than are actually present. In this case, however, the high-impedance current probes that are used reach signal levels of several hundred volts, and many secondaries may be recaptured. In any event, since the iris allows only a small fraction of the ions to reach the probes, and since the charge state spectrum of the heavy ions is unknown, the actual particle currents cannot be inferred from the probe data. The important features that are evident from the results shown in Fig. 2 and Table I may be summarized as follows: (1) The velocity of the fastest ions appears to be independent of the ion mass and is approximately $0.1c$, corresponding to a maximum energy of 4.6 MeV per nucleon. (2) Significantly higher probe current is observed for protons than for heavier ions, perhaps because protons have a higher charge-to-mass ratio than do even highly stripped heavy ions. (3) When the hydrogen data is disregarded, the peak current as well as the total integrated charge $\int I(t)dt$ for each ion pulse does not change appreciably with the ion mass number.

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[1] V. I. Veksler, in Proceedings of the CERN Symposium on High-Energy Accelerators, Geneva, 1956 (unpublished), Vol 1, p. 80; G. I. Budker, *ibid.*, p. 68; At. Energ. 1, 9 (1956).

[2] *Collective Methods of Acceleration,* edited by N. Rostoker and M. Reiser, (Harwood Academic Publishers, New York, 1979).

[3] C. L. Olson and U. Schumacher, *Springer Tracts in Modern Physics: Collective Ion Acceleration,* edited by G. Höhler (Springer, New York, 1979), Vol. 84.

[4] S. E. Graybill and J. R. Uglum, J. Appl. Phys. 41, 236 (1970).

[5] J. S. Luce, Ann. N. Y. Acad. Sci. 20, 336 (1973).

[6] W. W. Destler, R. F. Hoeberling, H. Kim, and W. H. Bostick, Appl. Phys. Lett. 35, 296 (1979).

[7] W. W. Destler, H. S. Uhm, H. Kim, and M. Reiser, J. Appl. Phys. 50, 3015 (1979).

[8] W. W. Destler, L. Floyd, and M. Reiser, IEEE Trans. Nucl. Sci. 26, 4177 (1979).

Observation of Collisional Velocity Changes Associated with Atoms in a Superposition of Dissimilar Electronic States

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Photon-echo measurements in atomic Na perturbed by He provide the first demonstration of the contribution of velocity-changing-like effects to the transverse relaxation of atoms in superposition of two states even *when the states follow different post-collision trajectories.* The apparent anomaly that broadening cross sections derived from either absorption line widths or photon-echo relaxation measurements are smaller than the total cross section for scattering of atoms in either pure state is explained.

The ability to study sub-Doppler collisional broadening of spectral lines, which has arisen concomitant to the development of high-resolution laser-spectroscopic techniques, has stimulated a thorough reanalysis of the basic concepts of collisional-broadening theories.[1] In particular the notion that a radiating atom (i.e., an atom in a linear superposition of two energy eigenstates) can generally experience identifiable collisionally induced velocity changes has been called into question.[2,3] The basis for the objection is that subsequent to a collision, mediated by a *state-dependent interaction,* the radiating atom finds itself in a *"superposition" of two trajectories* corresponding to the paths which would have been followed by an atom purely in one or the other of the two energy eigenstates. This leads to ambiguity in the concept of a past-collision atomic velocity, and raises questions as to the velocity-changing effects expected to be seen. If the collisional interaction is identical in both eigenstates only one final trajectory is expected and the ambiguity in final velocity disappears. In such cases the velocity-changing aspect of collisions leads to effects such as Dicke narrowing[4] and nonexponential decay of photon-echo intensity versus excitation-pulse separation.[5] Recently, it has come to be widely assumed that collisions, which affect atoms (or molecules) in a superposition of dissimilar electronic energy states, do not lead to the effects associated with collisional velocity changes, and attempts to observe such effects have yielded negative results.[6,7] In this Letter, however, we present the results of an experiment which utilizes the unique spectroscopic capabilities of the photon echo to provide for the first time an unambiguous demonstration of the velocity-changing aspect of such collisions. By measuring the decay of the photon-echo intensity as a function of perturber-gas pressure at various fixed excitation-pulse separations, τ, and using broadbandwidth laser excitation, we are able to determine the effect of collisions *without regard to either Doppler or natural broadening.* Working on the $3S_{1/2}$-$3P_{1/2}$ transition of Na perturbed by He, we find that while for short τ the echo decay is dominated by inelastic collisions and collisional phase changes, the contribution of the velocity-changing aspect of collisions grows as τ^3, and at the longest τ studied constitutes an important factor in the echo decay. Extrapolating to very long τ, collisional changes in velocity become the most important source of echo decay.

