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State-Selected Kinetics from Laser-Excited Fluorescence

Energy transfer and chemical reaction rates can be measured for individual molecular energy states.

C. Bradley Moore and Paul F. Zittel

Measurements of the rates of energy transfer, chemical reactions, and radiationless transitions of molecules in selected states can be made by using laser sources (*1–3*). Knowledge of the rate constants for processes connecting individual quantum states and their variation with rotational, vibrational, and electronic quantum numbers can greatly increase our understanding of chemical kinetics. Such measurements are detailed probes of the potential surfaces, dynamics, and coupling forces which operate in isolated molecules and in molecular collisions. To the extent that chemical reaction rates vary with reactant excitation it may be possible to select products and increase reaction rates in a practical way by laser excitation (*4–6*). Laser-photochemical separation of stable isotopes has been demonstrated and promises drastic reductions in stable isotope prices (*7, 8*). The most extensive application of laser state-selection to date has been in the field of vibrational energy transfer (*1, 2*). A great many processes involving energy transfer from vibration to vibration (V → V) and vibration to translation and rotation (V → T, R) have been studied. Their rates contain information on the internal coordinate dependence of the intermolecular potential. Energy transfer processes play a crucial role in the kinetics and mechanism of chemical and molecular lasers. Energy transfer is important in naturally occurring nonthermal distributions of states in the upper atmosphere, in shock waves, in combustion, in electrical discharges, and in the interstellar medium.

It is the monochromaticity, power, collimation, and short pulse duration of the laser which make it an ideal tool for state selection. Large numbers of molecules may be excited to a single rotation-vibration-electronic energy level or to a well-defined group of levels. Concentrations of various energy states as a function of time may be monitored spectroscopically or reaction end products sampled chemically. Laser state-selection may be used in combination with molecular beam techniques. Laser sources now cover the wavelength range from about 1100 angstroms out to the microwave klystron at a few millimeters (*3*). Tunable sources are now available over much of this range and are continuing to develop rapidly.

The power and coherence of laser sources give us a variety of methods for reaching a desired state. The simplest is to have a laser operating at the frequency of an appropriate absorption transition (Fig. 1a). Two-photon processes give Raman-type selection rules (*9*). Both excitation at the difference frequency between two lasers (Raman transition, Fig. 1b), and at the sum frequency (simultaneous absorption of two photons, Fig. 1c) are possible. When the intermediate or virtual state is near a real one, the intensity of these processes is enhanced. Two-step processes, with a real intermediate level, are also useful. With high-power lasers very substantial excited populations may be created by using these two-photon methods (*10*). The application of laser fluorescence techniques is illustrated below by a few examples.

Laser Experimental Techniques

Fluorescence from excited states populated by absorption of laser light of one frequency has been used to study vibrational and rotational energy transfer, electronic energy transfer, and photochemical reactions. Figure 2 illustrates a typical vibrational relaxation experiment for hydrogen chloride. A pulse with an intensity of a few kilowatts and a duration of several microseconds from an HCl chemical laser excites molecules in a gas sample from the ground vibrational level ($v = 0$) to the first excited vibrational state ($v = 1$) (*11*). Many rotational energy levels are excited by the laser, and in most cases collisions serve to bring about an equilibrium rotational distribution in a time short compared to the laser pulse duration. The concentration of molecules with $v = 1$ is monitored by observing the infrared fluorescence near 3.4 micrometers accompanying the transition $v = 1 \rightarrow v = 0$. In mixtures of HCl with other molecules fluorescence may be observed from any vibrations active in the infrared which became excited during the relaxation process (*12, 13*). Processes may be studied as a function of vibrational quantum number by direct laser excitation of $v = 2$ or $v = 3$ (*14, 15*). Selective excitation of either $H^{35}Cl$ or $H^{37}Cl$ may be achieved (*14*). In this way many V → T, R and V → V processes involving HCl have been studied (*12–19*). Similarly, there have been extensive studies with methane, carbon dioxide, and hydrogen fluoride (*2*). With vibrational excitation of polyatomic molecules energy transfer is observed among the modes of the molecule, as well as from molecule to molecule and from vibration to translation and rotation. The coinci-

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Dr. Moore is professor of chemistry at the University of California, Berkeley 94720. Dr. Zittel, formerly a graduate student at Berkeley, is now at the Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder 80302.

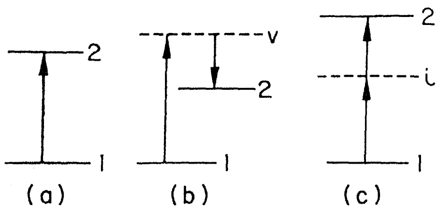


Fig. 1. Laser excitation processes. (a) Direct absorption of a single photon. (b) Raman transition: excitation occurs at the difference between two laser frequencies. (c) Two-photon absorption: simultaneous absorption of two photons excites transitions at the sum frequency. The dashed lines denote the intermediate or virtual states in the presence of the optical field.

dences between fixed-frequency lasers and molecular absorptions are being exploited to excite the vibrations of at least 16 different molecules in the gas phase (*2, 20, 21*). Vibrational relaxation of molecules isolated in matrices at low temperatures is beginning to be studied (*22*). The growing availability of tunable laser sources in the infrared allows almost any infrared-active transition to be selectively excited (*2, 14*).

