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Cluster-induced photochemistry of CH₃I at 248 nm

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We have carried out a systematic study of the 248 nm excimer-laser photodissociation of small methyl iodide clusters in a free jet expansion. Ground electronic state I_2 is formed from the photolysis of methyl iodide dimers and detected via the laser induced fluorescence (LIF) excitation spectrum of the (B-X) transition. The internal energy of the I_2 is approximately 2.5 kJ/mol and is the same for CH₃I seeded in CO₂, Ar, Xe, O₂, and He, as well as for the neat expansion and deuterated sample. A room temperature flow cell experiment shows that the reaction channel $I^* + CH_3I \rightarrow I_2 + CH_3I$ does not contribute to the measured I_2 signal. The results strongly imply that a cluster-induced *cooperative effect* is responsible for the I_2 -producing chemistry.

INTRODUCTION

A recurring theme in chemistry is the attempt to control a reaction by selectively breaking a chemical bond to yield products. Many new technologies and experimental methods have been employed in such an approach and many elegant experiments have been carried out.^{1,2} The cases of successful control have been largely limited by a rapid loss of the initial excitation through intramolecular processes. Recent experiments by the groups of Crim,³ Valentini,⁴ and Zare⁵ offer much promise in this direction, however. A different approach towards chemical control is achieved through the use of clusters and van der Waals (vdW) molecules. These systems provide a degree of control, albeit governed by the potential surfaces of the molecules involved, over the initial orientations, collision energies, and impact parameters of reaction species. They also provide the ability to simulate reactions from gas phase to condensed phase in a controlled manner so that new products may be produced.

The reaction of clusters or vdW molecules can differ significantly from that of two isolated molecules since several new effects may be introduced.⁶ In a cluster or a vdW molecular complex, molecules or atoms other than the reactants can act as a catalyst by introducing extra terms in the reactive potential. Also, in such a system, the presence of a "solvent" can relax restrictions due to momentum and energy conservation laws, and new channels for products may be opened. The existence of a solvent can give rise to an increase in the effective density of states of the reacting complex, lengthening its lifetime and allowing relatively complicated processes to occur. In addition, the aligning effect of the intermolecular potential may also change the reaction pattern, perhaps leading to a new chemistry. Finally, it is possible that more than one reaction takes place, i.e., an endothermic reaction that is energetically prohibited may be initiated by an exothermic reaction. It is not surprising that the study of the reaction dynamics in small clusters has been a rapidly

growing field.⁷⁻¹⁰ Other approaches to "solvation control" of chemical reaction are also fruitful, as the Polanyi group¹¹ has demonstrated. They observed Br_2 and Cl_2 as the products of a photoinitiated reaction: $2HX \rightarrow H_2 + X_2$ (X represents Br or Cl) taking place on LiF surfaces, which may act as catalyst by aligning the HX molecules.

Due to the difficulties in determining cluster size distributions unambiguously, many such studies have focused on ion-molecular clusters.¹² For instance, the Lineberger group¹³ has performed picosecond time-resolved measurements of the photodissociation and recombination dynamics of I_2^- interacting with a specific number of CO₂ molecules in mass selected $I_2^-(CO_2)_n$ clusters. For neutral clusters, two types of experimental methods have been used. One scheme for initiating reactions in the cluster is to electronically excite an atom inside the cluster. Soep and co-workers¹⁰ have used this method to investigate the electronic and geometric effects for several reactions of electronically excited mercury atoms $Hg({}^{3}P_{1})$ with Cl_{2} and H_{2} . Another scheme for such studies is to dissociate a molecule inside the cluster and then allow the radical to react with other molecules present in the cluster. With this method, first described by Wittig and coworkers,⁸ the scope of photochemistry is expanded dramatically. Recently, the Zewail group¹⁴ has extended femtosecond-transition-state-spectroscopy (FTS) method to the real-time probing of reactions in *clusters*. The experiments by the Wittig group¹⁵ and those of Soep¹⁶ are aimed at understanding entrance channel effects and the importance of orbital alignment and orientation on reactivity. Other experiments^{17,18} have detected S_2 from photoexcitation of (OCS)₂ and $(CS_2)_2$ using mass spectrometric detection.