For fixed pulse separation we find the photon-echo intensity decays with perturber-gas pressure P as

$$I_e(P) \propto \exp(-\beta P), \tag{1}$$

independent of the type of collisions affecting the echo atoms. Here β is a function of τ. If all collisions produce only phase- or state-changing effects, it is expected that[5]

$$\beta P = 4\Gamma_{\mathrm{ps}}\tau, \tag{2}$$

where Γ_{ps} is the total collision rate. Equation (2) indicates that β will vary linearly with τ. In the presence of collisions which only have the effect of introducing velocity changes it is expected that[5]

$$\beta P = \tfrac{2}{3}\Gamma_{\mathrm{vcc}}\tau(ku_0\tau)^2, \tag{3}$$

where k is the magnitude of the wave vector of the excitation pulses and the photon echo, Γ_{vcc} is the total velocity-changing collision (vcc) rate, and u_0 is the average change in axial velocity introduced by a single vcc. In writing Eq. (3) it is assumed that $ku_0\tau \ll 1$. In contrast to the case of phase- or state-changing collisions Eq. (3) indicates that the β resulting from vcc varies as τ^3. Note that in our experiment Γ_{vcc} represents the rate of vcc affecting atoms in a linear superposition of energy states each of which would normally be associated with a different post-collision trajectory. Previous attempts[6,7] to measure a Γ_{vcc} associated with atoms in a superposition of dissimilar states have yielded results consistent with $\Gamma_{\mathrm{vcc}} = 0$. The rates Γ_{ps} and Γ_{vcc} can be related to effective collisional cross sections σ_{ps} and σ_{vcc} through the relations

$$\Gamma_{\mathrm{ps}} = n\bar{v}\sigma_{\mathrm{ps}}, \quad \Gamma_{\mathrm{vcc}} = n\bar{v}\sigma_{\mathrm{vcc}}, \tag{4}$$

where n is the perturber-gas number density, $\bar{v}$ is the average echo-atom–perturber-atom relative speed and is given by $(8k_BT/\pi\mu)^{1/2}$, k_B is Boltzmann's constant, T is the absolute temperature, and μ is the echo-atom–perturber-atom reduced mass.

In the absence of a comprehensive theoretical treatment of the combined effect of collisional phase and velocity changes, we adopt a phenomenological collision model in the spirit of that proposed by LeGouët and Berman.[8] It is assumed that close collisions effectively randomize the phase of the atom's superposition state. Atoms experiencing such close collisions cannot contribute to the echo signal. Other statistically independent collisions occurring at larger impact parameters, where collisional phase changes are too small to appreciably degrade the echo, are taken as entirely velocity changing in nature. This collisional model predicts that

$$\beta = \beta_1 + \beta_3, \tag{5}$$

where β_1 (β_3) corresponds to echo decay resulting from the effect of phase- and state-changing collisions (velocity-changing collisions). Following Eqs. (2) and (3) we write $\beta_1 = b_1\tau$ and $\beta_3 = b_3\tau^3$, where b_1 and b_3 are constants.

In our experiments, a 3.5-nsec-long N_2-laser-pumped dye-laser pulse of 1-Ghz spectral width is optically split to provide the necessary two-pulse excitation sequence. An optical delay line is used to precisely determine the pulse separation τ. The pulses, of a few watts peak power, are collimated to a $\cong$ 2-mm diameter as they traversed the heat-pipe–type Na cell, which was maintained at 415 ± 15 K. After the Na cell, the excitation pulses, which have orthogonal linear polarizations, are blocked (to prevent detector saturation) by a series of two Pockels-cell optical shutters. To ensure that τ is not limited on the short side by the optical shutters $\cong$10-nsec switching time, the first optical shutter's input polarizer is oriented normal to the second pulses's polarization.