Excited electronic states of atoms and molecules have also been studied by laser fluorescence techniques. In steady-state fluorescence experiments diatomic molecules such as I_2 (*23*), Na_2 (*24*), and Li_2 (*25*) are excited to a single vibration-rotation level of an excited electronic state. Rates of vibrational and rotational energy transfer in collisions and of electronic quenching are measured against the radiative lifetime of the excited state. Short pulses from tunable dye lasers have been used to measure fluorescence decay times for single electronic-vibrational (vibronic) levels of electronically excited molecules (*26–30*). In this way rates of radiationless transitions and collisional processes may be studied as a function of vibrational excitation. Distributions of molecules among the vibrational states of the products of chemical reactions have also been measured (*31*). Single excited states of atoms may be prepared by laser excitation (*15*). Laser photodissociation may be used to prepare atomic reagents in specific electronic states and with known translational velocities (*32*). This has proved to be a convenient method of producing reactive atoms for measurements of chemical reaction rates (*33*) and vibrational relaxation rates (*34*). The availability of tunable radiation from 2,600 Å to 10,000 Å and the high sensitivity of photomultiplier detection make experiments on electronic excited states particularly favorable.

Fluorescence is not the only method of monitoring kinetic processes following laser excitation. When individual vibration-rotation levels need to be resolved, absorption spectroscopy with a laser source, as developed in the laboratories of Javan (*35*) and Steinfeld (*20, 36*), is often more sensitive than fluorescence. For fast processes, especially on the picosecond time scale, fluorescence yields are small and absorption techniques are again more sensitive (*37*). Energy deposition in translation may be monitored through changes in refractive index (*10, 38*) or detected with a microphone (*39*).

The Raman effect has been used by Ducuing and co-workers (*10, 40*) to excite infrared-inactive vibrations in molecules such as H_2, O_2, and N_2. Figure 3 shows an experiment in which a ruby laser is used to pump a dye laser such that the difference between the laser frequencies is equal to a vibrational frequency of the gas. The two beams are focused together into a small focal zone in which excitation occurs. The most successful detection scheme has been to follow translational temperature through the change in refractive index of the focal zone with time (*10, 40*). Lauberau and Kaiser (*41*) have used Raman excitation combined with Raman detection to study vibrational relaxation in liquids on the picosecond time scale. Yeung and Moore (*42*) have used simultaneous absorption of two photons to measure fluorescence decay times for two vibronic levels of formaldehyde. Freund and Oka (*43*) have demonstrated two-photon pumping by using an infrared laser and a microwave klystron source.

Energy Transfer in HCl

Studies of vibrational relaxation in HCl illustrate the sort of information about molecular collisions that is obtained in laser fluorescence experiments. Vibrational energy is transferred into translation and rotation

$$\mathrm{HCl}\ (v=1) + \mathrm{M} \rightarrow \mathrm{HCl}\ (v=0) + \mathrm{M} + \Delta E$$

where M is another molecule and ΔE, the energy removed from vibration, is 2886 reciprocal centimeters. This has been studied for HCl and for DCl in many mixtures at room temperature (Table 1). These data are a solid basis for conclusions regarding the mechanics of V → T, R relaxation in HCl.

Table 1. Vibrational relaxation of HCl and DCl: $\mathrm{HCl}(v=1) + \mathrm{M} \rightarrow \mathrm{HCl}(v=0) + \mathrm{M} + \Delta E\ (\mathrm{R,T})$. The probability of energy transfer per gas kinetic collision, $P = k/k_{\mathrm{kin}}$, where k is the rate constant; $k_{\mathrm{kin}} = 2.55 \times 10^6\ \bar{\sigma}^2/m^{1/2}$ per second per torr; $\bar{\sigma} = (\sigma_{\mathrm{HCl}} + \sigma_{\mathrm{M}})/2$ is the collision diameter; σ_{HCl} and σ_{M} are the gas kinetic diameters of HCl and M; and m is the translational reduced mass in atomic mass units. The gas kinetic diameters, in angstroms, for He, Ne, Ar, HCl, Cl_2, Cl, and H_2 are 2.6, 2.8, 3.4, 3.3, 4.2, 3.3, and 2.9, respectively. The abbreviations p-H_2 and n-H_2 stand for para-hydrogen and the normal hydrogen mixture (three-quarters ortho, one-quarter para). The numbers in parentheses are references.

