taken into account.

The level scheme of ^{212}Po as given in Fig. 2 and the configuration as derived from the $B(E2)$ value of the $(8^+)\rightarrow(6^+)$ transition may be compared with prediction of shell-model calculations.[4,6,7] Glendenning[4] suggested that the low-spin yrast states may be dominated by the $\nu i_{11/2}{}^2$ configuration thus producing a 10^+ isomer. This prediction is not supported by the present results. Later Glendenning and Harada[6] proposed that a 10^+ isomer of $[(\pi h_{9/2}{}^2)_{0^+}(\nu g_{9/2}, i_{11/2})_{10^+}]_{10^+}$ configuration may exist around 1.2 MeV. This isomer should have a lifetime of $\approx 10^{-6}$ s and decay by α emission.[6] Such an α line was not observed in the present experiments. Auerbach and Talmi[7] suggested that the low-spin yrast states may have mixed $[(\pi h_{9/2}{}^2)_{0^+}(\nu g_{9/2}{}^2)_{I^+}]_{I^+}$ and $[(\pi h_{9/2}{}^2)_{I^+}(\nu g_{9/2}{}^2)_{0^+}]_{I^+}$ configurations with spins $I = 0, 2, 4, 6, 8$ in agreement with the conclusions drawn from the experimental observations.

The present results seem to support the interpretation of the ^{212}Po high-spin isomer in terms of the $[(\pi h_{9/2}{}^2)_{8^+}(\nu g_{9/2}{}^2)_{8^+}]_{16^+}$ configuration.[7,8] However, the $[(\pi h_{9/2}{}^2)_{8^+}(\nu i_{11/2}{}^2)_{10^+}]_{18^+}$ configuration[4,5] cannot be excluded since the $\nu i_{11/2}{}^2$ configuration may play a role at higher excitation energies. It seems to be unlikely that the high-spin isomer has the $[(\pi h_{9/2}{}^2)_{8^+}(\nu g_{9/2}\nu i_{11/2})_{10^+}]_{18^+}$ configuration,[6] since the corresponding 10^+ isomer has not been observed.

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Collisionless Intramolecular Vibratonal Relaxation in SF_6

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Time-resolved spectroscopy is applied to the problem of collisionless intramolecular relaxation within the ground electronic state of polyatomic molecules. The redistribution of vibrational energy within a molecule may be monitored by the different anharmonic shifts which occur when the energy is localized in the different modes. Picosecond infrared-laser–absorption saturation-recovery measurements on SF_6 show that the relaxation time, for statistical behavior to set in, falls within the limits 1 psec $< T_1 <$ 30 psec.

There has always been great interest in the limits of applicability of statistical mechanics. For example, the point is often made that statistical concepts describe macroscopic systems very well. On the other hand, a tiny dynamical system such as a single isolated molecule may behave in a nonergodic manner.

While the question of ergodicity may seem high-

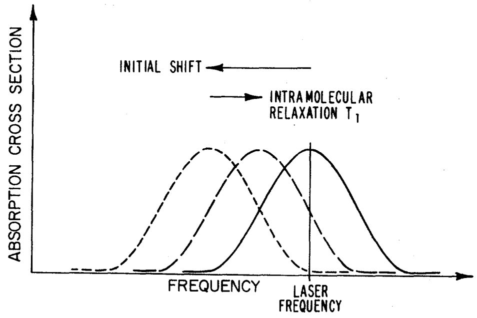

FIG. 1. Behavior of the ν_3 spectrum under infrared pumping by a powerful ultrashort CO_2-laser pulse. The strong initial redshift is followed by a partial return shift to the original position due to intramolecular relaxation.

ly theorectial, it has rather direct experimental consequences. Consider, for concreteness, the resonant excitation[1] of the ν_3 vibrational mode in SF_6 by an ultrashort infrared laser pulse. As a result of the energy deposition, the fundamental absorption spectrum will experience an anharmonic shift. There are two possibilities for the spectral shift: (1) For energy localized within the ν_3 mode, the anharmonic shift will be ~5 cm^{-1} per 1000 cm^{-}. This *self*-anharmonicity is known from the overtone spectrum[2] of the ν_3 mode. (2) For energy randomly distributed in all the modes, the anharmonic shift will be 2.6 cm^{-1} per 1000 cm^{-1}. This *cross* anharmonicity is determined from the temperature shift of the fundamental ν_3 spectrum.

