lifetime, $\tau_r = 4.20 \pm 0.13$ nsec.[17] The other time constant yields a production rate essentially proportional to the square of the pressure, indicating a three-body reaction with rate coefficient $(2.8 \pm 0.3) \times 10^{-33}$ $\mathrm{cm}^6/\mathrm{sec}$. This suggests a production reaction of the form $\mathrm{Ar}^* + 2\mathrm{Ar} \rightarrow \mathrm{Ar}_2^* + \mathrm{Ar} + E_K$. Weime and Weime-Lenaerts suggested that this reaction is also important in the production of the argon 1_u molecule at pressures less than 50 Torr.[7] They show that the production rate of the slowly decaying 1_u state agrees well with the destruction rate of atomic $\mathrm{Ar}(^2P_{3/2})4s[\frac{3}{2}]_2$ which is the dissociation limit of the 1_u molecule.[18] On the other hand, the three-body production rate we obtain for the fast decaying 0_u^+ state agrees with that measured by Hurst for the destruction of the $\mathrm{Ar}(^2P_{1/2})4s[\frac{1}{2}]_1$ atomic state.[6] The excited atom in the dissociated limit of 0_u^+ is, however, $\mathrm{Ar}(^2P_{3/2})4s[\frac{3}{2}]_1$, for which the three-body destruction rate has not been reported. Thus we are unable to conclude which atomic state is responsible for the production of the argon 0_u^+ molecule.

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[17] This pressure independence of the 0_u^+ lifetime rules out significant collisional mixing of the 0_u^+ and 1_u states; the data place an upper limit of about 6×10^{-18} cm^2 on the $0_u^+ + \mathrm{Ar} \rightarrow 1_u + \mathrm{Ar}$ de-excitation cross section. Qualitatively, a similar argument applies to xenon, although the data for the 0_u^+ state are insufficient to establish so stringent an upper limit.

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Discrete and Diffuse Emission Following Two-Photon Excitation of the E State in Molecular Iodine

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We studied the fluorescence spectrum of $E \rightarrow B$ transitions in molecular iodine following two-photon absorption. Discrete re-emission lines terminating in B-state levels ranging from $v = 0$ to the dissociation limit were observed in addition to a series of broad diffuse lines. These diffuse lines represent the first observation of Condon "internal diffraction" resulting from a *single* vibronic state, and therefore the variation of the bands directly displays the variation of the Franck-Condon factor.

Since the development of the laser considerable attention has been given to multiple-photon spectroscopy. The earlier investigations of simultaneous multiple-photon absorption utilized high-powered pulsed lasers. Recently the use of cw lasers for Doppler-free high-resolution spectroscopy of atomic gases has stimulated renewed interest in the field.[1] Furthermore, the recent availability of tunable lasers has now created interest in stepwise (sequential) multiple-photon spectroscopy in which the detailed investigation of high-energy and parity-forbidden states is possible. Advantage of two-photon sequential excitation has been taken to measure fine structure[2] and hyperfine structure[3] in atomic gases, to separate isotopes in atomic beams,[4] to measure excited-state lifetimes,[5] and to produce excited-state fluorescence in iodine monochloride vapor.[6]

In this Letter we report the re-emission observed after a sequential two-photon absorption process in molecular iodine. Two-photon processes have the potential advantages of reducing Doppler broadening and of allowing the investigation of certain states which are symmetry forbidden in one-photon spectroscopy. Although we did not utilize the first advantage we did make use of the second. The final state, labeled E, of this two-photon absorption in I_2 has the same parity as the ground state making it forbidden in a one-photon transition. In the past, population of the E state could only be accomplished by high-energy excitation (electrical discharges, etc.) in which many other electronic states were simultaneously excited. The subsequent re-emission has therefore been extremely complicated and the assignments have been at best ambiguous.[7] In contrast, in the two-photon experiment the E state can be selectively populated and its fluorescence properties studied without interference from other electronic states. In addition only one vibrational-rotational level of the upper electronic state is excited. The re-emission spectrum is then extremely simple and free of even those unwanted lines often present in conventional one-photon absorption-fluorescence spectroscopy, where more than one vibrational-rotation state is often populated. Because of the simplicity of the re-emission spectrum, we have been able to observe very clearly "internal-diffraction" bands predicted by Condon[8] in 1928.