M	*P* (293°K)	
	HCl	DCl
HCl	1.3×10^{-4} (*11*)	8.9×10^{-5} (*12*)
DCl		3.2×10^{-5} (*13*)
n-H_2	9×10^{-6} (*11*)	3.9×10^{-5} (*13*)
p-H_2	9×10^{-6} (*11*)	3.4×10^{-5} (*13*)
HD		1.9×10^{-5} (*13*)
D_2		4.6×10^{-6} (*13*)
^{3}He	3.3×10^{-7} (*17*)	5.0×10^{-7} (*17*)
^{4}He	1.6×10^{-7} (*17*)	1.6×10^{-7} (*17*)
Ne	1.4×10^{-7} (*17*)	4.9×10^{-8} (*17*)
Ar	2.1×10^{-8} (*17*)	1.1×10^{-8} (*17*)
Cl_2	2.5×10^{-5} (*34*)	
Cl	2×10^{-2} (*34*)	

Models of energy transfer from vibration to translation (*44*) imply a strong dependence of the energy transfer probability on the translational reduced mass of the collision partners and on the amount of vibrational energy released to translation. In contrast, the relaxation probabilities for HCl and DCl in Table 1 involving chemically similar species are remarkably similar in magnitude. In particular, deactivation by the rare gases depends relatively little on translational reduced mass. This suggests that the perturbation which causes vibrational energy transfer is not predominantly due to translational motion, but rather to the rotational motion of the vibrating halide (*45*). Similarly, the comparable probabilities for deactivating HCl ($\Delta E = 2886\ \mathrm{cm}^{-1}$) and DCl ($\Delta E = 2091\ \mathrm{cm}^{-1}$) by a particular collision partner and the greater probabilities for HCl compared to DCl as a collision partner support the conclusion that rapid rotational motion is the predominant cause of energy transfer (*11, 13, 17*). Studies of several other hydride and deuteride systems have led to similar conclusions (*45–48*).

In suggesting models for the coupling of vibration and rotation that leads to energy transfer, it is necessary to consider the rotational motion of both the vibrating molecule and its collision partner, as well as the relative translational motion. A simple model (*46, 49*) pictures asymmetrically shaped molecules (Fig. 4) in which vibration, rotation, and translation are coupled through the changing degree of intermolecular electron overlap which these motions simultaneously create. In this model electron overlap is represented by the overlap of the asymmetrical contours of equal electron density of the free molecule. When vibrational motion is represented as a simple expansion of the molecular contour with little distortion of the molecular shape, it is possible to show quantitatively how rotations and translation perturb the vibrational potential. This approach has led to an expression for an effective collisional reduced mass, $\mu\dagger = (m^{-1} + A_1\mu_{R,1}^{-1} + A_2\mu_{R,2}^{-1})^{-1}$, which replaces the translational reduced mass in a simple energy transfer theory (*46*). In this expression m is the translational reduced mass, A_i is related to the asymmetry of the molecular contour of molecule i, and $\mu_{R,i}$ is the rotational moment of inertia of molecule i divided by the square of the distance from the molecular center of mass to the peripheral light atom. Although a well-defined molecular shape is a convenient assumption for a simple model, the actual distortion of molecular shape which occurs during a highly asymmetric, polyatomic vibration may be considerable. A strong relationship between vibration and molecular shape—and thus between vibration and the rotational dependence of the intermolecular potential—could strongly couple vibration to rotation, even for molecules that are quite spherical in the ground vibrational state. Present experiments give a strong qualitative, but not yet a precise quantitative, measure of how vibration and rotation are coupled in collisions.

Models for intermolecular potentials and collision trajectories involving hydrogen halides must deal not only with rotation, but also with strong dipolar and chemical interactions. The importance of the chemical identity of the collision partner is demonstrated by the thousandfold increase in the HCl relaxation probability between M = Ar and M = Cl_2 and between M = Cl_2 and M = Cl. In Fig. 5 the dependence of the vibrational energy transfer probability on temperature also illustrates another chemical effect. The HCl-He curve is typical of what one expects from simple, first-order theories of vibrational energy transfer for head-on collisions with a repulsive potential; that is,

$$P \approx C \exp(cT^{-1/3})$$

where P is the probability, C and c are constants, and T is temperature. The HF-HF and HCl-HCl curves exhibit a much different behavior, attributed to strong attractive forces. These forces may strongly affect translational and rotational trajectories for noncolinear collisions at low velocities. Successful theories must determine the nature of these attractive forces and precisely describe their effect on trajectories and vibrational potentials.

Vibration-to-vibration energy transfer processes such as

$$\mathrm{HCl}\ (v = 1) + \mathrm{HBr}(v = 0) \rightarrow$$
$$\mathrm{HCl}\ (v = 0) + \mathrm{HBr}\ (v = 1) + \Delta E$$

