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Multiple oscillations observed in the rotational state population of $I_2(B)$ formed in the photodissociation of $(I_2)_2$

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Several oscillations are observed in the rotational state population of $I_2B^{3}\Pi(0_u^+)$ produced in the photodissociation $(I_2)_2 + h\nu \rightarrow I_2(B_{v',J'}) + I_2(X)$. The initial excitation is above the dissociation limit of the I_2 B state. These oscillations are pronounced on some v' states, but not on others. For a given state v', the rotational state population oscillations essentially do not depend on the photolysis wavelength over the range of applied conditions.

The photodissociation of iodine in liquids, solids, and gases has been a key model system in molecular dynamics for a large part of this century.¹⁻³ The competition between dissociative and nondissociative pathways is related to the so-called cage effect. More recently the photodissociation of I_2 has been studied in small van der Waals clusters,⁴⁻⁹ for instance

$$\mathbf{I}_{2}\mathbf{M} + h\boldsymbol{\nu} \rightarrow \mathbf{I}_{2}(\boldsymbol{B}_{\boldsymbol{\nu}',\boldsymbol{J}'}) + \mathbf{M}.$$
 (1)

Previous studies have reported on the distributions of v' for both polyatomic and monoatomic "solvents" M. Significantly different dynamics is found when photodissociating $I_2 M$ above the B state dissociation limit^{5,6} as compared to the vibrational predissociation from rovibrational levels below the dissociation limit.⁷ In the former case,⁶ a very large fraction (up to 30%) of the energy available to the products of reaction (1) goes into translational energy between the $I_2(B)$ and M photofragments. Most of the remaining energy goes into vibrational energy of the $I_2(B)$. Only a small fraction goes into rotational energy of $I_2(B)$.^{8,9} For M = Ar, Kr, Xe, N_2 , and O_2 , the rotational state population distributions in the electronically excited iodine generally resemble a Boltzmann distribution for the lower rotational states (up to J' is about 35). The higher rotational states show a population in excess of that given by these rotational "temperatures" as can be seen in Fig. 1. Furthermore, in some cases, a nonstatistical distribution of odd and even J' is observed.^{8,9} Here we report on marked multiple oscillations in the J'populations observed mainly for the case of $M = I_2$, i.e., in the reaction

$$(\mathbf{I}_{2})_{2} + h\nu \to \mathbf{I}_{2}(B_{\nu',J'}) + \mathbf{I}_{2}(X).$$
⁽²⁾

The experimental setup has been described in some detail previously.^{6,8,9} Briefly, a free jet of I_2 diluted with He is

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crossed with a laser beam from a line tunable c.w. argon ion laser with a nominal output power of 20 W (all lines visible). The crossing point is within the laser cavity so as to profit from the significantly higher intracavity light intensity. The fluorescence from $I_2(B)$ product molecules is picked up by a lens system at right angles to both the laser beam and the free jet and focused on the slit of an f = 1 m monochromator for dispersion. The maximum resolution obtained with a 2400 line per mm grating in first order is 0.007 nm at 550 nm. The light intensity passing through the monochromator is measured by a photomultiplier cooled to -30 °C, the signal of which is processed by a single photon counting system and registered by a multichannel analyzer. This is done while the monochromator is slowly scanned by a synchronous motor at a speed of the order of 0.1 nm per hour.

The raw spectra are evaluated in the following way: relative emission intensities including the Hönl–London factors and rotationally dependent lifetimes¹⁰ are calculated for the *P* and *R* transitions originating from all J' levels and convo-



FIG. 1. Rotational populations distribution in v' = 35 obtained from the dissociation of I_2 Kr at 488 nm. P_0 (Kr) = 0.35 bar, $P_0(I_2) = 2.7$ mbar, $T_0 = 345$ K. $N_{J'}$ is the relative population, g_{sn} is the correction factor for the spin of the nuclei, and (2J' + 1) is the degeneracy of the rotational level. A pure Boltzmann distribution would give a straight line on such a plot.

