Laser-Assisted Intermolecular Energy Transfer between Electronic States of Carbon Monoxide in the Vacuum Ultraviolet

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We report the first observation of laser-assisted collisions in molecules. Cross sections for such intermolecular processes involving high-energy ($E \sim 11$ eV) Rydberg states in carbon monoxide are shown to be larger than 10^{-16} cm^2 at the laser intensities approaching 10^{10} W/cm^2. Our experiments clearly illustrate the care necessary in interpreting multiphoton spectra taken at high laser powers.

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Optical processes involving the near simultaneous events of a collision and absorption of laser radiation have recently been shown to occur with significant cross sections[1] and in a wide range of atomic media.[2] We report the first observations of analogous phenomena in a molecular system, where we have demonstrated laser-assisted intermolecular energy transfer in carbon monoxide (CO). There are significant differences to be encountered in the molecular case, since the detailed rotational and vibrational energy-level structure must be included in the interpretation of both the frequency dependence and the magnitude of the laser-assisted transfer. Thus, laser-induced collisional phenomena[3,4] are an important new probe for molecular dynamics and the concepts developed in these studies may ultimately lead to "transition state" spectroscopy in both fragmentation and reactive scattering processes.

In spite of the fact that the rovibronic energy levels in a molecule "dilute" the electronic transition probabilities, the cross sections for these laser-assisted energy-transfer phenomena can approach those observed in atomic media, and in CO were measured to be $> 10^{-16}$ cm^2 at a power density of 8×10^9 W/cm^2. Moreover it must be appreciated that when working at high power densities, where the laser-induced cross section deviates from a linear intensity dependence, the frequency dependence scales as $1/\Delta\omega$ rather than $1/\Delta\omega^2$. Thus in molecular systems much of the structure due to individual rotational states may be smeared out into a "quasicontinuous" spectrum arising from laser-assisted collisional phenomena. Such effects therefore could play an important role in multiphoton absorption at high laser intensities since they serve to eliminate rotational bottlenecks and hence must be included in the interpretation of multiphoton studies of the electronic structure of polyatomic molecules.

The laser system for these studies produced two independently tunable and time synchronized dye-laser pulses. This was achieved by using a Nd-doped yttrium aluminum garnet oscillator and dividing the output into two beams which were amplified, frequency doubled, delayed with respect to each other, and then used to pump the two dye lasers. Typical performance for the first laser at 5570 Å (Rhodamine 560) was 50 mJ in a 10-nsec pulse with a linewidth of 0.8 cm^{-1}. This radiation was then frequency doubled in deuterated potassium dihydrogen phosphate (KD*P) to yield 6 mJ in an 8-nsec pulse at 2784 Å. The second laser at $\lambda \sim 5800$ Å (Rhodamine 590) was narrower in linewidth ($\Delta\nu < 0.06$ cm^{-1}) and produced a 10-nsec-duration 25-mJ pulse, delayed by 12 nsec with respect to the first pulse. The two laser beams were counterpropagating and focused into a stainless-steel cell with LiF windows to a 200-μm waist oriented parallel to the slit of a 1-m vacuum ultraviolet monochromator. The detector was an EMI solar-blind photomultiplier (CsI cathode) and the absolute sensitivity calibration of this system has been already described.[5] In the present experiment the output of the photomultiplier was amplified in a Tektronix model-1A7A amplifier, then passed through a 50-nsec coincidence gate set to overlap the transfer laser, and finally to a discriminator and counter.

The types of laser-assisted energy transfer processes which were studied in CO are as follows:

$$\mathrm{CO}(1)\{A^1\Pi, v_1 = 5\} + \mathrm{CO}(2)\{X^1\Sigma^+, v_2 = 0\} + \hbar\omega \rightarrow \mathrm{CO}(1)\{X^1\Sigma^+, v_1 = 1\} + \mathrm{CO}(2)\{B^1\Sigma^+, v_2 = 0\}, \tag{1a}$$