Fragment angular and internal energy distributions may give one insight into the detailed dynamics in the dissociation process. For example, the S₂ product of (OCS)₂ photochemistry at 222 nm has been probed using laser-induced fluorescence detection;¹⁹ the S₂ internal state distributions are the same as those produced in the unclustered species: $S(^{1}D) + OCS \rightarrow S_{2} + CO$, indicating that the reaction dynamics are the same in the two cases. This is not always the

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case, however; the reaction between energetic H atoms and N_2O , photoinitiated in $HX \cdot N_2O$ clusters,¹⁵ gives rise to different product state distributions and branching ratios than do the unclustered reactions. Likewise, the "end-on" collision of H with CO_2 results in a much lower reaction probability than the "broadside" attack.¹⁵

Although there are numerous studies on the photodissociation of the methyl iodide monomer,²⁰ few such studies have been carried out for its clusters. There have been two reports of I₂ product formation from methyl iodide cluster dissociation, following excitation of the "A" band of the monomer. Sapers et al.²¹ first observed I_2^+ from 248 nm excitation of small CH₃I clusters via time-of-flight mass spectrometry. However, they could not establish the origin of the I₂⁺ unambiguously. More recently, Syage and Steadman²² have reported picosecond, two-color multiphoton ionization spectroscopy and electron-impact ionization studies of the same system at 266 nm. They determined neutral cluster chemistry to be the origin of the I_2^+ signal and proposed that after absorption of one photon by CH₃I, a methyl group is ejected and immediately abstracts a second methyl, forming ethane and I_2 in a concerted process. There has also been one study of CH₃I cluster dissociation following excitation of the first Rydberg state of the monomer near 200 nm. Wang et al.²³ observed several anti-Stokes transitions of I₂ in a resonance Raman experiment on small CH₃I clusters. They measured the relative intensities of the anti-Stokes peaks and obtained an estimated vibrational "temperature" of 925 K. I₂ was proposed to be the product of reaction between spin-orbit excited I*, formed via dissociation of one of the CH₃I units, and an adjacent CH₃I.

This article is an extension of our earlier report²⁴ on the laser-induced fluorescence (LIF) of I_2 produced in the photodissociation of methyl iodide clusters. We describe here systematic measurements of the internal energy distribution in the I_2 product of (CH₃I)₂ and (CD₃I)₂ photodissociation using a variety of carrier gases in the free jet expansion. Combined with the result of a room temperature flow cell experiment, a consistent picture of the photodissociation dynamics of methyl iodide clusters emerges. We suggest that some form of cluster-induced *new chemistry* is responsible for the I_2 product.

EXPERIMENT

A detailed description of the experimental setup can be found elsewhere.²⁴ The experiment is a two laser, pump and probe arrangement, in which the pump laser photolyses methyl iodide clusters, and the probe laser detects I_2 via a laser induced fluorescence (LIF) spectrum of the *B*--X transition. CH₃I clusters are generated by supersonic expansion from a commercial 0.2 mm diameter pulsed nozzle. The vapor pressure of methyl iodide is varied by changing the bath temperature of the CH₃I reservoir. The pump laser, a weakly focused KrF excimer laser operating at 10 Hz, and the probe laser, a 20 Hz Nd:YAG pumped dye laser, enter the reaction chamber from opposite directions, intersecting the molecular beam about 20 nozzle diameters down stream from the nozzle throat. The typical delay time between the two lasers is 30 ns. Typical excimer laser pulse energies used are 1–2 mJ. I₂ fluorescence excited by the probe laser is collected in a fiber optic bundle and transmitted through a colored glass filter to a red-sensitive photomultiplier detector, whose signal is averaged in a boxcar averager and sent to a lab computer. The boxcar is operated such that its averaged output represents the signal due to both lasers firing minus the signal due to only the probe laser firing. The CH₃I from Kodak and the deuterated sample (99.5 + at % D), purchased from Aldrich Chemical Company, Inc., are used as obtained. All carrier gases are Matheson research grade and used directly from their cylinders.