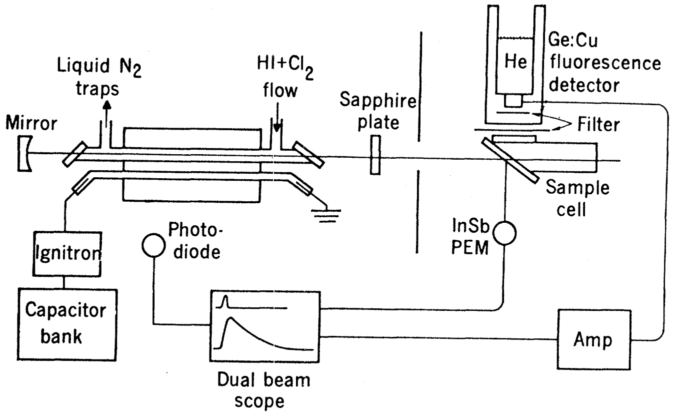
where $\Delta E = 327$ cm^{-1}, have been studied for a great many mixtures with HCl and DCl [see (*12, 13*) and a recent review (*2*)]. Measurements of energy transfer among the vibrational levels in pure HCl gas have given results for (*14, 19*)

$$\mathrm{HCl}\ (v = 2) + \mathrm{HCl}\ (v = 0) \rightarrow$$
$$2\mathrm{HCl}\ (v = 1) + \Delta E$$

where $\Delta E = -102$ cm^{-1} and $P = 1.5 \times 10^{-2}$, and (*14*)

$$\mathrm{H^{35}Cl}\ (v = 1) + \mathrm{H^{37}Cl}\ (v = 0) \rightarrow$$
$$\mathrm{H^{35}Cl}\ (v = 0) + \mathrm{H^{37}Cl}\ (v = 1) + \Delta E$$

where $\Delta E = 2$ cm^{-1} and $P = 1.0 \times 10^{-1}$. Such rates are of particular importance in studies of laser-induced chemical reactions, isotope separation (*8, 15*), and chemical laser systems (*12*).



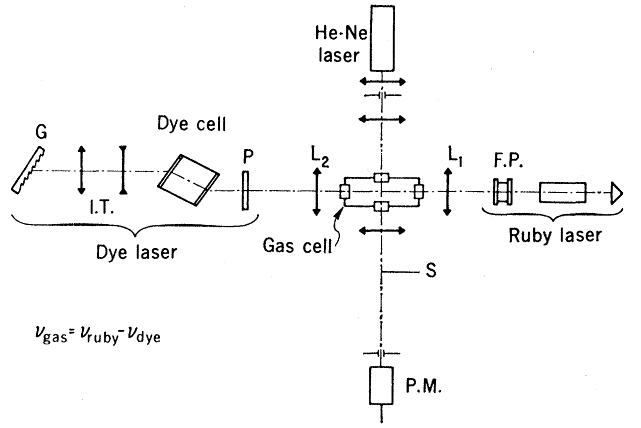


Fig. 2 (left). Apparatus for laser-excited vibrational fluorescence to measure the vibrational relaxation of HCl. A $Cl_2 + HI$ chemical laser pumped by a flashlamp produces a short pulse of light at the 3–2, 2–1, and 1–0 vibrational transition frequencies of HCl. The 1–0 radiation is absorbed by HCl gas at room temperature in the sample cell. The Ge:Cu photoconductive infrared detector monitors fluorescence from HCl ($v = 1$) molecules as a function of time. The laser and detector outputs are photographically recorded from an oscilloscope. An interference filter at a low temperature inside the detector Dewar decreases the detector noise level and reflects scattered laser light (*2*). The abbreviation *PEM* stands for photoelectromagnetic infrared detector; *Amp*, amplifier. Fig. 3 (right). Stimulated Raman excitation of molecular vibrations (*40*). Light from the Q-switched ruby laser (pulse duration, 20 nsec) is focused by lens L_1 into the gas cell, is recollimated by L_2, and is absorbed in the dye cell. The dye laser output, tuned by rotation of grating *G*, is also focused in the center of the gas cell. Strong vibrational excitation occurs in this focal region. Vibrational relaxation is detected by the expansion of the focal zone as energy is released to translation. Expansion causes a change in the refractive index which scatters light from the He-Ne laser onto the photomultiplier *P.M.* Other abbreviations are: *I.T.*, internal telescope; *S*, stop; *F.P.*, Fabry-Perot interferometer.

Polyatomic V → V Transfers

For diatomic molecules we have discussed the transfer of energy from vibration into translation and rotation, from the vibration of one kind of molecule to the vibration of another, and from one vibrational energy level to another of the vibrational degree of freedom of a single kind of molecule. For polyatomic molecules we are also concerned with the transfer of energy among the several vibrational degrees of freedom of the molecule itself. Since the probabilities of energy transfer processes generally decrease rapidly as the amount of vibrational energy transferred into translation and rotation increases, V → V transfers usually channel vibrational excitation into the vibrational mode with the lowest frequency and then into translation. For example, when the asymmetric stretching vibration (3020 cm^{-1}) of CH_4 is excited, CH_4-CH_4 collisions transfer energy to the bending modes (1533 and 1306 cm^{-1}) with a probability of 1.4×10^{-2} (*47*). The probability for V → T, R transfer is only 7×10^{-5}. By exciting bending vibrations and observing fluorescence from both bending and stretching vibrations, Flynn and co-workers (*48*) have studied the rate at which energy is transferred up the energy level ladders of a molecule. This type of process governs the distribution of vibrational excitation in a laser-irradiated gas and the types of gas-phase chemical reactions that may be induced by intense laser radiation.

