Tango and Zare's dipole strength ($\frac{1}{3}$ of their $|\langle\Pi|R|\Sigma\rangle|^2$) versus r; the $|R(r)|^2$ scale of Callender *et al.* is arbitrary and we have chosen a scale factor which keeps their data on the graph. In comparing our results with those of Tango and Zare it should be noted that they used $n^*=2$ only for simplicity. An "exact Coulomb" calculation[10] using $n^*=2.1$ would change the radial scaling and reduce the $r\to 0$ and $r\to\infty$ asymptotes slightly (see p. 81 of Ref. 10).

The results of Callender *et al.* disagree strongly with our results and those of Tango and Zare. It is unclear at what point the theory or experiment of Callender *et al.* is inadequate. Their use of a two-state model for a molecular transition neglects the dependence of $\langle v'|R|v''\rangle$ on vibrational wave functions but this may not be serious since the vibrational spacing $\omega_e \sim 150$ cm^{-1} is smaller than $kT \sim 430$ cm^{-1} and the vibrational structure may be negligible. They also assumed that all molecules having an energy greater than that of the atomic p state, $\epsilon_2(\infty)$, will dissociate and produce atomic fluorescence; this assumption neglects both the electronic potential barrier[11] and the rotational energy barrier which exist at large r and which can prevent dissociation. There may also be experimental uncertainties associated with radiation trapping, etc.

In summary, we find a 30% variation in the transition moment over the range 2.6–5.0 Å. We find that the r-centroid technique is valid over this range of r and that three independent measurements give the same value for the relative r dependence, α. The absolute value of $R(r)$ was determined from the lifetime data of Baumgartner, Demtroder, and Stock and the resulting $|R(r)|^2$ agrees qualitatively with the calculations of Tango and Zare but disagrees strongly with the results of Callender *et al.*

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Velocity Selection by Doppler Shift: A General Method for Studying Excited-State Collisions*

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We show that the Doppler shift can provide velocity resolution in excited-state molecular-collision experiments which is comparable to that obtainable in molecular-beam machines. In addition, the state of the quasimolecule formed in the collision can be selected.

Excited-state atomic and molecular collision processes such as excitation transfer,[1] fine-structure-changing collisions,[2] electronic-to-vibrational energy transfer,[3,4] and rotational energy transfer[5] have long been studied with the use of spectral lamps, resonance lamps, and more recently gas lasers as sources of the light to provide the initial excitation. Many investigators have realized that tunable lasers open new avenues in this research by offering high intensity and increased selectivity of state (fine[4] and hyperfine in atoms, vibrational and rotational in molecules). In this Letter we present a method by which single-frequency tunable lasers operating in the visible region of the spectrum can extend these studies in two new and qualitatively different ways: The collision cross sections may be measured *in a gas cell* with a velocity resolution approaching that obtainable with colliding beams (5 to 20%), and the internal state of the quasimolecule formed during the collision may be chosen by polarizing the light relative to the incident *collision axis.*

Our technique is based on velocity selection by Doppler shift (VSDS). If a single-frequency laser beam has a frequency ν which differs slightly from a resonance frequency ν_0 of the molecules (or atoms) in the gas through which it passes, the Doppler shift will make the laser radiation appear exactly on resonance only for those molecules whose component of velocity along the laser beam is

$$v_{1z} = c(\nu - \nu_0)/\nu_0, \tag{1}$$

where the laser beam travels in the z direction. Since the linewidths of good cw dye lasers and typical atomic systems are about 10^7 Hz, and ν_0 is roughly 5×10^{14} Hz, the range of v_{1z} of the excited molecules is very small, roughly 600 cm/sec, and v_{1z} may be regarded as being perfectly determined by the laser frequency. All other degrees of freedom of the collision system are independent, so that the distribution of relative velocity $\vec{u}$ is

$$P(\vec{u}) = \frac{\mu}{2\pi kT}\left(\frac{m_2}{2\pi kT}\right)^{1/2} \exp\left(-\frac{\mu}{2kT}(u_x^2+u_y^2)\right) \exp\left(-\frac{m_2}{2kT}(v_{1z}-u_z)^2\right), \tag{2}$$

where the subscripts 1 and 2 refer to the excited and target particles, respectively, and the reduced mass is $\mu = m_1 m_2/(m_1+m_2)$. One can show from this that the energy resolution is

$$\frac{\Delta E_{\mathrm{rms}}}{\langle E\rangle} = 2\left(\frac{m_1}{\alpha m_2}\right)^{1/2}\left(1+\frac{m_1+m_2}{\alpha\mu}+\frac{1}{2}\frac{m_1}{\alpha m_2}\right)\left(1+\frac{2m_1}{\alpha\mu}+\frac{m_1}{\alpha m_2}\right), \tag{3}$$

where $\alpha \equiv m_1 v_{1z}^2/kT$, and the resolution of relative speed is approximately

$$\frac{\Delta S}{\langle S\rangle} = \left(\frac{m_1}{\alpha m_2}\right)^{1/2}\left(1+\frac{1}{\alpha}\frac{m_1+m_2}{\mu}\right)^{1/2}\left(1+\frac{1}{\alpha}\frac{m_1}{\mu}\right).$$