A detailed description of our flow cell experimental setup is also found elsewhere.²⁵ The flow cell is typically kept at a pressure of 500 mTorr using a 50 ft³/min mechanical pump. Under these conditions, the gas in the cell is pumped out completely between the 20 Hz laser pulses. The lasers and electronics are operated in the same configuration as the jet experiment. Several experimental parameters are varied to search for I₂ signal. The delay time between the pump and the probe lasers is tuned from 30 ns up to $10 \,\mu$ s, long enough to allow many collisions between species in the cell. Cell pressures up to 100 Torr and excimer laser energies from 0.5 to 10 mJ are also used.

RESULTS

Our earlier results are summarized in Figs. 1 and 2. I_2 is observed promptly after the pump laser fires. Figure 1 shows LIF spectra of I_2 from 591 to 596 nm as a function of the delay time between the two lasers. The band heads of the (10,0), (12,1), (14,2), (16,3), (18,4) vibronic bands of the $B({}^{3}\Pi_{O_{u}^{+}}) \leftarrow X({}^{1}\Sigma_{g}^{+})$ transition bands appear near 591.5 nm; and those of the (9,0), (11,1), (13,2), (15,3), (17,4) bands at around 595.7 nm. For these runs, room temperature CH₃I is seeded in Ar at a stagnation pressure of 660



FIG. 1. LIF spectra as a function of the delay time between excitation and probe, Δt . CH₃I is seeded in Ar and the total stagnation pressure $P_{tot} = 660$ Torr. (a) $\Delta t = 10$ ns, (b) $\Delta t = 30$ ns, (c) $\Delta t = 1 \mu$ s.



FIG. 2. LIF intensity as a function of excitation laser pulse energy. CH_3I is seeded in He, $P_{tot} = 1300$ Torr.

Torr. Signal is observed at 10 ns following the excimer laser trigger, peaks at around 30 ns and drops monotonically with time to about 1/3 of the peak level at 1 μ s. Since the excimer laser has a pulse width of ~15 ns and the dye laser one of 8 ns, it is clear that within our experimental time resolution I₂ is born instantly after 248 nm excitation. Under the conditions prevailing in the expansion, we estimate (*vide infra*) that at least 1-3 μ s are required for reactive collisions to occur between even highly energetic species in the jet. Therefore the prompt I₂ signal cannot be the result of reactions which involve monomer dissociation fragments, and must be due to the photodissociation of clusters.

The relation between the excitation laser pulse energy and the intensity of the I_2 signal is depicted in Fig. 2. The signal intensity shown is the signal at 592 nm (peak) minus the signal at 591.5 nm (background). The clear linear dependence of LIF signal on excimer pulse energy suggests that I_2 is born in a one-photon process. The requirement that both lasers be fired to generate any emission indicates that no electronically excited I_2 is being produced.

Figure 3 shows representative spectra of I_2 in the 591– 596 nm spectral range for CH₃I seeded in various different gases. These spectra are taken with room temperature CH₃I (P = 350 Torr); the total stagnation pressure is about 1300 Torr. We have tried nine different carrier gases: He, Ar, Kr, Xe, CO₂, O₂, N₂, SF₆, and freon-14 (CF₄). Rather interestingly, no I_2 is detected using either SF₆ or CF₄ as the seeding gas. However, this may not be due to any influence they have on CH₃I cluster photochemistry, since expanding I₂ with these gases also results in no LIF signal. For all other seeding gases, the spectra are not noticeably different as a function of the gas used. The shape of the spectrum is also independent of the nozzle diameter (between 0.2-0.8 mm), and the total stagnation pressure. The intensity of the signal is a linear function of the total stagnation pressure in the range 100-1600 Torr using both He and Xe as carrier gases. These results indicate that the I_2 signal is not due to the dissociation of $(CH_3I)_m \cdot X_n$ clusters, where X is the seeding gas.



FIG. 3. Representative spectra measured with different seeding gases, (a) He, (b) O_2 , and (c) Xe.