In the experiment two laser beams were sent from opposite directions into a cell containing molecular iodine at about 0.25 Torr. One beam was from a tunable (5600–6300 Å) rhodamine-6G dye laser. This beam induced transitions from the $X(^1\Sigma_{0^+g})$ state of iodine to specific vibrational-rotational levels of the $B(^3\Pi_{0^+u})$ state. The second beam was the multimode 28 514-cm^{-1} uv output from a krypton-ion laser. This beam induced transitions from the now populated B-state level to a specific vibrational-rotational level of the E state. The relative positions of the potential functions and the laser energies are illustrated in Fig. 1. Although the specific electronic assignment of the E state is not yet known,[7] it is thought to be either $^1\Sigma_{0^+g}$ or $^3\Pi_{0^+g}$. The scattered light re-emitted from the selectively populated vibrational-rotational level of this state to the various levels of the B state was analyzed with a Spex double monochromator.

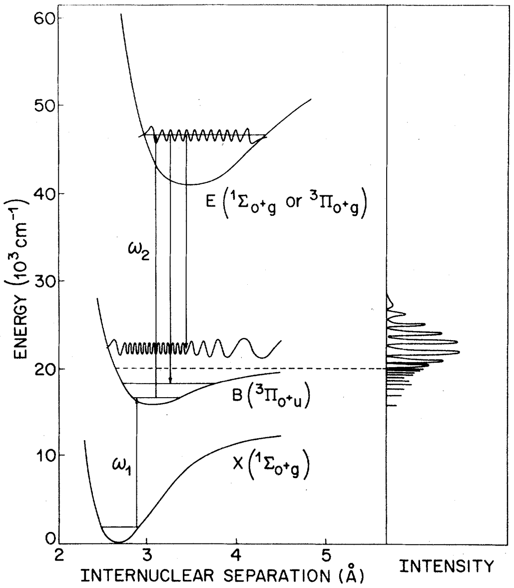

FIG. 1. The energy levels of molecular iodine. The upward arrows represent the optical absorptions of the dye laser (ω_1) and the uv laser (ω_2). The downward arrows correspond to the $E \rightarrow B$ fluorescence. The B dissociation limit is indicated by the dashed line. In the fluorescence, the re-emission terminating in the bound levels of the B state gives a discrete line spectrum indicated schematically on the right-hand side of the figure. Re-emission terminating in dissociative levels gives a diffuse spectrum because of the Condon "internal-diffraction" effect.

In order to locate resonant $E \leftarrow B$ absorptions, the monochromator was set to the region of the expected $E \rightarrow B$ fluorescence and the slits were opened wide. The frequency of the dye laser was then tuned, thereby making a search for B-state energy levels which are separated from E levels by exactly 28 514 cm^{-1}. Numerous resonant transitions were observed.[9] The B-state vibrational-rotational levels of the strongest of these transitions were $v = 11, J = 38$; $v = 16, J = 15$; and $v = 17$, $J = 87$. Qualitatively the spectra resulting from each of the transitions had similar features —namely a series of sharp lines followed by a series of broad lines. As indicated schematically on the right-hand side of Fig. 1, the sharp lines result from transitions between the populated level of the E state and the various vibrational levels of the B state; and the broad lines

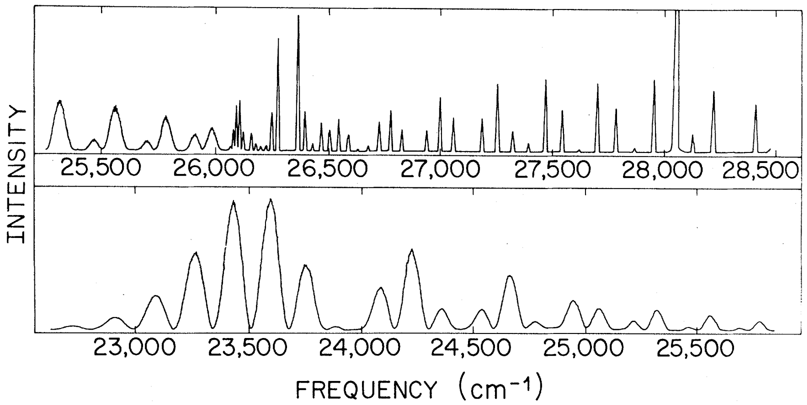

FIG. 2. Fluorescence spectrum of an $E \rightarrow B$ transition. The top spectrum was obtained at ten times the sensitivity of the bottom spectrum but corrections have not been made for the spectrometer and photomultiplier response. The excitation frequency of the laser for the $E \leftarrow B$ transition was 28 514 cm^{-1}. The strong line in the spectrum at 28 058 cm^{-1} is an additional laser line oscillating simultaneously.

occur for transitions terminating in continuum levels of the B state. The broad band structure in this region results from the variation of the overlap factors between the discrete and continuum wave functions.