Chemical Forces

Unusually large observed probabilities of V → T, R energy transfer have for many years been attributed to special chemical interactions between the collision partners. In collisions between relatively inert closed-shell molecules the dominant forces are repulsive and the collision exerts only a weak perturbation on the vibrational coordinates. The situation is very different when a chemical bond may be formed between two collision partners. The strongly attractive potential accelerates the collision and intermolecular forces change on a time scale that approaches a vibrational period. The approaching collision partner may cause a large shift in the equilibrium bond length of the vibrating molecule. For example, when an oxygen atom approaches O_2 the O–O bond length changes from 1.21 to 1.28 Å. This creates a large force on the oscillator as the system approaches the configuration of ozone. The approach to O_2 of a neon atom moving with the thermal velocity barely perturbs the O–O bond. A multiplicity of electronic curves is involved in collisions between partners such as H and CO or Cl and HCl, and relaxation mechanisms may involve coupling between electronic, vibrational, and translational modes (*50*). Measurements in shock tubes at high temperatures have yielded data on a number of systems (*51, 52*). Laser fluorescence techniques are beginning to be applied to this problem [see (*34, 52*)].

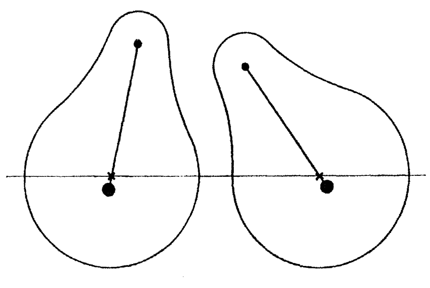


Fig. 4. A model for energy transfer from vibration to rotation and translation during the collision of two asymmetric molecules. The molecular centers of mass are shown (×), and the molecular shapes are represented by contours of equal electron density of the free molecules. When rotational and translational motion bring the molecules rapidly into repulsive overlap, vibrational motion is coupled to rotation and translation.

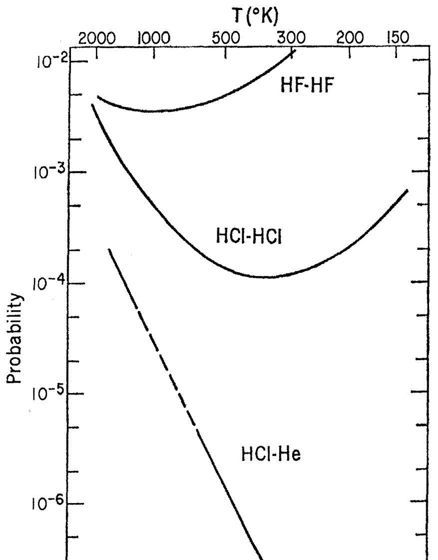


Fig. 5. Transfer of vibrational to translational and rotational energy in the hydrogen halides. The relaxation probability per kinetic collision as a function of the −⅓ power of the temperature (*T*) is shown for HF ($v = 1$) deactivated by HF and for HCl ($v = 1$) deactivated by HCl and by He. The data are from (*17, 18, 52*).

It will be of special interest to determine relaxation rates for molecular vibration in some reactive collision systems. For example, the chemical reaction

$$Cl + HI \rightarrow HCl\ (v = 1,2,3,4) + I$$

has been studied by using crossed molecular beams, infrared chemiluminescence, laser flash photolysis, and classical trajectory calculations (*33, 53*). The reaction rate, the angular distribution of the products, and the vibration-rotation states of the HCl produced appear to be primarily determined by the shape of the Cl + HI entrance half of the potential surface (*53*). Collisions of I atoms with HCl ($v = 1,2,3$) at average thermal velocities will sample the HCl + I exit half of the surface. Collisions with HCl ($v = 4$) will have sufficient energy to sample both halves of the surface. Smith and Wood (*54*) point out that in this case, and for high-velocity collisions with lower vibrational states, vibrational relaxation and reverse reaction (I + HCl → Cl + HI) are simultaneously possible. Thus, energy transfer measurements on reactive systems should lead both to a knowledge of the vibrational relaxation mechanism and to a fuller understanding of the chemical reactions themselves.

State Selection in Reactions

The rates of chemical reactions, particularly endothermic ones, may be sensitive to vibrational excitation of the reactants. Odiorne *et al.* (*4*) have used an HCl chemical laser to excite a molecular beam of HCl. When the molecular beam is crossed by a beam of potassium atoms the reaction cross section for formation of KCl is about two orders of magnitude larger for the $v = 1$ state than for the $v = 0$ state of HCl. One might hope to observe and take practical advantage of laser state-selection in bulk gases to promote specific reactions or to produce isotopically selected products (*5, 6, 8, 15*). The competition between relaxation and reaction processes is a severe limiting factor for chemical schemes involving laser induction. In practice it is often difficult to establish whether the products are the result of reactions involving states specifically excited by the laser or are the result of normal thermal reactions in a laser-heated gas (*6*).