In order to quantify the methyl iodide cluster sizes of importance, we measure the I₂ signal intensity as a function of the CH₃I vapor pressure. The total stagnation pressure is regulated at 1250 Torr while the reservoir temperature, and hence the methyl iodide vapor pressure, is varied. Figure 4 shows the results corresponding to the vapor pressure range 35–400 Torr (-30 to 25 °C). In this figure again the signal intensity shown represents the signal at 592 nm (peak) minus the signal at 591.5 nm (background). The dashed line through the points is a quadratic function of CH₃I pressure. The inset shows a log–log plot of the low pressure region ($p_{CH,I} < 100$ Torr). The slope of this plot is 2.04, indicating



FIG. 4. LIF intensity of I_2 as a function of the vapor pressure of CH₃I. The seeding gas is He and the total stagnation pressure is regulated at 1300 Torr. The dashed line represents a quadratic fit to the data below 120 Torr. The inset is a log-log plot of the same data below 120 Torr; the slope of the line is 2.04.

that it is the methyl iodide dimers which are most important to I_2 generation. At vapor pressures above about 100 Torr, the I_2 signal intensity shows no further increase with increasing pressure. This may be because the formation of larger methyl iodide clusters is parasitic on the dimer fraction present in the expansion. These results are consistent with those of Sapers *et al.*²¹ and of Syage *et al.*²² Both report that I_2 is first observed under conditions which favor CH₃I dimer formation.

Figure 5 exhibits spectra of I_2 observed after photolysis of both deuterated and protonated methyl iodide samples measured under the same experimental conditions. Within our experimental signal-to-noise ratio, the spectra are identical, suggesting identical formation mechanisms for the two samples.

Finally, we have attempted to measure the production of I₂ from the reaction of spin-orbit excited iodine, I*, with $CH_{3}I$. For this experiment, neat room temperature $CH_{3}I$ is photolyzed at 248 nm in a flow cell arrangement. Molecular iodine has been observed previously in the flow cell photolysis of 5-10 Torr CH₃I using 193 nm excitation.²⁶ In the present experiment, however, no I_2 product is observed under any pressure conditions. The CH₃I pressure is varied from 0.5–100 Torr and the pump/probe delay from 30 ns to $10 \,\mu$ s. The loss rate of I* in collisions with CH₃I is known²⁷ to be $(2.5 \pm 0.4) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹; under our conditions we probe up to five time constants for I* removal, at a number of total pressures. The lack of any I_2 signal even under extreme conditions gives us confidence that I* is not chemically quenched by CH₃I. This has been concluded previously.27

DISCUSSION

I₂ origin

Our results show that I_2 is formed from CH_3I dimers and small clusters in a one photon process and that it is born



FIG. 5. LIF spectrum of I₂ from dissociation of CD₃I dimers (a) in comparison with that of CH₃I dimers (b). The seeding gas is He at $P_{tot} = 1300$ Torr.

instantly (< 10 ns) within our experimental resolution. Recently, Syage and Steadman²² have reported that I_2 is formed within 10 ps in the dissociation of CH₃I clusters, a result which is consistent with ours. The short time between the excitation and the appearance of product eliminates any non-same-cluster related reaction channels. Specifically, these involve the reaction of photolysis products, CH₃, I, and I*, with other CH₃I molecules and clusters in the beam. As an example, if we assume that all the available energy from monomer photolysis goes into translation of the products I* and CH₃, the I* has 0.2 eV of translational energy, corresponding to a velocity of 5.3×10^4 cm/s. At 20 nozzle diameters downstream, and with 1400 Torr stagnation pressure, the mean free path in the beam is $\sim 3 \times 10^{-2}$ cm. Therefore, the minimum time required for collisions between I* and any other species in the jet (90% He) is 500 ns, too long to form any I₂ within 10 ns. Although the CH₃ fragment moves much faster, it is still too slow to collide with other potential reaction partners within such a short time under our beam conditions. This rules out the possibility that CH₃ reacts with CH₃I·I, which might be produced by the dissociation of a dimer or larger clusters.