To illustrate in greater detail the re-emission behavior, the spectrum from the vibrational level ($\approx v = 53$) of the E state populated by the absorption from the B-state level $v = 16, J = 15$ is displayed in Fig. 2. In the top spectrum the Stokes re-emission is shown ranging from the exciting line to beyond the dissociation limit. By looking on the anti-Stokes side of the exciting line, $E \rightarrow B$ transitions all the way down to $v = 0$ of the B state could be seen. This allowed an unambiguous determination of the vibrational quantum number of the initially populated B state to be made. In addition, by looking at high resolution, the doublets resulting from the $\Delta J = \pm 1$ selection rule for these transitions could be resolved allowing an independent determination of the B-state rotational quantum number to be made.

In Fig. 3 we show under higher resolution the region of the dissociation limit. Note that the distinguishable lines get closer and closer together until they may no longer be resolved by our instrumental resolution. Spectra obtained by a high-resolution instrument should allow an extremely accurate determination for any J of all the energy levels of the B state including those in the region of the dissociation limit. Furthermore, because the re-emission is being observed for transitions originating from only a single upper state the usual difficulty in assignment of the lines no longer exists in this type of experiment.

Beyond the dissociation limit at lower re-emission energies the fluorescence spectrum no longer contains the sharp discrete lines, but instead consists of a series of very broad lines (widths of up to 100 cm^{-1}). The spacing of these lines, as may be seen in the bottom spectrum and the left-hand side of the top spectrum in Fig. 2, ranges

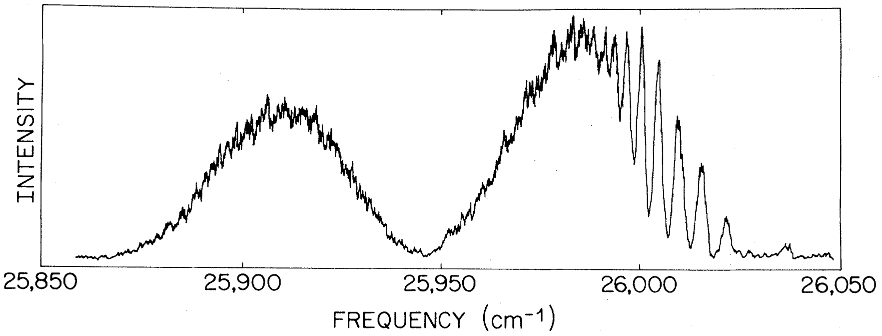

FIG. 3. Fluorescence spectrum of an $E \rightarrow B$ transition in the region of the dissociation limit.

from less than 100 cm^{-1} to about 200 cm^{-1}. These lines originate from the "internal-diffraction" effect first predicted by Condon.[8] The re-emission spectrum in this range results from transitions originating in the discrete level of the E state and terminating in the continuum levels of the B state. Although one might expect the spectrum in this region to be continuous and lack structure, the intensity variations occur because of the phase relationship between the initial and final wave functions, and thus Condon labeled the phenomenon "internal diffraction" in analogy to ordinary diffraction, which depends on phase relationships in a light field. The structure simply results from the variation in the Franck-Condon factor as a function of re-emission frequency. Indeed the variation of the fluorescence intensity in this region is a direct measure of the variation of the Franck-Condon factor.

Although a few other observations of the "internal-diffraction" effect have been made, the spectra were far more complicated because the re-emission from several states was superimposed in each case. In fluorescence from metastable He_2 molecules produced in a discharge, a series of diffuse bands have been observed.[10] Mies and Smith[11] interpreted the intensity variation in this emission as resulting from transitions from bound states to dissociative states. The spectra are, however, rather "washed out" because of the population of numerous initial states and because of the rotational distribution. In experiments on H_2 excited by flash discharges Dalgarno, Herzberg, and Stephens[12] explained the structure in the continuous emission observed as originating from discrete-continuum transitions. However, the spectra are also complicated because of the overlap of Lyman bands and because of the population of several initial discrete states. Finally, Mulliken[7,13] has interpreted part of the diffuse emission spectrum of I_2 after high-energy excitation (electrical or atomic line absorption) in terms of discrete-continuum transitions. Again the spectrum is very complicated because of the superposition of several transitions. The data reported in this Letter, however, represent the first observations of the Condon "internal-diffraction" phenomenon in which the re-emission spectrum results from transitions originating from a single vibronic state only. The observed bands are therefore very clean. The intensities at the minima between the bands are typically less than 0.1% of the intensities at the maxima. The absence of any fluorescent intensity between the maxima is an expected result since the minima result from the vibrational overlap factor passing through zero.