Therefore, we may anticipate the behavior shown in Fig. 1. An ultrashort infrared pulse will initially deposit energy in the ν_3 mode, causing a large anharmonic shift. Subsequently, the energy may randomize among all the vibrational modes, causing the infrared spectrum to shift part way back to the original position. Time-resolved vibrational spectroscopy can monitor the amount of energy deposited, its distribution among the modes and can provide an operational test for ergodicity. The anharmonic shifts in effect measure the probability distribution of the molecule in its phase space, thereby probing for ergodicity and the rate at which it sets in. The redistribution of energy from a driven mode should be regarded as a T_1-type relaxation process,[3] where the rest of the molecule acts as a heat bath.

In the experiments described below, SF_6 gas is pumped by a powerful CO_2-laser pulse. The drop in absorption cross section which results should not be regarded as a true two-level saturation effect. Instead the absorption saturation is best interpreted as due to a shift off resonance of the absorption spectrum as indicated in Fig. 1. We may hope to see a strong absorption effect when the ν_3 mode is initially excited, followed by a partial recovery of absorption as the vibrational energy is redistributed among the modes.

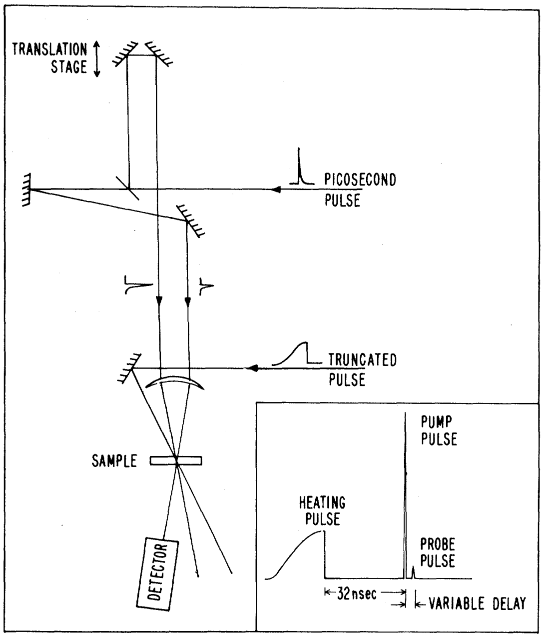

FIG. 2. Experimental setup. The sequence of pulses arriving at the sample is shown in the inset.

In this series of experiments the time-resolved saturation and partial recovery of absorption are probed at the same wavelength as the pump beam. The full saturation spectrum may be obtained by a simple extension of the techniques employed here.

The experimental apparatus is illustrated in Fig. 2. A single-mode Tachisto transversely-excited-atmosphere CO_2 laser is followed by a plasma shutter[4] which truncates the laser pulse. The beam then passes through an optical free-induction-decay[5] cell which generates the 30-psec pulses. This light source is employed in a standard[6] picosecond pump and probe arrangement, the time delay being supplied by a translation stage. The probe pulse was observed with a Ge:Au detector and averaged with a boxcar integrator.

In one of the experiments a comparison was made between the behavior of heated and unheated SF_6. Rather than using an oven, the preheating was accomplished by means of the truncated

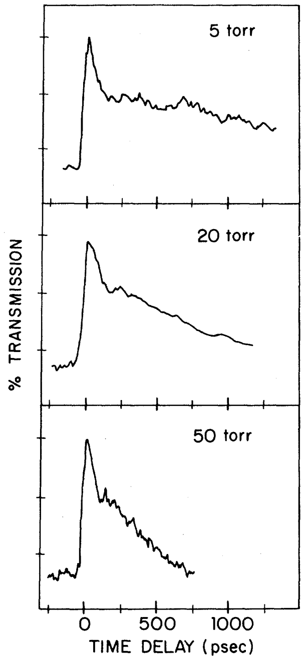

FIG. 3. Recovery of saturation is shown for three gas cell pressures. The experiments were with 50-psec pulses at a peak intensity of 66 MW/cm^2.

