$K(x) = \int_0^\infty \exp(-y^2) y^3 \sin(x/y) dy. \quad (7)$$

With this notation, (5) becomes

$$\langle {}_s P_{p,q} \rangle_{av} = \frac{1}{4} - \frac{1}{2} I(4bl/\alpha) + \cos \delta \left[\frac{1}{2} I(\lambda L/\alpha) - \frac{1}{4} I(4bl/\alpha + \lambda L/\alpha) - \frac{1}{4} I(4bl/\alpha - \lambda L/\alpha) \right] + \sin \delta \left[\frac{1}{2} K(\lambda L/\alpha) - \frac{1}{4} K(4bl/\alpha + \lambda L/\alpha) + \frac{1}{4} K(4bl/\alpha - \lambda L/\alpha) \right]. \quad (8)$$

The functions $I(x)$ and $K(x)$ have been tabulated by Kruse and Ramsey² and may be used to evaluate the transition probability.

The value of (8) depends not only on δ and λ but also on $2bl/\alpha$. As discussed in the previous paper,¹ the most suitable value of $2bl/\alpha$ for many purposes is 0.600π ;

² U. E. Kruse and N. F. Ramsey, J. Math. Phys. **30**, 40 (1951).

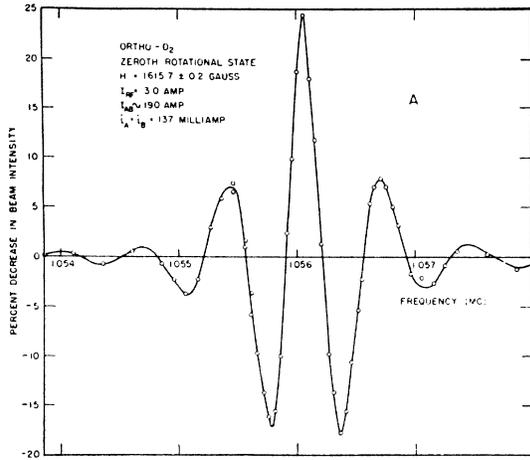


FIG. 2. Experimental change in beam intensity on removing 180° phase shift with ortho- D_2 in zeroth rotational state.

consequently all of the accompanying curves are for this value.

One of the most useful cases of the introduction of a relative phase shift δ is that in which the change in molecular beam intensity is measured as δ is changed from 0 to π -radians. Then

$$\langle {}_0P_{p,q} \rangle_{AV} - \langle {}_{\pi}P_{p,q} \rangle_{AV} \equiv A = I(\lambda L/\alpha) - \frac{1}{2}I(4bl/\alpha + \lambda L/\alpha) - \frac{1}{2}I(4bl/\alpha - \lambda L/\alpha). \quad (9)$$

This expression is plotted in Fig. 1 as a function of $(\nu_0 - \nu)L/\alpha$, where $\nu = \omega/2\pi$, with the value of 0.600π for $2bl/\alpha$. For comparison purposes, an experimental curve of the change in beam intensity for the nuclear resonance in ortho- D_2 is shown in Fig. 2.

The change in the ordinate between maxima and minima in Fig. 1 is just double that in Fig. 2 of the earlier paper¹ in which the change in beam intensity is to be observed when the oscillator is successively turned off and on. Therefore, the phase shifting method of observation provides the equivalent of a doubling of the beam intensity which can be of great value in experiments where the beam intensity is a limiting factor.

An additional feature of the method is that the rf amplitude is constant, which is an advantage if the beam detector is sensitive to rf "pickup." Also, the slowly varying first two terms of (8) are not observed since they are independent of δ . This may be an advantage in searching for resonances, particularly if lines are close together.

An alternative case of considerable interest is that in

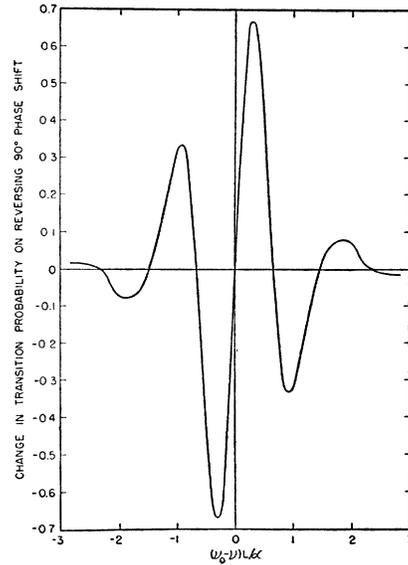


FIG. 3. Theoretical change in transition probability on reversing 90° phase shift.

which δ is changed from $\frac{1}{2}\pi$ to $-\frac{1}{2}\pi$. Then (8) becomes

$$\langle \frac{1}{2}\pi P_{p,q} \rangle_{AV} - \langle -\frac{1}{2}\pi P_{p,q} \rangle_{AV} \equiv B = K(\lambda L/\alpha) - \frac{1}{2}K(4bl/\alpha + \lambda L/\alpha) + \frac{1}{2}K(4bl/\alpha - \lambda L/\alpha). \quad (10)$$

The graph of this expression is plotted in Fig. 3. The curve can be seen to be of a dispersion type and to pass through zero at the resonance frequency. Since the curve is very steep as it passes through the resonance value, this technique provides a particularly sensitive means for experimentally locating the exact resonance frequency.

Theoretical curves for other phase shifts can be obtained from (8). However, the calculation can often be simplified by noting from (8), (9), and (10) that

$$\langle {}_{\delta}P_{p,q} \rangle_{AV} = \frac{1}{4} - \frac{1}{2}I(4bl/\alpha) + \frac{1}{2}A \cos\delta + \frac{1}{2}B \sin\delta. \quad (11)$$

For the value of $2bl/\alpha$ equal to 0.600π ,

$$\langle {}_{\delta}P_{p,q} \rangle = 0.383 + \frac{1}{2}A \cos\delta + \frac{1}{2}B \sin\delta, \quad (12)$$

where A and B can be obtained from Fig. 1 and Fig. 3.

In particular, from (12) one sees that

$$\langle {}_{\delta}P_{p,q} \rangle_{AV} - \langle {}_{-\delta}P_{p,q} \rangle_{AV} = B \sin\delta. \quad (13)$$

Therefore, a curve passing sharply through zero at resonance can be obtained even if the phase shift departs somewhat from $\frac{1}{2}\pi$ provided only that the one phase shift is exactly the negative of the other.