On the basis of the data presented here, it is clear that much old spectroscopic data from simple gases must be reanalyzed. The diffuse bands are very strong and, because of their regular spacing, it is easy to misassign this spacing to an upper-state vibrational manifold. For example, several diffuse bands in molecular I_2 were originally interpreted[14] as transitions from discrete vibrational manifolds to repulsive electronic states with flat potential curves. Although in reviewing the data, Mulliken[7] suggested that the diffuse bands in the 3200-Å region may result from the "internal-diffraction" effect, he explicitly excluded the bands between 3300 and 4800 Å from this interpretation. The observation of the series of diffuse bands in just this region reported here, which clearly must be interpreted as "internal-diffraction" bands, makes mandatory the reanalysis of the I_2 emission spectrum.

Two-photon excitation of the E state offers a definitive means of determining the electronic structure and the spectroscopic parameters of this state. It now becomes a simple task to measure the fluorescence lifetime of the various levels of the state to the $B(^3\Pi_{0^+u})$ state. From that measurement conclusions concerning the question of whether the electronic structure is $^1\Sigma_{0^+g}$, giving a spin-forbidden transition, or $^3\Pi_{0^+g}$ giving a fully allowed transition may be made. The detailed form of the potential curve and the spectroscopic parameters may be obtained from one of two techniques. First, since the potential function of the B state is very well known, any of the methods of inverting the data in order to determine, at least locally, the upper-state potential curve may be applied.[15] Secondly, instead of using a fixed-frequency uv laser to excite the $E \leftarrow B$ transitions, a tunable blue–near-uv laser could be used instead, and thereby determine the energy levels of the E state. This technique is particularly attractive since by first populating the B state with a narrow tunable laser a specific rotational state is selected. Then by tuning the uv laser through the E-state vibrational levels, the spectroscopic parameters may be unambiguously determined for the E state as a function of the originally selected J value. With a knowledge of these spectroscopic parameters, an accurate potential curve may be determined from a

Rydberg-Klein-Rees analysis.

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Line Shape of the 3*p* Excitation in the Electron Energy-Loss Spectrum of Nickel Metal

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The line shape of the electron energy-loss spectra due to $3p \rightarrow 3d$ excitation is reported for Ni. The observation is interpreted by a Fano-type interaction in which the excited configuration decays by Coster-Kronig processes into the continuum of excitations of the 3*d* band. These processes appear to hold generally for the transition metals in both electron scattering and soft-x-ray absorption.

The spectra of the transition metals Mn to Ni in the vicinity of the 3*p* core-level excitation (~60 eV) exhibit a highly asymmetric line shape, the origin of which has been a topic of conjecture.[1,2] These spectra have recently been studied both by optical absorption using a synchrotron light source,[1,3] and by electron energy-loss spectroscopy (ELS).[2,4] In the present paper we report detailed ELS measurements on the 3*p* line shape for Ni.

Compared with other transition metals, Ni presents a relatively simple case for interpretation because the $3p \rightarrow 3d$ excitation results mainly in the final-state configuration $3p^5 3d^{10}$. Thus it is not necessary to take account of the exchange interaction between the *p* and *d* holes which may split excited levels, in general a complicating factor.[5]

We interpret the ELS results in terms of the resonant interaction between an excitation to a discrete level and a continuum, and compute the spectral density from the general formalism for such interactions given by Fano.[6]

These considerations indicate that the excited electronic configuration consisting of a 3*p* hole and a 3*d* conduction electron interacts strongly with the continuum of configurations resulting from excitations from the 3*d* band. This configuration interaction, rather than the empty 3*d* state density, dominates the 3*p* line shape.

The electron energy-loss spectra were obtained with conventional four-grid low-energy-electron-diffraction (LEED) optics used as a retarding-potential analyzer. The experiment was done at normal incidence and all electrons emitted within 80° of the surface normal were collected. Both the energy distribution of scattered electrons $N(E)$ and its energy derivative $N'(E)$ were measured. Cathode modulation was used to suppress the "true-secondary" electron current and struc-