Condon Internal Diffraction in the $0_u^+ \rightarrow 0_g^+$ Fluorescence of Photoassociated Hg_2

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We have observed a well-resolved Condon diffraction pattern in the $0_u^+(v \approx 57) \rightarrow 0_g^+$(unbound) fluorescence of Hg_2. The upper state is excited by photoassociating mercury atoms with an ArF laser at 193 nm.

The bound-free fluorescence continuum from a vibronic state of high vibrational quantum number in an exciplex provides an opportunity to probe that inner portion of the ground-state repulsive wall which is energetically inaccessible to molecular-beam or line-broadening techniques. Such continua were shown by Condon[1] to have an oscillatory envelope which results from the interference of the bound upper-state wave function with those of the ground-state continuum—hence, the name "Condon internal diffraction." In particular, for a molecule with the potential curve configuration shown in the inset of Fig. 1, the undulatory envelope resembles the upper-state wave function as "reflected" by the lower-state potential curve.

Historically, exciplexes in gases have been excited via collisional processes involving, for example, the recombination of the atomic constituents of the excited state. In this case, the large number of collisionally populated vibronic levels may obscure the oscillatory structure of the subsequent fluorescence, or at least introduce ambiguities in its interpretation.[2] As a result, Condon diffraction bands have not generally been used to provide molecular data. Recently, however, there have been observations of well-resolved undulatory spectra which resulted from laser excitation from bound ground-state molecules.[3] However, the use of bound-bound excitation can limit the excitation to low vibrational levels (Fig. 1 shows a specific case) and to stable molecular systems with an appreciably bound ground state. In this Letter we show that Condon diffraction may also be observed if excitation is via free-bound absorption, i.e., photoassociation. Our results show that photoassociation, to a narrow band of vibronic states high in the upper-state potential well, can result in a well-defined Condon diffraction over a large range of internuclear distance. In particular, we have used the 193-nm output from an ArF laser to excite an oscillatory spectrum in the $0_u^+ \rightarrow 0_g^+$ band of Hg_2.

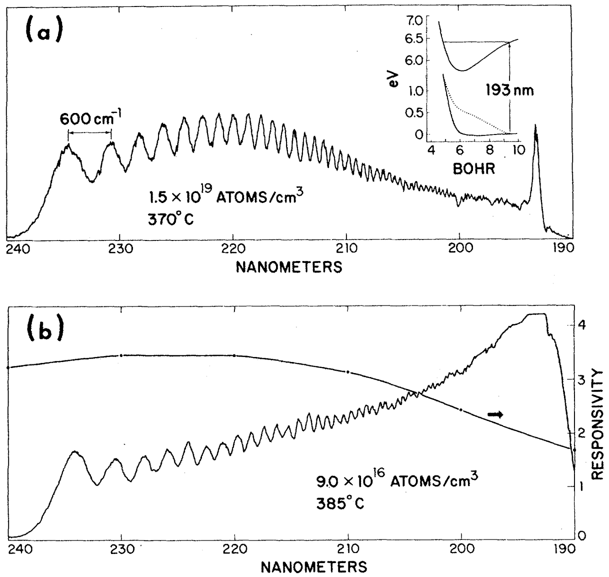

FIG. 1. Bound-free continua $0_u^+ \rightarrow 0_g^+$ resulting from laser excitation of the Hg_2 0_u^+ state. (a), (b) High and low density of Hg. The inset in (a) shows the estimated potential curves for the two relevant states; the minimum for the van der Waals well in the ground states is at approximately 7 bohrs.

As shown in the inset in Fig. 1 the difference between our photon energy and the difference potential[4] (the dotted curve) gives the fluorescence wave number as a function of internuclear distance, r, which is expected on the basis of the Franck-Condon (FC) principle and in the absence of relaxation of the upper states. At reasonable temperatures absorption to such high-lying vibrational levels will occur only for r in the immediate vicinity of the right-hand terminus of the difference potential. In this region, the depth of the lower-state potential is small compared to kT and the contribution of bound molecules to the total absorption cross section is small (~ 10%). Absorption at 193 nm for any smaller r will be extremely weak because of the FC requirement for conservation of nuclear momentum during an electronic transition. Thus free-bound absorption will dominate, as is experimentally confirmed (see below). The broad linewidth of the laser, 0.5 nm, will couple efficiently into the continuum absorption of the free-bound process.

In our experiment, high-purity Hg cells were prepared according to the procedure described by Drullinger and co-workers.[5] The cells were heated in a two-temperature oven, so that the Hg temperature and density could be independently controlled. The cells were irradiated with 4-mJ pulses of 193-nm radiation from an ArF laser which was weakly focused with a 75-cm–focal-length lens to an area of 0.2 cm^2 within the cell. Power densities at the cell were varied between 10^4 and 10^6 W/cm^2. The laser output was centered at 193.3 nm with a measured full width at half-maximum of 0.5 nm. Fluorescence from the cells was measured to within 0.2-nm resolution with a McPherson 1/3 monochromator. Calibration of the wavelength dependence of our monochromator-photomultiplier system was accomplished with a standard D_2 lamp source.