A simple kinetic analysis of the dimer formation reaction

$$CH_3I + CH_3I + M(=He,Ar,...) \rightarrow (CH_3I)_2 + M$$

indicates that the formation of dimer should depend quadratically on methyl iodide concentration, and linearly on that of the third body. Figure 4 shows a clear quadratic dependence of the I₂ signal on methyl iodide partial pressure up to \sim 120 Torr; its dependence on He or Xe is linear (at $P_{\rm tot} < 1600$ Torr). At values $p(CH_3I)$ greater than ~ 120 Torr, the I₂ LIF signal becomes approximately constant. We attribute this to the growing importance of higher clusters in the expansion under these conditions-I₂ may still be formed in such a cluster, but the fluorescence signal is rapidly quenched by the CH₃I neighbors. We conclude that the important species for I₂ generation from methyl iodide clusters in the low pressure regime is the methyl iodide dimer $(CH_3I)_2$. This does not imply that the dimer is the sole, or even the most important cluster present, only that the dimer is strongly implicated as the precursor of I₂. Supporting evidence is that apart from their intensity, the spectra of I_2 measured using both low (\sim 35 Torr) and high (\sim 400 Torr) methyl iodide partial pressures are identical, implying a common origin. At a total stagnation pressure above about 1600 Torr a quadratic dependence of LIF signal on total pressure is observed. This may be due to the participation of mixed clusters, such as $(CH_3I)_2 \cdot X$, where X is the seed gas. However, there is no marked difference in the observed I_2 spectrum under these conditions.

I₂ internal energy distribution

To analyze the I₂ internal energy distributions, we have carried out spectral simulations of the $B^{3}\Pi_{O_{u}^{+}} \leftarrow X^{1}\Sigma_{g}^{+}$ transition. The simulations use the I₂ molecular constants given in Huber and Hertzberg²⁸ and J-dependent Franck-Condon factors, given by Tellinghuisen.²⁹ To test the simulation, we can compare a predicted spectrum with an experimentally measured one, with known internal state distribution. Figure 6 displays a LIF spectrum of I₂ measured in a room temperature cell and a simulation, with $T_{\rm vib}$ = $T_{\rm rot}$ = 300 K and an effective resolution of 0.5 cm⁻¹.

Five ground state vibrational levels and 300 rotational levels are included in the simulation of the photolytically generated I₂. In order to reduce the number of unknown parameters, both the vibrational and the rotational distributions are assumed to be Boltzmann, each with a defining temperature. Extensive experimentation on the effects of the vibrational and the rotational temperatures on the appearance of the simulated spectrum shows that the relative intensity of the bandheads at \sim 591.7 nm to those at 591.9 nm is a sensitive function of the vibrational temperature and that the "steepness" of the shading of the band to the red is governed almost entirely by the rotational temperature. We use this insight to model the experimental spectrum which results from (CH₃I)₂ photolysis. Figure 7 displays the I₂ spectrum shown in Fig. 5(a) as well as a simulated spectrum with $T_{\rm vib} = T_{\rm rot} = 150$ K. Varying either or both of these temperatures within the range 150-200 K results in similar spectra, though not quite as good a match to experiment. Outside that range, the simulations appear quite different from the measured data. We conclude that insofar as the I_2 may be characterized by separate Boltzmann distributions in vibration and rotation, the internal energy distributions are well approximated using a "temperature" of ~150 K in each degree of freedom. This corresponds to a total internal energy of about 2.5 kJ/mol for the I_2 product, which is less than the energy disposal reported by Wang et al.,²³ who report \sim 3.8 kJ/mol in vibration alone. However, the experiments are performed at different excitation wavelengths, and access different electronic states of the CH₃I monomer.



FIG. 6. (a) LIF spectrum of I_2 obtained in a room temperature flow cell experiment. (b) Simulated LIF spectrum of I_2 with $T_{rot} = 300$ K, $T_{vb} = 300$ K.



FIG. 7. (a) LIF spectrum of I_2 from dissociation of CH₃I dimers. (b) Simulated LIF spectrum of I_2 with $T_{rot} = 150$ K, $T_{vib} = 150$ K.