Lasers are also useful in determining the internal energy states of reaction products. Zare and co-workers (*31*) have studied the BaO produced in the $Ba + O_2$ reaction by tuning a dye laser over the absorption spectrum of BaO. Since the excited electronic state is fluorescent, the amount of laser light absorbed is monitored by detecting visible BaO fluorescence. This spectrum then gives the relative concentrations of molecules formed in each of the BaO vibration-rotation levels. A potentially more general and sensitive method of state-selection spectroscopy for molecular beams is two-step photoionization (*15*). If one laser is tuned at high resolution over the absorption spectrum of a product molecule, a second laser may be used to ionize the molecules excited by the first. With sufficiently powerful lasers and an ion counter, nearly unit detection efficiency could be achieved. It will doubtless be some time before really practical sources are available for this difficult technique.

Excited Electronic States

Laser excitation of electronic states allows one to study electronic energy transfer, vibrational and rotational energy transfer among the levels of the excited state, radiationless transitions of isolated molecules and of molecules suffering collisions, and chemical reactions of excited states. Leone and Wodarczyk (*55*) have explored transfers of electronic to vibrational energy of the type

$$Br^* + HCl \rightarrow Br + HCl\ (v = 1)$$

The excited atoms (Br^*) are produced by laser photodissociation of Br_2, and the infrared fluorescence from HCl ($v = 1$) is observed.

Electronically excited alkali dimer molecules and I_2 have been studied in considerable detail by steady-state fluorescence spectroscopy (*23–25*). The changes of rotational and vibrational quantum numbers that occur in collisions with a variety of foreign gas molecules have been studied. Particularly interesting propensity rules for rotational transitions are found for the alkali dimers (*24, 25*). It is also found that rotational energy changes comparable to the thermal energy kT often occur notwithstanding the large changes in rotational quantum number required. In I_2 the loss of one quantum of vibrational energy does not appear to be accompanied by an increase in rotational energy. By contrast, for Li_2 it appears that a substantial fraction of the vibrational energy is transferred into rotation rather than translation. Extension of this type of study to other diatomic and polyatomic molecules will be greatly aided by a good ultraviolet tunable laser source.

Lifetimes of fluorescence decay from single vibrational levels have been measured by using pulsed tunable lasers for molecules such as ICl (*28*), NO_2 (*29*), formaldehyde (*27*), and glyoxal (*26*). Considerably higher resolution and sensitivity are possible with excitation by lasers rather than flashlamps and monochromators. It should be possible to obtain high enough concentrations of excited molecules to study the time dependence of their spectra and chemically analyze the end products. The competition among pathways for energy transfer, radiationless transition, photochemical rearrangement, dissociation, and excited state chemical reaction can be studied in detail as a function of the quantum state initially excited. If excitation selectivity can be translated into photochemical product selectivity, then laser photochemistry may become a chemical engineering method as well as a powerful research tool. In the case of formaldehyde it has already been shown that selective excitation of D_2CO in a mixture of H_2CO and D_2CO yields primarily D_2 molecules (*7*).

$$D_2CO^* \rightarrow D_2 + CO$$
$$D_2CO^* + M \rightarrow D_2 + CO + M$$

Many other laser-photochemical isotope separation schemes are possible in principle (*8, 15*). The use of laser sources in photochemistry promises to provide a great many exciting and important research opportunities.

In summary, state selection with lasers is a powerful tool for investigation of chemical phenomena. Only a few illustrative examples have been given from the many already in the literature. The development of reliable, tunable laser systems from vacuum ultraviolet to far infrared promises to open up broad new areas of application and to greatly expand those now under investigation.