Figures 1(a) and 1(b) show the laser-excited $0_u^+ \rightarrow 0_g^+$ spectra at high and low pressure, respectively. The solid curve superimposed on Fig. 1(b) gives the response curve of the monochromator-detector system. The peak in the signal intensity on the far right-hand side of Fig. 1(b) is due to laser scatter. In the high-pressure spectrum the relative decrease in the region of the spectrum from 220 to 190 nm is due to self-absorption which becomes appreciable at this density. However, the position of maxima and their depth of modulation were unchanged throughout the density range examined (10^{17}–10^{19} atoms/cm^3). The radiative lifetime of the 0_u^+ state, which correlates to one atom in the $^1\boldsymbol{P}_1$ state, has an estimated lifetime of $\leqslant 1$ ns.[6] As a result, it is probable that Fig. 1(b) represents a truly collisionless spectrum. The similarity of Figs. 1(a) and 1(b) indicates that significant collisional thermalization of the vibrational levels in the 0_u^+ state does not occur up to densities of 10^{19} atoms/cm^3.

For wavelengths less than 200 nm, the intermaxima spacing becomes less than our monochromator resolution and any oscillatory structure is lost. By extrapolation of the intermaxima spacing to 193 nm we estimate the total number of peaks to be ~57, a value which is consistent with the excess vibrational energy with which we form the 0_u^+ state divided by the estimated vibrational frequency. Notice that despite the fact that the laser has a linewidth (~150 cm^{-1}) which is greater than two vibrational quanta and that the thermal energy of the vapor is also large (400 cm^{-1}), the resulting bound-free continuum appears sharp.

The absorption at 193 nm as a function of mercury density at a fixed temperature exhibited a density-square dependence which is to be expected on the basis of either bound or unbound molecular absorbers. There was no perceptible change in the absorption for a temperature variation from 500–750°K at a fixed density. The classical quasistatic theory of Hedges, Drummond, and Gallagher[7] indicates that, for our potential curves and wavelength, bound-bound absorption should vary as $\sim 1/T$ whereas the free-bound case should have no significant temperature variation. This results from the fact that at the r for which the FC overlap for absorption at 193 nm is large, most of the thermally accessible phase space is occupied by unbound molecules. Thus our temperature-independent absorption confirms that the free-bound process is dominant. In addition, our observation that the oscillations in the fluorescence spectrum broaden insignificantly with temperature shows that this photoassociation is the major source of the fluorescing molecules. No evidence of saturation of the absorption was seen at the maximum energies and lowest densities used in this experiment (~50 mJ/cm^2) which is again consistent with a free-bound process. The two-body absorption coefficient which was measured to be 3×10^{-38} cm^{-1} $(\text{atom}^2/\text{cm}^6)$ is in reasonable agreement with the coefficient which can be interpolated from Fig. 4 of Mrozowski.[8]

Thus far we have given only indirect evidence that the spectra of Fig. 1 are a manifestation of Condon internal diffraction. We can, however, use a semiclassical treatment of the spectrum along with the best estimates of the excited-state potentials to show directly that the predicted intermaxima spacings are in agreement with our experimental measurements. In the WKBJ approximations[9] the wave function is given by

$$\Psi \approx \{C/[k_j(r)]^{1/2}\}\cos\varphi_j(r), \tag{1}$$

where C is a normalization constant and $k_j(r)$ is the local wave number of the molecule. Also $\varphi_j(r)$ is the phase given by $\varphi_j(r) = \int_{r_j}^{r} k_j(r)dr - \frac{1}{4}\pi$, where r_j is the left-hand turning point, and the subscript j denotes the upper, u, and ground, g, states. The wave number of the molecule is related to the potential energy curves by $k_j^2(r) = 2\mu[E_j - U_j(r)]/\hbar^2$, where μ is the molecular reduced mass, E_j is the *maximum* value of the potential-energy curve, $U_j(r)$ (at the left-hand turning point), and $\hbar$ is Planck's constant divided by 2π. We may ignore the effect of rotation as long as the lower state is strongly dissociative.[2,3] Then, the chief effect of adding the rotational potential is to shift both the upper and lower curves upward by approximately equal energies and to reduce somewhat the modulation in Eq. (1). The transition dipole moment, M, is expected to be only weakly dependent on r, a fact verified by the calculations of Miles, Stephens, and Krauss[10] and thus the transition amplitude is

$$M\langle\Psi_g|\Psi_u\rangle. \tag{2}$$

For a heavy molecule this integral peaks sharply around $r=r^*$, where $k_u(r^*)=k_g(r^*)\equiv k$, which is simply the FC principle. As a result the FC overlap integral can be shown to be