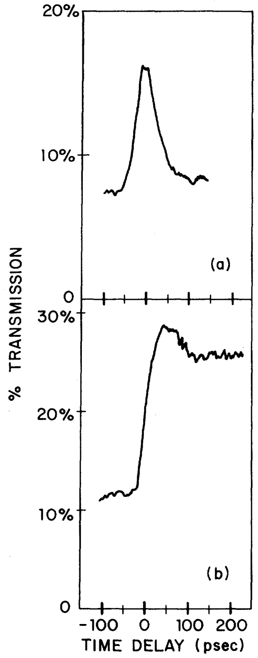

FIG. 4. Saturation recovery scans for (a) p-Ge at an intensity of 150 MW/cm^2, (b) 20 Torr of SF$_6$ at 0.3 GW/cm^2. 30 psec pulses were employed in these scans.

optical pulse from the plasma shutter. An optical delay of 32 nsec after the heating pulse allowed collisional equilibration before the picosecond pump and probe pulses arrived. The irradiation sequence experienced by the molecules is shown in the inset of Fig. 2. However, most of the experiments were performed at room temperature with the preheating beam not in use.

In this type of experiment it is important to separate out collisional effects and to operate in a pressure regime where they are negligible. Figure 3 shows a series of pump probe saturation scans which were performed at three different SF$_6$ gas pressures. The graphs show a strong absorption saturation followed, as anticipated, by a partial recovery on a rapid collisionless time scale and then a slow pressure-dependent recovery. The pressure-dependent recovery time constant is 13.5 ± 3 nsec Torr. This corresponds to a very large gas kinetic cross section, indicating the care that is necessary for operation in a truly collisionless regime.

Previous workers,[7,8] who observed a saturation recovery in the nanosecond regime, speculated that they might be seeing collisionless effects. The improved time resolution in our experiments shows that those effects were most likely collisional in nature. Deutsch and Brueck[9] have seen some interesting effects even on a microsecond time scale. It is clear from our measured pressure-time constant that their observations were firmly in the collision-dominated time scale.

The scans shown in Figs. 4 and 5 were taken at a sufficiently low pressure as to have a negligible effect on the results. Figure 4, showing data taken with 30-psec pulses, compares the saturation recovery in SF$_6$ with that observed in the saturable absorber p-Ge.[10] This semiconductor crystal is known to have a saturation recovery time of $\lesssim 1$ psec which is essentially instantaneous on the time scale of our experiments. Therefore, Fig. 4(a) is a type of pulse autocorrelation scan and it enables us to fix an accurate zero of time delay.

The saturation recovery of SF$_6$ under three different conditions of excitation is shown in Fig. 5. The scan in Fig. 5(a), which resembles those of Figs. 3 and 4(b), was taken under conditions where on the average, $\lesssim 1000$ cm^{-1} of energy was deposited per molecule by the pump pulse.[11] In Fig. 5(b), the pump power was increased so as to deposit ~3000 cm^{-1} per molecule on average. A steady state reached 50 psec essentially during the laser pulse, and the fast recovery com-

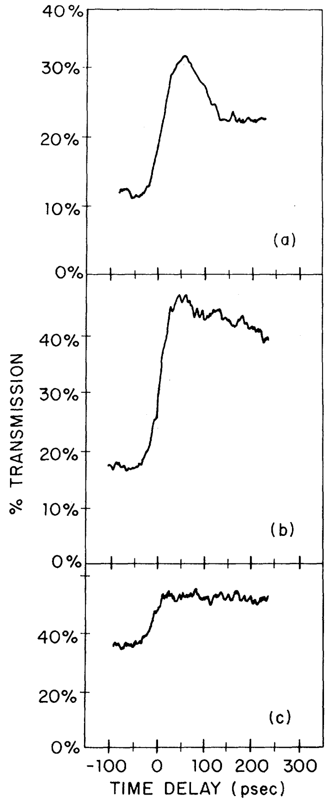

FIG. 5. Saturation recovery scans to show the disappearance of the initial fast component as the internal vibrational energy of the SF_6 molecules is increased. Experiments were done at 20 Torr of SF_6 in a 3.7-mm cell with 50-psec pulses. (a) Less than 1000 cm^{-1} energy deposited by the pump pulse. (b) $\gtrsim 3000$ cm^{-1} energy deposited. (c) Molecules thermally excited to 650°K or 3500 cm^{-1} by a preheating pulse.

ponent is absent. In Fig. 5(c) the experiment was repeated[12] in SF_6 preheated to 650°K, a temperature at which the average internal vibrational energy is equivalent to ~3500 cm^{-1}. Once more, a steady state is reached within 50 psec, essentially during the laser pulse, and the fast recovery component is absent.