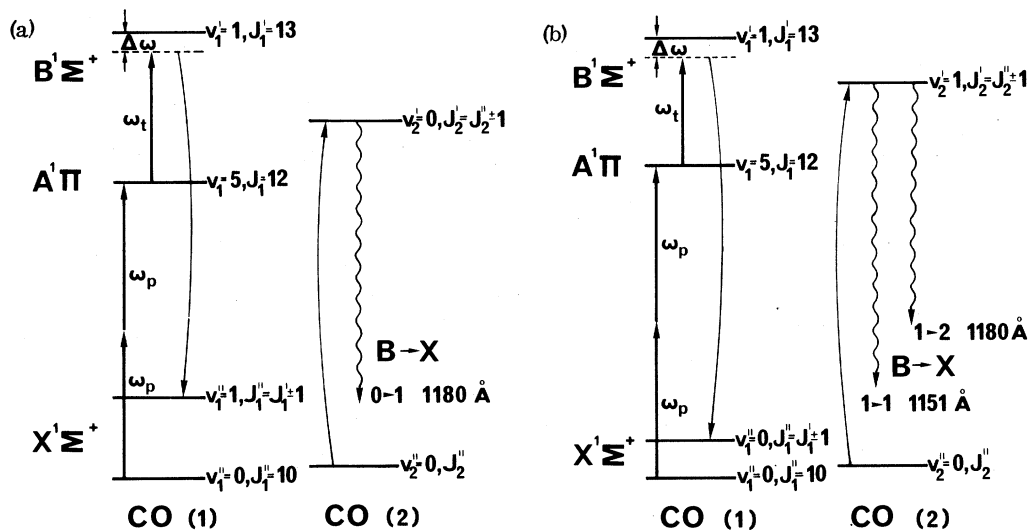$$\rightarrow \mathrm{CO}(1)\{X^1\Sigma^+, v_1 = 0\} + \mathrm{CO}(2)\{B^1\Sigma^+, v_2 = 1\}, \tag{1b}$$

FIG. 1. Energy-level scheme for laser-assisted intermolecular energy transfer in CO. (a) and (b) correspond to processes (1a) and (1b) described in text.

and these are indicated in Figs. 1(a) and 1(b). The first laser ($\lambda = 2784$ Å) at $t = 0$ creates population ($> 10^{13}$ cm^{-3}) in a rovibronic level ($v = 5$, $J = 12$) of the $A^1\Pi$ state via two-photon absorption. After a 12 nsec delay the transfer laser prepares a dressed state[6] (indicated by the dotted line) which can transfer its energy to another CO molecule if it *simultaneously* makes a collision. In the strong-field regime, the cross section for this process is given[1,3a] by

$$\sigma = 1.4 \, \frac{3\pi}{\sqrt{3}} \, \frac{\mu_1 \mu_2 \mu_3}{\hbar^2 \bar{v} \, \Delta\omega} \, E , \qquad (2)$$

where μ_1, μ_2, and μ_3 are matrix elements corresponding to $B \leftarrow A(1, 5)[CO(1)]$, $B \leftarrow X[CO(1)]$, and $B \leftarrow X[CO(2)]$, respectively (including rotational line strength factors). $\Delta\omega$ is the detuning from a real rovibronic level in the B state, and E is the transfer-laser field strength. It should be noted that the deviation from the E^2 dependence observed at lower laser intensities is not a saturation phenomenon, corresponding to an equalization of populations. Rather it arises because the magnitude of the laser-induced avoided crossing is becoming large enough that at very-high fields the dressed states never cross.[3b]

Since all the input parameters for Eq. (2) are available[7,8] for CO, it is possible to make estimates of the cross sections for processes (1a) and (1b). Allowing for the 10 cm^{-1} deutuning from a rovibronic level in the $B^1\Sigma^+$ state and a factor of $\frac{1}{3}$ for the orientational average[3a] with respect to the linearly polarized transfer laser,

at a power density (P/A) of 8×10^9 W/cm^2 we estimate $\sigma = 17 \times 10^{-16}$ cm^2 for (1a) and $\sigma = 3 \times 10^{-16}$ cm^2 for (1b).