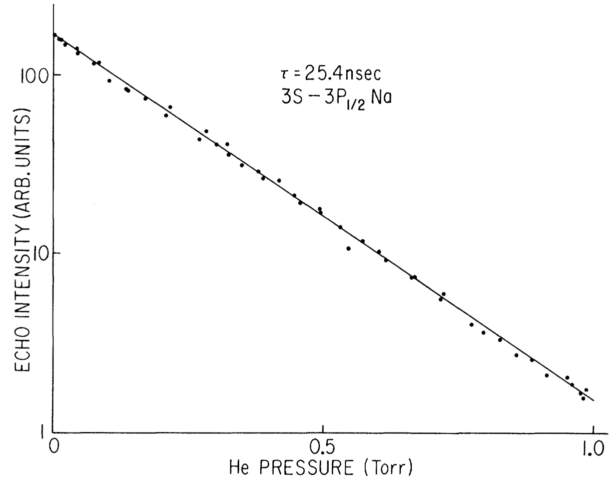

FIG. 1. Photon-echo intensity vs He pressure. The echo intensity and He pressure are computer monitored as the He pressure first increases and then returns to its initial value. Each point represents an average of 75 echoes. The straight line represents a least-squares fit to $I_e(P) = I(P=0)\exp(-\beta_i P)$. The β's given in Table I represent an average of the β_i's obtained in four to six independent runs (as shown above) for each value of τ.

TABLE I. Observed values of β for various excitation-pulse separations τ.

τ (nsec)	β (Torr^{-1})
7.5	1.25(2)
12.1	2.06(3)
25.4	4.61(4)
38.7	7.84(7)

This prevents transmission of the second pulse even when the shutters are open. While excitation pulses of crossed polarization enable us (by eliminating second-pulse-induced detector saturation) to make short-τ measurements, they produce (because of nuclear spin effects) an echo only one-tenth as intense as that produced by excitation pulses of parallel polarization.[9] As described elsewhere[10] our measurements are performed by monitoring the simple exponential decay [see Eq. (1) and Fig. 1] of the photon-echo intensity as a function of He pressure ($0 < P < 3$ Torr) at fixed τ. The nature of the collisional effects responsible for the echo decay can be determined by measuring β at a number of different values of τ. The maximum τ used in our experiments is limited by the radiative decay of the 16-nsec-lifetime $3P_{1/2}$ state, which at $\tau = 38.7$ nsec already accounts for more than a hundredfold degradation in echo intensity.

The results of our measurements are presented in Table I, and we plot the quantity β/τ vs τ^2 in Fig. 2. If Eq. (5), which states that $\beta/\tau = b_1 + b_3\tau^2$, is applicable, the data points in Fig. 2 should fall along a straight line. The fact that they do provides a clear indication that collisional velocity changes are contributing to the echo decay. A least-squares fit to the data of Fig. 2 reveals that $b_1 = 1.66\times10^8$ (Torr sec)$^{-1}$ and $b_3 = 2.45\times10^{22}$ (Torr sec^3)$^{-1}$. Although the data points in Fig. 2 fortuitously fall almost exactly on the fitted line shown, the error bars (which represent the standard deviation of the mean of our measurements) are to be taken as more representative of the ac-

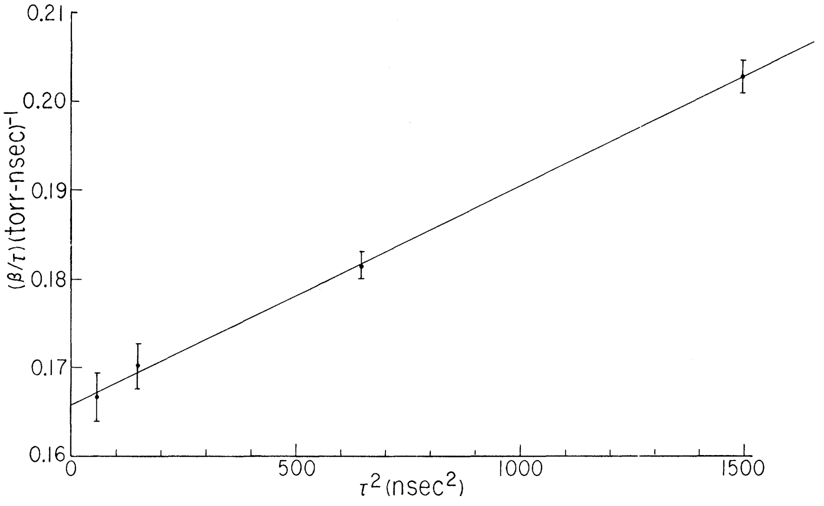

FIG. 2. Plot of β/τ vs τ^2. The straight line is a least-squares fit by $\beta/\tau = b_1 + b_3\tau^2$.

curacy of our experiment.