$$[C'/(kV')^{1/2}]\cos[\varphi_u(r^*)-\varphi_g(r^*)], \tag{3}$$

where C' is again a constant, $V'=[(\partial/\partial r)(U_u-U_g)]_{r=r^*}$. In principle, the spacing between the maxima can be obtained from this expression by determining the values of r^* for the zero of its derivative. However, the resulting expression is in general complex and not readily soluble. If, however, we confine ourselves to that region of r for which the derivative of the lower curve is much greater than that of the upper, it can be shown that the FC factor has zeros at $\varphi_u-\varphi_g=-\frac{1}{4}\pi, \frac{3}{4}\pi$, etc., and that the spacing, ΔE, between these maxima is given by

$$\Delta E=(\pi/k)[\partial U_g/\partial r]_{r=r^*}. \tag{4}$$

Examination of the curves for Hg_2 indicates that the assumption leading to this result will be invalid for $r\gtrsim 5.7$ bohrs. In this region of the spectrum Eq. (4) will tend to underestimate the true intermaxima spacing.

In order to apply (4) to our data we have used the ground-state potential generated by Baylis[11] and a modified version of the semiquantitative 0_u^+ potential estimated by Mies, Stephens, and Krauss.[10] We have retained the shape of this curve and scaled the well depth to match earlier absorption data on the 0_u^+ state.[8,12] An independent test of the accuracy of these curves is provided by a comparison of the predicted with the measured maximum redshift of the fluorescence. The measurement gives the precise value for the spacing of the upper and lower potentials at the left-hand turning point on the 0_u^+ curve (at 6.4 eV). We find that the experimental quantity is 42 000 cm^{-1}, which is acceptably close to the 38 000 cm^{-1} value predicted from the above curves.

In Fig. 2 we display the measured maxima spacing as a function of wave number; since

$$\nu(r^*)=[U_u(r^*)-U_g(r^*)]/\hbar c, \tag{5}$$

this plot is essentially a graph of ΔE as a function of internuclear spacing. In this figure, we also give the calculated values at the same wave numbers [in the region of internuclear distance for which (4) is valid]. The agreement is satisfactory in light of the approximate nature of (4) and the uncertainties in the potential curves.

If the 0_u^+ potential were well known, our spectra in conjunction with numerical calculation of the FC factors would immediately yield the lower-state potential over an internuclear range of 3 bohrs. However, even in the absence of this knowledge, it can be shown both the 0_g^+ and the 0_u^+ potentials can be determined by the use of two excitation frequencies. The second frequency necessary for this technique can be generated by Raman shifting the ArF output in either gaseous N_2 or H_2.[13]

An important aspect of our experiment is that despite the excitation of several vibronic levels in each of the 21 isotopes of Hg_2, we still obtain a sharp diffraction structure. At present we are investigating the details of the origin of this sharpness; however, the essential features can be outlined here. In our case, excitation is to a set of levels having an energy spread ($\sim kT$) which is much narrower than their average vibrational energy, E_0, in the upper state; i.e., $E_0 \gg kT$. The spectrum from each of these levels has a periodicity in λ which is very close to that of a

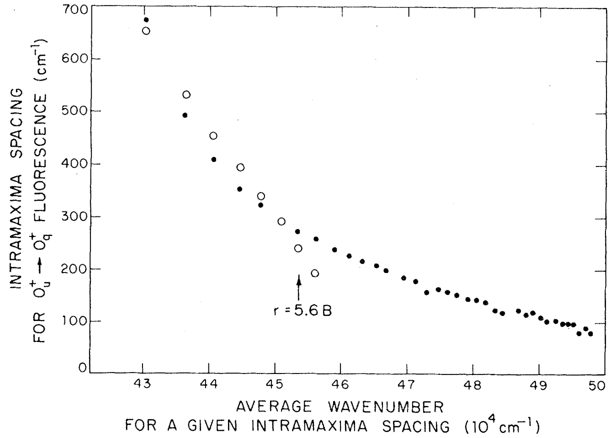

FIG. 2. Intermaxima spacing from the $0_u^+ \to 0_g^+$ fluorescence as a function of the average wavelength of the two respective wavelengths. The open circles are the computed spacings based on Eq. (4).

spectrum from a level at E_0 (see Tamagake and Setser[2] for a discussion of this point). Also since for our excitation energy the shift in the wavelength of the first (red) maxima is small, the composite pattern will start with a high contrast ratio between maxima and minima. This is the region of r which was analyzed with our WKBJ treatment. Then in moving toward the blue the periodicity in λ will remain that of a pattern from a level at E_0, but the depth of modulation will decrease as the small differences in the periodicity accumulate.

In conclusion, we have shown that photoassociative excitation is a useful technique for generating clear Condon diffraction bands from vibrational levels high in the excited-state well and that analysis of these bands can give unambiguous data on previously inaccessible regions of the ground-state repulsive wall. A direct extension of this approach to similar metal van der Waals molecules (vis., Cd_2, Zn_2) can be made and with some care it can be used to study exciplexes with transient or reactive atomic constituents such as many of the rare-gas halides.

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