At low intensities of the transfer (10^5 W/cm^2), we observe only the direct (intramolecular) excitation of the $B^1\Sigma^+(v' = 1) \leftarrow A^1\Pi(v'' = 5)$ transition. As predicted from consideration of the detailed rotational-state selection rules for this two-step, three-photon absorption, only P and R lines[9] (labeled with respect to the $A^1\Pi$ state) are observed. As can be seen from the lower trace of Fig. 2 ($p_{CO} = 30$ Torr) we are populating primarily $J = 12$ in the $A^1\Pi$ state with a small contribution from $J = 13$, but with no $J = 11$ (both $J = 12$ and 13 are excited simultaneously because the bandwidth of the pump laser is comparable to their separation at the S-branch $A \leftarrow X$ bandhead). Even for pressures as high as 100 Torr there is no evidence from these excitation spectra for any rotational relaxation in this relatively unperturbed[10] vibrational level of the $A^1\Pi$ state. Measurement of the $B \leftarrow X$ fluorescence spectrum originating from $v' = 1$ gave a branching ratio for (1, 1), (1, 2), and (1, 3) emission of 4:1:0.3, which is in good agreement with the calculated ratio of Franck-Condon[8] factors of 4:1.3:0.4.

Under conditions of high transfer-laser intensity (8×10^9 W/cm^2) we observe a dramatic change in the excitation spectrum. If we detect only the emission from $v' = 1$ of the B state [(1, 1) at 1151 Å], then the sharp lines observed at low intensity become asymmetrically broadened with a linewidth $\Delta\nu = 3.7 \pm 0.3$ cm^{-1}. Although we do indeed
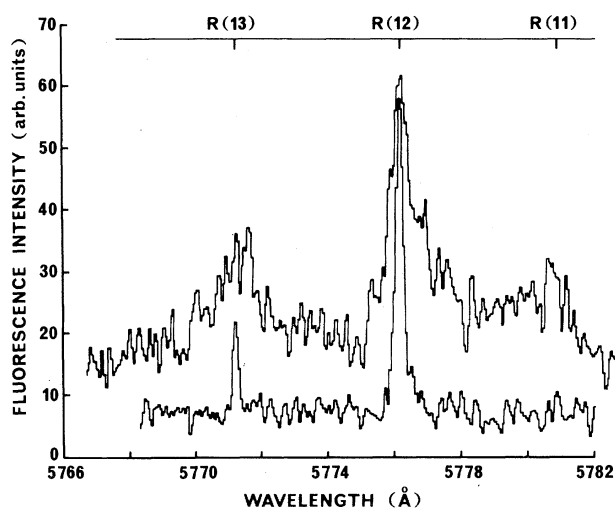
FIG. 2. Excitation spectra (scanning the transfer laser λ_t) of CO, detecting $B \rightarrow X$ fluorescence $[(0, 1) + (1, 1) + (1, 2)]$. Transfer laser is delayed by 12 nsec with respect to the pump laser. Lower trace: $P/A = 10^5$ W/cm^2, signals registered between the R lines correspond to the *background* level observed without the transfer laser. Upper trace: $P/A = 8 \times 10^9$ W/cm^2. $p_{CO} = 30$ Torr.

FIG. 3. Intensity dependence of the switched collision process, $p_{CO} = 100$ Torr and $\lambda_t = 5778.2$ Å. Solid and broken lines represent slopes $\frac{1}{2}$ and 1, respectively.

observe a red wing to the line, it is probably premature to interpret this as being directly analogous to the quasistatic wing observed in atomic media.[2]

In Fig. 2, we show the excitation spectrum taken while simultaneously monitoring the fluorescence from both the $v' = 0$ and the $v' = 1$ levels of the $B^1\Sigma^+$ state. This choice was made because (0, 1) emission lies too close ($\Delta\lambda = 0.5$ Å) to the (1, 2) emission to be resolved with our monochromator and because we also wish to emphasize that both processes (1a) and (1b) are occurring simultaneously. As well as the asymmetric line shape around the real transition noted above, there is also an additional set of peaks of lower intensity but *reproducible* in position. Furthermore the emission spectra obtained when exciting at 5776 Å (near resonance) and 5778.2 Å (at one of the new spectral features noted) gave different intensity ratios at 1151 Å [(1, 1) emission] and 1180 Å [(0, 1) + (1, 2) emission], namely, 4:1 vs 2:1, corroborating the additional presence of (0, 1) emission resulting from process (1a).