Explanations of the observed nonlinear behavior of $\beta(\tau)$ which do not invoke vcc have not been successful. The loss of Na atoms from the excitation region is not expected to be important both because few atoms leave the $\cong$2-mm beams even for $\tau = 38.7$ nsec, and because our measurements, performed at fixed τ, are automatically normalized by the $P=0$ measurements to account for whatever loss of Na that does occur. The use of excitation pulses of finite duration could conceivably require that our experiment be analyzed with an effective pulse separation τ' which differs from τ (τ represents the excitation-pulse separation measured between pulse centers) by an amount equal to or less than the 3.5-nsec excitation-pulse duration. With the assumption that τ does require a correction, β will vary nonlinearly with τ, but the nonlinearity will be most pronounced at short τ. Since the measured β varies linearly with τ for short τ, we conclude not only that the excitation pulse duration is not responsible for the nonlinearity in our data, but also that any corrections to τ must be small.

With the use of Eqs. (2) and (4), b_1 can be utilized to obtain a collision cross section corresponding to the combined effect of phase- and state-changing collisions through the relation $\sigma_{\mathrm{ps}}(\mathrm{cm}^2) = b_1 P/4n\bar{v} = (1.036\times10^{-19}) b_1 T/4\bar{v}$. For the value of b_1 given above we find that $\sigma_{\mathrm{ps}} = 111(1)$ Å^2. This is to be compared to the cross section derived from measurements of the He-broadened $3S$-$3P_{1/2}$ absorption line[11] which yield a broadening cross section of $\sigma(T = 415°\mathrm{K}) = 110(9)$ Å^2. Measurements[12] indicate that with He as the perturbing gas the cross section for fine-structure-changing collisions affecting the $3P_{1/2}$ state is $\cong 80$ Å^2. Since a 80-Å^2 depopulation collision cross section represents only a 40-Å^2 contribution to the photon-echo decay cross section, it follows that collisionally induced phase changes constitute a major contribution to photon-echo relaxation for short τ.

Using Eqs. (3) and (4), we find that b_3 can be related to a total vcc cross section according to

$$\sigma_{\mathrm{vcc}} = (1.55\times10^{-19}) b_3 T/\bar{v}(ku_0)^2. \tag{6}$$

Since β_3 is found to vary as τ^3 for all τ considered in our experiment, and since (as discussed in Ref. 5) Eq. (3) is only valid for $ku_0\tau \ll 1$, we must conclude that $u_0 \ll (k\tau_{\mathrm{max}})^{-1} \cong 250$ cm/sec. Inserting $u_0 = 250$ cm/sec in Eq. (6) we find that $\sigma_{\mathrm{vcc}} \gg 138$ Å^2. The fact that σ_{vcc} is found to be relatively large resolves the paradox, discussed in Ref. 13, that the cross section for photon-echo relaxation, measured without considering the effects of vcc, is found to be smaller than the total cross section for either Na($3S$)-He or Na($3P_{1/2}$)-He scattering, which are, respectively, 176 and $\cong 450$ Å^2. The inclusion of vcc effects makes the total photon-echo cross section $\sigma_{\mathrm{tot}} = \sigma_{\mathrm{ps}} + \sigma_{\mathrm{vcc}} \gg 249$ Å^2. The $\cong$450-cm/sec value of u_0 obtained in Na($3S$)-He scattering is found to be large compared to the <250-cm/sec u_0 observed in the present experiment.

We note that earlier photon-echo experiments, performed between different electronic levels in molecular I_2, found no evidence for vcc.[6] Although not explicitly stated, the range of τ investigated appears to have been large compared to that studied in our experiment. This fact taken together with the fact that measurements made exclusively in the $ku_0\tau \gg 1$ regime cannot distinguish the effects of vcc from those of phase-changing collisions leads us to infer that the I_2-I_2 collisional relaxation results from the combined effect of phase-changing *and* vcc collisions.

In conclusion, we have observed for the first time effects related to velocity changes which occur in the collision of an atom in a superposition of two dissimilar atomic-energy states with a perturber atom. This demonstrates that collisional velocity changes are important even in the presence of collisional phase changes. We find that the cross section for collisions whose primary effect is to produce a velocity change is larger than the corresponding cross section for primarily phase-changing collisions. The average axial velocity change per collision is found to be small in support of the contention that only weak distant collisions produce observable velocity-changing effects. It would be particularly interesting to perform experiments with atoms (or molecules) in which the excited state has a lifetime long enough to allow measurements in the regime $ku_0\tau > 1$. In this regime the total vcc cross section could be unambiguously determined.