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luted with the line shape measured on a single unblended rotational transition. The line positions being known,¹¹ this gives a set of theoretical emission spectra (one for each J'). The coefficients of the linear combination of these spectra which gives the best fit to the measured spectrum are obtained by a linear least-squares technique; they represent the desired population distribution. These relative populations may then be reported directly as a function of J'. Alternatively they may be corrected for rotational degeneracy (2J' + 1)and nuclear spin statistics (for the *B* state of iodine g_{sn} = 5/12 when J' is odd and g_{sn} = 7/12 when J' is even) to produce a so-called "Boltzmann plot".

As in the case of the v' population distribution measurements,⁶ one must assure that the observed J' populations come from the photodissociation of $(I_2)_2$ rather than from other clusters which may be present in the free jet. In this case, we use the stagnation pressures of I_2 and He for which recent experiments measuring v' distributions^{6(b)} have shown that the fluorescence signal is predominantly due to the dissociation of $(I_2)_2$. Furthermore we checked that the observed rotational spectra are independent of the distance between the nozzle and the laser beam (for 20 < x/D < 80, where x is the distance and D the nozzle diameter) and of the vacuum chamber residual pressure (from the normal working pressure of $p < 10^{-3}$ mbar up to p = 0.2 mbar). This rules out the possibility of rotational relaxation of $I_2(B)$ by collision with molecules of the jet or from the background gas.

Figure 2 shows (a) the raw spectral data obtained from a typical measurement of the dissociation of $(I_2)_2$ at $\lambda = 488$ nm and (b) the spectrum calculated with the relative populations obtained by the linear least-squares technique. The stagnation conditions are $P_0(I_2) = 16$ mbar, $P_0(He) = 1.1$ bar, and $T_0 = 375$ K. The relative J' populations obtained



FIG. 2. (a) Rotationally resolved emission spectrum of the transition from v' = 31 to v'' = 0 in the dissociation of $(I_2)_2$ at 488 nm and (b) the simulated spectrum obtained by least-squares fit. The resolution is 0.015 nm and the stagnation conditions are $P_0(I_2) = 16$ mbar, $P_0(He) = 1.1$ bar, and $T_0 = 375$ K.

from this measurement on v' = 31 are shown in Fig. 3; the open and full circles correspond, respectively, to the even and odd J' levels.

The error bars in these results are difficult to determine since below J' = 10 the incomplete resolution causes the uncertainty in the population to increase, whereas for high J', the populations are small and once again the uncertainty increases due to the unfavorable signal-to-noise ratio. However, the rotational population distributions were measured several times at intervals of days or weeks, and in each case, the oscillating structure (or its absence) was found to be reproducible. Figure 4 shows two examples of such test comparisons: (a) one with oscillations and (b) one without.

A systematic study of the appearance of these oscillations on different vibrational levels v' at several wavelengths of photoexcitation was undertaken. The results are summarized in Table I. Unfortunately, due to spectral congestion, i.e., severe overlap of the emission spectra of more than a single $B(v') \rightarrow X(v'')$ transition, not all desirable measurements can lead to usable results. From Table I, it appears that:

(i) The oscillations in the J' state populations produced in the photodissociation of $(I_2)_2$ are strong on certain vibrational states, for instance v' = 31 and 34; they are less marked on v' = 32 and 35, and are not distinguishable on v' = 30 and 33; in these two latter cases, the rotational population distribution is similar to that of Fig. 1.

(ii) The oscillations depend little on the excitation wavelength in the range of $\lambda = 496.5-476.5$ nm, which corresponds to a change of about 20% in the recoil velocities between the two iodine photodissociation fragments.

(iii) The maxima in the rotational populations always appear roughly at the same levels and they are separated by about 10 rotational quantum numbers.

In all the $I_2 M$ systems we studied, we found only two other cases where there was some indication of such oscillations in the J' populations. These were the cases where M was diethyl ether and the case of I_2M_n with M = Kr and n > 1.



FIG. 3. Relative rotational populations extracted from the spectrum of Fig. 2. The even J'(O) and odd J'(O) populations are reported directly as evaluated. Their systematic difference is due to the nuclear spin statistics.



FIG. 4. Comparison of rotational distributions measured under identical conditions at intervals of several days (a) $(I_2)_2$ dissociated at 488 nm with observation of the 31-0 vibrational band; (b) $(I_2)_2$ dissociated at 496.5 nm with observation of the 30-0 vibrational band; in the latter case, the bump near 30 cm⁻¹ is due to the overlap with the 33-1 vibrational band.