A detailed theoretical analysis of the rotational-state dependence [taking into account the Boltzmann distribution of acceptor states of CO(2) in the X state] of processes (1a) and (1b) reveals an extremely dense spectrum of switched colli-
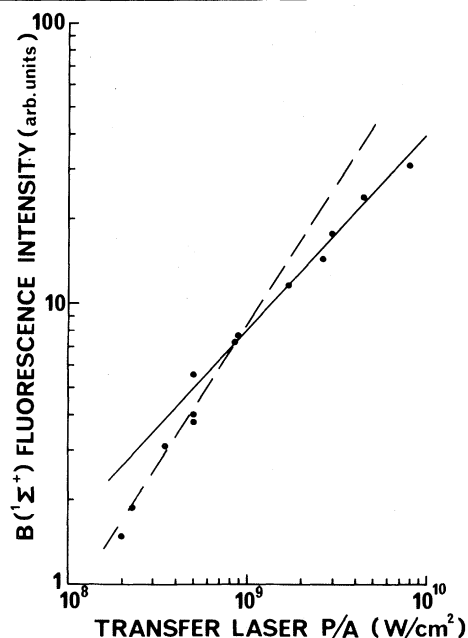
sions with $\Delta\omega$ extending ± 200 cm^{-1}, and we have observed similar quasicontinuous spectral features, well above the background level, as far as 150 cm^{-1} from any real $B \leftarrow A(1, 5)$ transition.

The intensity dependence of the spectral features due to laser-assisted collisional energy transfer is given in Fig. 3 (data are for $\lambda_t = 5778.2$ Å, $\Delta\omega = 6.6$ cm^{-1}). It is initially linear in P/A and then goes over to $(P/A)^{1/2}$ dependence at high intensities as predicted by theory. This behavior was observed at several different wavelengths, except in a 0.4-cm^{-1} region around the intramolecular transitions shown in the low-intensity scan in Fig. 2. On resonance the intramolecular transition is saturated with the signal reduced by a factor of ~10 compared to that extrapolated from low laser intensities, but this would account only for a total width < 0.2 cm^{-1}, far less than observed.

An intramolecular process which could account for the observed emission is the production of anti-Stokes radiation induced by the transfer laser. Several reasons lead us to believe that an anti-Stokes process can be eliminated. Firstly, the frequency dependence of anti-Stokes radiation must *smoothly* follow the intramolecular excitation as shown in the lower trace of Fig. 2. Secondly, it must be symmetric with respect to the

frequency detuning. Finally, the emission spectrum (vibrational intensities) must be independent of the wavelength of the transfer laser. All of these properties are in direct contrast to what is actually observed.

It is possible to make an estimate of the cross section observed experimentally for the sum of processes (1a) and (1b). We calculate that 2% of the $A^1\Pi$ state is transferred to the $B^1\Sigma^+$ state via this laser-assisted collisional process at 8×10^9 W/cm. This corresponds to a total cross section of $\sigma_{a+b} = 5 \times 10^{-16}$ cm^2 compared to our estimate of $\sigma_{a+b} = 20 \times 10^{-16}$ cm^2. Agreement is reasonable considering the total uncertainties in the input parameters.

This work shows the important role that laser-assisted collisional phenomena can play in laser spectroscopy studies at high laser intensities. As the first observation of switched collisions to achieve inelastic energy transfer in a molecular system, it is an important step in developing and understanding models for laser field effects in molecular dynamics, and provides the basis for exploring dressed-state chemistry in other areas such as photofragmentation and even reactive scattering. Finally, the large cross sections achieved in these experiments establish the feasibility of future applications, as for example exciting vacuum ultraviolet lasers.

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Transition to Chaotic Behavior via a Reproducible Sequence of Period-Doubling Bifurcations

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We present the results of measurements of the vertical and horizontal temperature gradients in a Rayleigh-Benard cell. By an appropriate preparation of the initial state, the system can be brought into a single-frequency oscillatory regime. Further stepwise increase in the imposed temperature gradient makes the system go through a reproducible sequence of period-doubling bifurcations up to $f_1/16$. The Feigenbaum δ and μ universal numbers are determined.

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A recent theory by Feigenbaum[1,2] suggests that nonlinear systems which can be led into chaotic behavior via a sequence of period-doubling bifurcations will exhibit universal behavior. As the stress parameter λ is increased, the bifurcation points λ_n occur in such a way that the ratio