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[1] Broadening theories are reviewed by W. R. Hindmarsh and J. M. Farr, Prog. Quantum Electron. 2, 139 (1972); R. G. Breene, Jr., Rev. Mod. Phys. 29, 94 (1957); S. Y. Chen and M. Takeo, Rev. Mod. Phys. 29, 20 (1957); F. Schuller and W. Behmenburg, Phys. Rep.

12C, 273, (1974).

[2] P. R. Berman and W. E. Lamb, Phys. Rev. A 2, 2435 (1970), and 4, 319 (1971).

[3] P. R. Berman, Phys. Rev. A 5, 927 (1972), and 6, 2157 (1972), and references therein.

[4] S. G. Rautian and I. I. Sobel'man, Sov. Phys. Usp. 9, 701 (1967) [Usp. Fiz. Nauk. 90, 209 (1966)].

[5] P. R. Berman, J. M. Levy, and R. G. Brewer, Phys. Rev. A 11, 1668 (1975).

[6] R. G. Brewer and A. Z. Genack, Phys. Rev. Lett. 36, 959 (1976).

[7] Ph. Cahuzac, J. L. LeGouët, P. E. Toschek, and R. Vetter, Appl. Phys. (Germany) 20, 83 (1979).

[8] J. L. LeGouët and P. R. Berman, Phys. Rev. A 17, 52 (1978).

[9] The effect of excitation pulse polarization on photon-echo intensity has been discussed in certain cases by I. D. Abella, N. A. Kurnit, and S. R. Hartmann, Phys. Rev. 141, 391 (1966); J. P. Gordon, C. H. Wang, C. K. N. Patel, R. E. Slusher, and W. J. Tomlinson, Phys. Rev. 179, 294 (1969).

[10] A. Flusberg, T. Mossberg, and S. R. Hartmann, Opt. Commun. 24, 207 (1978).

[11] D. G. McCartan and J. M. Farr, J. Phys. B 9, 985 (1976). The cross section obtained in this reference was misquoted in J. Pascale and R. E. Olson, J. Chem. Phys. 64, 3538 (1976).

[12] Pascale and Olson, Ref. 11.

[13] T. Mossberg, A. Flusberg, R. Kachru, and S. R. Hartmann, Phys. Rev. Lett. 42, 1665 (1979).

Thermodynamic Model and Sum Rules for Three-Phase Coexistence near the Tricritical Point in a Liquid Mixture

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Two sum rules for order-parameter susceptibilities are derived for the classical theory of the three-phase region near a tricritical point in ordinary liquid mixtures. The classical theory can also be fitted in a quantitative way to the composition data of Lang and Widom near the tricritical point in the mixture ethanol + benzene + water + ammonium sulfate.

In principle, it should be possible to obtain a wealth of information about tricritical points by carrying out experiments on ordinary liquid mixtures.[1] Variations in composition, temperature, and pressure permit one to alter thermodynamic parameters whose counterparts at a typical symmetry-breaking tricritical point (such as in $FeCl_2$ or ^3He-^4He mixtures) are not under experimental control. However, in practice it is difficult to interpret experimental data for ordinary mixtures near tricritical points precisely because of the large number of thermodynamic degrees of freedom: Four variables must be adjusted to achieve the tricritical state, in place of the two which suffice for a symmetry-breaking system, and phase diagrams should, ideally, be drawn in four dimensions! Thus the task of understanding such experiments can be greatly assisted by the development of *quantitative* theoretical and phenomenological descriptions which can be compared with, or applied to, the laboratory data.

In this Letter we report two results which should be quite useful in interpreting experimental data in the region of three-phase coexistence near a tricritical point. The first is a pair of sum rules for the order-parameter susceptibility. Experimental tests of these sum rules are reported in an accompanying Letter.[2] The second is a practical method of choosing parameters in a thermodynamic model to fit data on compositions of three coexisting phases in a four-component mixture. We have applied it to the data of Lang and Widom[3] for the mixture ethanol + benzene + water + ammonium sulfate, and the results near the tricritical point are very encouraging.

Both results are based on the classical theory[4] of tricritical points and thus do not include nonclassical effects such as the expected logarithmic corrections to scaling.[5,6] Thus far there has been no clear-cut experimental evidence of nonclassical tricritical effects in ordinary mixtures. Of course, one way of looking for such effects is to find where the predictions reported here break down.

In the classical theory the stable thermodynamic state is given by that value of an order parameter ψ which minimizes a free energy Ψ which we assume is a polynomial of the form

$$\Psi = \sum_{j=0}^{6} a_j \psi^j . \tag{1}$$