Figure 1 shows the speed resolution as a function of α for several values of m_1/m_2—the advantage of using a heavy target is obvious. The overall velocity resolution obtainable with the use of the VSDS technique is generally somewhat poorer than in molecular-beam scattering experiments (where 10% overall velocity resolution is not uncommon); however, this is partially offset by the fact that the velocity distribution in a VSDS experiment is known exactly [Eq. (2)], permitting one to deconvolute the true cross section from the measured one with greater confidence.

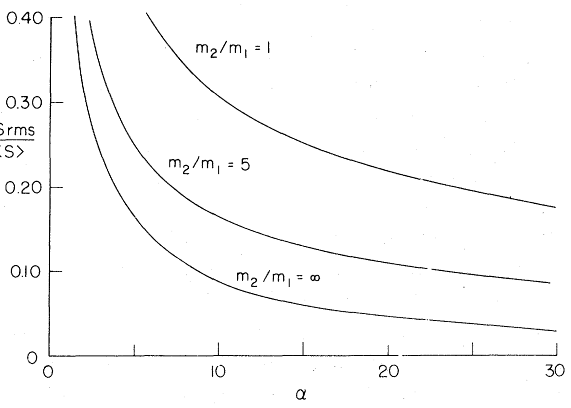

FIG. 1. Speed resolution as a function of $\alpha = m_1 v_{1z}^2/kT$ for various ratios of target mass, m_2, to excited-particle mass, m_1.

In practice the maximum value of α at which useful data may be obtained, and hence the maximum obtainable resolution, is limited by the fact that the signal decreases as $e^{-\alpha/2}$ because of the Maxwell-Boltzmann velocity distribution. In an experiment which is limited solely by this exponential decrease in signal, the limiting value of α will typically lie between 20 and 40. In experiments where the low-velocity cross section is significant there is an additional limitation due to the off-resonant excitation of slow molecules. Since the probability for this off-resonant excitation decreases only as α^{-1} (under the assumption of a Lorentzian line shape), the density of excited slow-moving molecules eventually exceeds the density of velocity-selected ones. This occurs at about $\alpha = 17$ in the worst case.

The VSDS technique offers another novel means of control over collisions occurring in gas cells, namely, selection of the molecular state of the unbound molecule formed by the collision partners during the collision. This may be achieved by polarizing the laser so that the atoms which it excites have a definite projection of electronic orbital angular momentum, m_l, along the laser-beam axis. Since the relative velocity of the colliding atoms, and hence the initial direction of the internuclear axis of the molecule formed by the atoms during the collision, is also preferentially oriented along this axis when the VSDS technique is in use, the projection of the electronic angular momentum along the internuclear axis of this molecule, Λ, is determined by m_l (particularly where the target atom has $L = 0$). In many cases (Hund's cases *a* and *b* for molecules), Λ determines the nature of the molecular potential, and hence governs the results of the collision; for example, a transfer of excitation from one atom to another would generally proceed via a curve crossing involving only one curve with a particular value of Λ. Similar control of collision dynamics can be obtained when the excited particle is a molecule. If molecules which are excited are initially in a low-J state, it should be possible to observe effects arising from the anisotropic nature of the potential between this molecule and the target by using the polarization of the laser to align J relative to the collision axis in the manner discussed above for atoms. Striking effects similar to the ones above, but arising from the final rather than the initial state of the collision system, have been observed in ion-atom scattering.[6] We would not expect similar effects to be as strong in VSDS experiments because of the larger impact parameters and greater angular deflections characteristic of thermal-energy collisions.

The experimental procedure for a typical VSDS experiment involves shining a single-mode cw tunable laser into a gas cell containing both a species to be excited and a target species. The velocity dependence of the cross section for the production of a particular excited state is then determined by measuring the ratio of fluorescence from this state to the laser-excited resonance fluorescence as the frequency of the laser is swept. The method may be used to measure cross sections for change of state of the excited species, for transfer of excitation to the target species, or for the production of new excited species through chemical reaction.