References and Notes

1. J. I. Steinfeld, in *MTP International Review of Science, Series 1*, vol. **9**, *Gas Kinetics*, J. C. Polanyi, Ed. (Butterworths, London, 1972), p. 247; C. B. Moore, *Accounts Chem. Res.* **2**, 103 (1969).
2. C. B. Moore, *Advan. Chem. Phys.* **23**, 41 (1973).
3. ———, *Annu. Rev. Phys. Chem.* **22**, 387 (1971).
4. T. J. Odiorne, P. R. Brooks, J. V. V. Kasper, *J. Chem. Phys.* **55**, 1980 (1971).
5. N. G. Basov, E. P. Markin, A. N. Oraevskii, A. V. Pankratov, A. N. Skachkov, *JETP Lett.* **14**, 165 (1971).
6. M. I. Buchwald, R. McFarlane, S. H. Bauer, in preparation.
7. E. S. Yeung and C. B. Moore, *Appl. Phys. Lett.* **21**, 109 (1972); V. S. Letokhov, *Chem. Phys. Lett.* **15**, 221 (1972).
8. C. B. Moore, *Accounts Chem. Res.* **9**, 323 (1973).
9. W. M. McClain, *J. Chem. Phys.* **58**, 324 (1973).
10. J. Ducuing, C. Joffrin, J. P. Coffinet, *Opt. Commun.* **2**, 245 (1970).
11. H. L. Chen and C. B. Moore, *J. Chem. Phys.* **54**, 4072 (1971); H. L. Chen, *ibid.* **55**, 5551 (1971).
12. H. L. Chen and C. B. Moore, *ibid.* **54**, 4080 (1971); H. L. Chen, J. C. Stephenson, C. B. Moore, *Chem. Phys. Lett.* **2**, 593 (1968).
13. P. F. Zittel and C. B. Moore, *J. Chem. Phys.* **58**, 2922 (1973).
14. S. R. Leone and C. B. Moore, *Chem. Phys. Lett.* **19**, 340 (1973).
15. R. V. Ambartzumian and V. S. Letokhov, *Appl. Opt.* **11**, 354 (1972); V. S. Letokhov, *Science* **180**, 451 (1973).
16. M. Margottin-Maclou, L. Doyennette, L. Henry, *Appl. Opt.* **10**, 1768 (1971), and references cited therein.
17. R. V. Steele, Jr. and C. B. Moore, in preparation.
18. P. F. Zittel and C. B. Moore, in preparation.
19. B. M. Hopkins and H. L. Chen, *J. Chem. Phys.* **57**, 3816 (1972); I. Burak, Y. Noter, A. M. Ronn, A. Szöke, *Chem. Phys. Lett.* **17**, 345 (1972).
20. P. L. Houston, A. V. Nowak, J. I. Steinfeld, *J. Chem. Phys.* **58**, 3373 (1973).
21. J. C. Stephenson, in preparation; W. H. Green and J. K. Hancock, in preparation.
22. V. Bondybey and J. W. Nibler, *J. Chem. Phys.* **56**, 4719 (1972); H. Dubost, L. Abouaf-Marguin, F. Legay, *Chem. Phys. Lett.* **17**, 269 (1972).
23. A. N. Schweid and J. I. Steinfeld, *J. Chem. Phys.* **58**, 844 (1973), and references cited therein.
24. K. Bergmann and W. Demtröder, *Proc. Phys. Soc. London At. Mol. Phys.* **5**, 1386 (1972).
25. C. Ottinger and D. Poppe, *Chem. Phys. Lett.* **8**, 513 (1971).
26. J. T. Yardley, *J. Chem. Phys.* **56**, 6192 (1972).
27. E. S. Yeung and C. B. Moore, *ibid.* **58**, 3988 (1973).
28. G. W. Holleman and J. I. Steinfeld, *Chem. Phys. Lett.* **12**, 431 (1971).
29. P. B. Sackett and J. T. Yardley, *J. Chem. Phys.* **57**, 152 (1972).
30. J. T. Yardley, G. W. Holleman, J. I. Steinfeld, *Chem. Phys. Lett.* **10**, 266 (1971).
31. A. Schultz, H. W. Cruse, R. N. Zare, *J. Chem. Phys.* **57**, 1354 (1972).
32. K. R. Wilson, in *Excited State Chemistry*, J. N. Pitts, Jr., Ed. (Gordon & Breach, New York, 1970), p. 33.
33. F. Wodarczyk and C. B. Moore, in preparation.
34. N. C. Craig and C. B. Moore, *J. Phys. Chem.* **75**, 1622 (1971).
35. C. K. Rhodes, M. J. Kelly, A. Javan, *J. Chem. Phys.* **48**, 5730 (1968).
36. I. Burak, A. V. Nowak, J. I. Steinfeld, D. G. Sutton, *ibid.* **51**, 2275 (1969); *ibid.* **52**, 5421 (1970).
37. P. M. Rentzepis, *Science* **169**, 239 (1970); *Advan. Chem. Phys.* **23**, 189 (1973).
38. F. R. Grabiner, D. R. Siebert, G. W. Flynn, *Chem. Phys. Lett.* **17**, 189 (1972).
39. I. Burak, P. Houston, D. G. Sutton, J. I. Steinfeld, *J. Chem. Phys.* **53**, 3632 (1970); L. B. Kreuzer and C. K. N. Patel, *Science* **173**, 45 (1971).
40. R. Frey, J. Lukasik, J. Ducuing, *Chem. Phys. Lett.* **14**, 514 (1972).
41. A. Lauberau and W. Kaiser, *Phys. Rev. Lett.* **28**, 1162 (1972).
42. E. S. Yeung and C. B. Moore, in *Fundamental and Applied Laser Physics: Proceedings*