The spectral shifts depicted in Fig. 1 may result not only from the internal redistribution of energy, but also from the loss of molecular energy due to adiabatic decay of level populations which follow the decaying laser pulse. This loss of internal energy simply reduces the anharmonic shift. We interpret the fast recovery component which is seen in Figs. 3, 4(b), and 5(a) as due to the adiabatic decay of level populations in an energy region where the vibrational level density is relatively sparce.[13] It is readily seen from Fig. 4 that the fast recovery component roughly follows the autocorrelation function.

On the other hand, Figs. 5(b) and 5(c) are typical of experiments on molecules with > 3000 cm^{-1} excitation. This is the so-called quasicontinuum regime[14] where the vibrational level density is very high. In these cases, there is no fast recovery component and the saturation approaches steady state during the laser-pulse duration.

In either of the above cases, the saturation level achieves a final steady state during or immediately following the laser pulse. The conclusion seems inescapable therefore that the intramolecular damping occurs within 30 psec. The proper interpretation of this point requires a clear conceptual picture of intramolecular damping.

Ignoring spontaneous emission, dissociation, and collisional effects, the energy levels of the exact vibrational Hamiltonian, though they may be very dense, are rigorously discrete. A molecule with energy localized in a given mode is inherently nonstationary due to anharmonicity and must be described as a coherent superposition of discrete stationary states of differing energies. Therefore the line shape of intramolecular damping is best regarded as the *envelope* function of those discrete levels which contribute to the nonstationary superposition. The reciprocal of the width of that envelope function is the intramolecular damping time.

The experimental conclusion is that the linewidth of the envelope function of such a nonstationary state must be greater than the reciprocal of 30 psec. If the envelope function were any narrower, then the decay of the coherent superposition would produce temporal structure on a time scale longer than the pulse duration. Thus the redistribution of energy from the driven normal mode must occur within an upper limit of 30 psec.

A lower limit of 1 psec may be determined from the absorption linewidth[15] of heated SF_6 which is never much greater than ~20 cm^{-1}. Therefore, the intramolecular relaxation time must fall within the limits 1 psec $< T_1 <$ 30 psec.

Although the final steady state is achieved very rapidly, this experiment does not establish that the final state is necessarily exactly ergodic. Indeed, no one individual measurement[16] is sufficient for this purpose. The accessible vibrational phase space contains thousands of cells and therefore thousands of different experiments would be required to show that each cell is occupied with equal probability.

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Electron Scattering by Laser-Excited Barium Atoms

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Inelastic and superelastic scattering of 30- and 100-eV electrons by laser-excited $6s6p\,^1P$ and subsequent cascade-populated $6s6p\,^3P$, $6s5d\,^1D$, and $6s5d\,^3D$ Ba atoms have been observed for the first time. Absolute differential cross sections for the singlet and relative scattering intensities for the triplet species have been determined in the 5°–20° angular region. Under the present conditions excitations dominate over de-excitations.

Few observations have been made concerning electron scattering by excited atoms due primarily because of the difficulties associated with generating such species. However, such information is crucial to the understanding of a broad range of laser and plasma systems. Through the utilization of lasers the experimental difficulties can be overcome. Λ and χ parameters, representing relative magnetic sublevel cross-section ratios and phases for the Na $3^2P \rightarrow 3^2S$ and 3^2P-4^2S processes, have been determined utilizing laser-excitation and electron-scattering techniques.[1,2] More recently recoil techniques[3,4] have been utilized to generate total electron scattering cross sections from the laser-excited Na 3^2P state. Neither of these measurements yielded, or could yield, new cross sections for specific inelastic processes associated with the excited atomic species and no such cross sections exist for any laser-excited species at the present time.

We report here the first measurements concerning electron scattering by laser-excited Ba atoms and the first set of normalized differential cross sections (σ) for transitions among excited states of any atom. This research has been greatly facilitated by the construction of a new electron impact spectrometer which uses unique tandem double-hemispherical energy analyzers. This approach improves the system energy resolution and signal-to-noise ratio and, in particular, greatly reduces direct electron beam contributions at low scattering angles. The details of this apparatus have been described elsewhere.[5]