Let us now look at a possible VSDS experiment in more detail in order to illustrate its application. We consider an experiment similar to Ottinger and Zare's[5]; that is,

$$M^*(v,j) + X \rightarrow M^*(v',j') + X,$$

where the molecule M^* has been excited to a particular vibrational and rotational state by laser excitation, and then undergoes the state-changing collision with an inert target, X. The final state of the molecule is determined by analyzing the fluorescence from the final state with a spectrometer and photomultiplier. We will assume that the experiment is done in a 1-cm^3 volume, with a density of M and X such that 10^{16} photons/sec are absorbed from a laser beam with a power density of 100 mW/cm^2. This can be achieved without saturating the transition if the density of M is about 10^{14}/cm^3 and the density of X is 3×10^{15}/cm^3. The target-gas density must have roughly this value to prevent the laser from burning a hole in the ground-state velocity distribution of the molecules M. We assume here that about 5×10^{-3} of the molecules M are in the particular vibrational and rotational ground state we wish to excite from, and that 10^{-2} of these have the right velocity to be excited by the laser. The Frank-Condon factor for the excitation transition is taken to be about 0.03, and the kinetic cross section for redistributing the velocity of M on collision with X is assumed to be 10^{-13} cm^2. Under these conditions the velocity distribution of the excited molecules will not be seriously perturbed before they radiate. With these experimental parameters about 0.1% of the excited molecules will make an inelastic transition to a particular v',j' level (cf. Fig. 3 of Ref. 5). Therefore, the fluorescence from molecules having a particular final state is about 10^{13}/sec cm^3. A typical spectrometer will require a slit width of 0.02 cm (for 1-Å resolution), restricting the volume of gas observed to 0.02 cm^3, and will collect only 2×10^{-3} of the light ($f/7$ optics) from this volume. Assuming reasonable values for the Frank-Condon factor of the observed transition (0.1), the transmission of the optical system (0.2), and the quantum efficiency of the detector (0.15) gives a counting rate of 10^6 counts/sec in the most intense fluorescence line from the inelastically scattered excited-state molecule. This counting rate will be reduced by $e^{-\alpha/2}$ as the laser is tuned to select larger velocities, suggesting that measurements up to $\alpha \cong 20$ should be possible. Experiments requiring lower resolution or ones in which an interference filter can be used to analyze the scattered light will give larger counting rates.

The velocity-selective interaction of monochromatic radiation with gas molecules upon which the VSDS method is based also forms the basis of Lamb-dip and saturated-absorption spectroscopy in which only those molecules having essentially zero velocity along the direction of the laser beams are observed. Recently this selective interaction with radiation from infrared gas lasers has been used to measure the width of the Lamb dip for molecules having a nonzero velocity along the laser beam by using acousto-optic modulation to shift the laser frequency away from exact resonance.[7] In another experiment[8] CO_2 molecules were pumped into an excited vibrational-rotational state by one laser, and another laser was used to look at the velocity changes which accompanied a collision-induced change of rotational state. In contrast to the method proposed above, these experiments all involve the interaction of the molecules with two monochromatic laser fields, and information about collision processes has been determined from the width of the resonance observed as the probe beam is frequency tuned. In the method proposed above the atoms interact with only one laser beam and the effects of the collision are determined by examining the fluorescence; consequently the technique is simpler and inherently more sensitive.

Studies of collision processes involving electronically excited molecules have produced valuable and interesting information, in spite of the fact that they have been done without the velocity resolution characteristic of recent molecular-beam experiments on collisions of ground-state molecules. The VSDS technique offers a simple method for achieving this resolution in excited-state collision studies. In addition it affords an opportunity of extending the energy range of these experiments well into the superthermal region (up to 1 eV in some cases), and it allows selection of the internal state of the collision complex.

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Thermal Detection of Nuclear Spin-Symmetry Conversion of Tunneling Methyl Groups

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Nonequilibrium populations of proton spin-symmetry species of methyl groups undergoing tunneling rotation occur in a sample which has been thermally quenched to helium temperatures. When the external magnetic field is adjusted to bring the Larmor frequency of impurity electrons into coincidence with the methyl-group tunneling frequency, cross relaxation releases the stored mechanical energy of tunneling rotation to heat the sample.

Tunneling resonances have been reported[1-3] in the magnetic field dependence of proton spin relaxation in γ-irradiated samples containing molecular groups undergoing tunneling rotation at low temperatures. The resonances occur when the Larmor frequency of impurity unpaired electron spins is equal to the molecular rotational tunneling frequency. They arise from transitions which involve a flip of the electron spin in the external magnetic field and a simultaneous change