of the Esfahan Symposium, 1971, M. Feld, N. Kurnit, A. Javan, Eds. (Wiley-Interscience, New York, 1973), p. 223.
43. S. M. Freund and T. Oka, *Appl. Phys. Lett.* **21**, 60 (1972).
44. R. N. Schwartz, Z. I. Slawsky, K. F. Herzfeld, *J. Chem. Phys.* **20**, 1591 (1952).
45. T. L. Cottrell and A. J. Matheson, *Trans. Faraday Soc.* **58**, 2336 (1962); C. B. Moore, *J. Chem. Phys.* **43**, 2979 (1965).
46. C. B. Moore and P. F. Zittel, *J. Chem. Phys.* **58**, 2004 (1973).
47. J. T. Yardley and C. B. Moore, *ibid.* **49**, 1111 (1968).
48. R. C. L. Yuan and G. W. Flynn, *ibid.* **57**, 1316 (1972); E. Weitz, G. W. Flynn, A. M. Ronn, *ibid.* **56**, 6060 (1972); J. T. Knudtson and G. W. Flynn, in preparation.
49. G. A. Kapralova, E. E. Nikitin, A. M. Chaikin, *Chem. Phys. Lett.* **2**, 581 (1968); E. E. Nikitin, *Teor. Eksp. Khim.* **3**, 185 (1967).
50. E. E. Nikitin and S. Ya. Umanski, *Discuss. Faraday Soc.* **52**, 7 (1972).
51. R. E. Center, *J. Chem. Phys.* **58**, 5230 (1973), and references cited therein.
52. J. F. Bott, *ibid.* **57**, 96 (1972); L. S. Blair, W. D. Breshears, G. L. Schott, *ibid.*, in press.
53. C. A. Parr, J. C. Polanyi, W. H. Wong, *ibid.* **58**, 5 (1973), and references therein.
54. I. W. M. Smith and P. M. Wood, *Mol. Phys.* **25**, 441 (1973).
55. S. R. Leone and F. Wodarczyk, in preparation.
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Ecological Genetics and Natural Selection in Molluscs

Climatic selection has an important effect on some patterns of gene distribution in snail populations.

J. S. Jones

Recent investigations of protein polymorphism which suggest that up to 40 percent of all gene loci may be polymorphic in animals as diverse as *Limulus* and man (*1*) have led to a resurgence of interest in the mechanisms which are responsible for the maintenance of genetical variation in natural populations. Ecological genetics is the study of the relationship of such variation to the environment. Unfortunately, much research which is intended to refer to the ecological genetics of a system suffers from the weakness of the investigation of Chinese metaphysics by the Dickensian character who obtained his information by combining encyclopedia articles on China and on metaphysics. We have adequate information on the genetics of some organisms and on the ecology of others, but in relatively few cases is sufficient data available on both variables to justify a realistic amalgamation. Resolution of the long-standing disagreement between those who think that natural selection is the main factor affecting genetic variation in natural populations and those who emphasize the importance of random processes has therefore been delayed by a lack of suitable information.

Ecology and Genetics of Land Molluscs

Polymorphic land snails are excellent material for research into the interactions of ecology and genetics. Individual species may live in a wide range of environments, their shells can easily be marked for identification, and empty shells (whose appearance may give an indication of the cause of death) leave a record of some of the genes which the animal possessed when alive. The low mobility of most land snails also means that populations sharing a common gene pool are small and can be studied in detail. These factors make it relatively easy to study the ecology of snail populations. *Cepaea nemoralis*, a common European helicid, is the most widely investigated species. Information is now available on its food, reproduction, growth rate, survival, movement, activity, actual and effective population size, and predators (*2*). Much work has also been conducted on the genetics of its visible polymorphism.

The shell may be yellow, pink, or brown, and bears up to five dark or partly pigmented bands. The genes for shell color are allelic. A locus controlling the presence or absence of bands is closely linked to the color locus, and several other loci controlling intensity of band and lip pigmentation are linked to these loci to form a "supergene." Two loci reducing the number of bands on the shell to less than five are not linked to this supergene (*3*).

The complexity of the visible polymorphism in *C. nemoralis* is matched by its ubiquity. I have records of only 26 monomorphic colonies out of more than 4000 sampled in Britain and France. *Cepaea hortensis*, which is closely related to *C. nemoralis*, is also highly polymorphic, and the visible polymorphism of the two species is homologous to such an extent that dominance relations are preserved in interspecies crosses (*4*). Polymorphism in *C. hortensis* is not as extensive as in *C. nemoralis*, 11.7 percent of British colonies being monomorphic for shell color and banding. *Cepaea sylvatica* and *C. vindobonensis* are continental European species which have considerably simpler systems of shell polymorphism. The ecology and genetics of several other molluscs have also been investigated (*5*).

Ecological Genetics of Cepaea

The extreme local variations in morph frequency found in *Cepaea* populations were for many years quoted as examples of the importance of random processes in determining population structure. On the basis of a survey of *C. nemoralis* populations in France, Lamotte (*6*) also concluded that genetic drift is the major factor affecting gene frequencies because he could find no associations of morph frequency with environment, and because analysis of his data suggested that they were in accordance with Wright's (*7*) predictions for populations whose structure is primarily determined by random processes.

More recently, however, natural selection has been shown to be important in affecting the distribution of genes in

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The author is lecturer in biology at the Royal Free Hospital School of Medicine, University of London, 8 Hunter Street, London WC1N 1BP.