There are several reports in the literature where some form of structure in rotational quantum state distributions has been observed.¹² Such structure has been ascribed to chemical reactions,^{12(a)} rotational rainbows,^{12(a)-12(d)} quantum interference,^{12(b)} symmetry selection rules,^{12(b)} the nodal structure of the bending wave function,^{12(g)} and intermediate resonances inducing a sequential intramolecular vibrational relaxation process.^{12(h)} Only in the latter two cases were multiple oscillations observed, similar to the presently reported ones. The rotational distribution of NO in the dissociation of NOCl shows as much as three distinct maxima, the positions of which are very sensitive to the photolysis

TABLE I. Maxima in the rotational populations distributions.

System $\backslash \lambda_{exc}$	496.5 nm	488.0 nm	476.5 nm
(I ₂), 30-0	None	None	
$(I_2)_2 31-0$	12,22,32,41,51,60	12,22,31,40,51,60	
$(I_2)_2$ 32-0	14,22,31,42		
$(I_2)_2 33-0$	None		
$(I_2)_2 34-0$		12,20,29,40,50	14,24,31,40,48
(I ₂), 35-0		13,21,32	12,20,30
I ₂ Kr, 35-0	12,22,30		
I,Et,O 19-1		None	
I ₂ Et ₂ O 20-0			None
I, Et, O 20-1			None
$I_2 Et_2 O 23-1$			12,24,34,46,58

wavelength,^{12(g)} and the Cl₂ product distribution in the $\Delta v' = -2$ vibrational predissociation of Cl₂Ar^{12(h)} displays six maxima. The present measurements differ significantly from those of Ref. 12(h) in that only a small fraction of the total energy shared among the product degrees of freedom goes into rotational energy, which is not the case in the $\Delta v' = -2$ vibrational predissociation of ArCl₂.

Two striking features of our rotational population distributions are the strong dependence on the vibrational level v' at constant photolysis wavelength and the weak dependence on the photolysis wavelength for a given vibrational level v'. A semiclassical scattering theory, as developed by Schinke for direct photodissociation¹³ and applied by Waterland et al.¹⁴ for the vibrational predissociation of ICl-He, could give rise to several maxima in the rotational distribution; since for a homonuclear diatomic molecule the excitation function $J(\gamma)$ is symmetric about $\gamma = 90^\circ$, multiple maxima can only occur if the wave function $\Psi(\gamma)$ [and therefore the weighting function $W(\gamma) = \Psi^2(\gamma) \cdot \sin \gamma$ has several maxima. In the iodine dimer, this can be imagined, due to the number of possible geometries for the complex. However, this kind of model apparently cannot reproduce the observed large differences in rotational distribution between levels as close as v' = 33 and v' = 34 (63 cm⁻¹ apart, as compared with the 1700 cm^{-1} excess energy given by the exciting photon).

In another possible model, one considers the energy repartition between the fragments. The oscillations in the rotational populations have generally been observed in cases where the invisible (nonfluorescing) fragments can accommodate some internal energy. Such a process is more probable if there is a close match of the rotation/vibration frequencies and relatively strong coupling between I₂ and M (i.e., iodine in its ground electronic state and diethyl ether are expected to be very favorable partners). In such a model resonances leading to oscillations in the population distribution could be expected. Even the case of the I₂ Kr_n complex could fit into this scheme if the dissociation takes place stepwise, as is the case, for instance, for the vibrational predissociation of I₂He₂.¹⁵

Finally, the possibility of an internal energy redistribution in which a significant fraction of the energy is transferred to the van der Waals modes and/or to the vibration or rotation of the $I_2(X)$ prior to dissociation cannot be ruled out here, nor can the mechanism proposed by Beswick *et al.*¹⁶ involving initial excitation to the ¹ Π repulsive state followed by transfer to the *B* state.

In summary, the multiple oscillations observed in the rotational state populations in the photodissociation of $(I_2)_2$ appear to point to a novel, not yet well-understood phenomenon in chemical dynamics. This will be born out by detailed model calculations and further experiments.

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