Reaction dynamics

The timing of the appearance of I_2 rules out all but a same-cluster reaction mechanism. We now discuss the possibility that I_2 is formed in methyl iodide dimers as a consequence of the dissociation of one CH₃I unit into I* + CH₃, followed by a chemical reaction between I* and the remaining CH₃I. This reaction is slightly exoergic, unlike the corresponding reaction with ground state I atoms; the total energy available, including translation imparted by the photolysis, is ~ 20 kJ/mol. This probably represents an upper limit to the energy, since it ignores vibrations in the CH₃ photofragment; as well Loo *et al.*³⁰ report observing slower I* from the photolysis of CH₃I clusters than from monomers.

Although energetically possible, this reaction has not been unambiguously seen in the unclustered environment. There have been several measurements of I* quenching by CH_3I .^{27,31} The total quenching rate constant is reported to be 2.5×10^{-13} cm³ molecule⁻¹ s⁻¹ at 300 K for the following channels:²⁷

$$I^* + CH_3I \rightarrow CH_3I + I$$

$$\Delta H^0_{300} = -92 \text{ kJ/mol}$$
(A)

$$I^* + CH_3I \rightarrow CH_3 + I_2$$

$$\Delta H_{300}^0 = -4.2 \text{ kJ/mol}, \qquad (B)$$

and decreases with increasing temperature. The mechanism for the protonated molecule is attributed *exclusively* to an electronic to vibrational energy transfer into a manifold of acceptor states in CH_3I , i.e., channel (A); and not I* loss via chemical reaction (B).²⁷ The temperature dependence of the quenching implies that it is even less efficient at the higher collision energies available to photolysis products. The results of our cell experiment confirm that (B) is an unobservable channel under our conditions.

It is possible that I_2 is produced from reactions of high

kinetic energy ground state I, perhaps produced in the E-V,R,T relaxation of I*. To consider the likelihood of this mechanism, it is helpful to compare our experiment with those of the reverse reaction $CH_3 + X_2 \rightarrow CH_3X + X$, where X is I, Br, and Cl. In an early crossed molecular beam study by McFadden *et al.*,³² at a 4.6 kcal mol⁻¹ collision energy the CH₃I product was predominantly backscattered into $\theta \sim 150^\circ$ with a small cross section for the reaction, about 0.5 to 5 Å². Similar results were obtained for all CH₃ + X₂ reactions. In another study of the reaction $CH_3 + Br_2$ and Cl_2 by Kovalenko and Leone,³³ about 50% of the exoergicity appeared in product vibration, and the reaction rate was enhanced considerably by an increase in the translational energy of CH₃. These studies suggest that there is an "early" barrier in the reaction and the energy release to CH₃X is "mixed."³⁴ This means that for the reverse reaction, $I + CH_3I \rightarrow I_2 + CH_3$, there will be a late barrier, implying that translational energy alone will be ineffective at overcoming the endoergicity.

For the deuterated sample, it has been reported²⁷ that the total depletion rate of I* [reaction (A) and (B)] is 4.8×10^{-13} molecule⁻¹ s⁻¹ at 300 K. This rate is 2 orders of magnitude lower than that of the protonated sample and represents an upper limit to the reaction rate in the deuterated methyl iodide. Therefore, if the I₂ is formed from the reaction I* + CH₃I occurring in methyl iodide dimer, we expect to see a dramatic difference in the signal intensity between these two samples. However, this is not the case: We observe identical signals for CH₃I and CD₃I samples. This further indicates that this reaction channel is not followed.

The difference between the reaction $I^* + CH_3I \rightarrow I_2 + CH_3$ in a cell and in a cluster might be rationalized if we assume a "late" barrier on the reaction coordinate. This barrier could be overcome by dimer formation if, when I* is born from the dissociation of a monomer unit in the cluster, it is already on the product side of the barrier, allowing the reaction to proceed. Such a picture is consistent with studies of spin-orbit effects in reactions involving halogen atoms with hydrogen halides and halogen molecules³⁵

$$X + HY \rightarrow HX + Y,$$

$$X + YZ \rightarrow XY + Z.$$

These studies show that the lower spin-orbit state is more reactive, both in the H atom and the halogen atom transfer reactions in most cases. Generally, the spin-orbit excited state of the reactants correlated with the excited states of the products; reactions giving ground state products, if they occur at all, must follow a nonadiabatic pathway, which gives rise to an effective barrier to the reaction.

Such a barrier seems unlikely in the present case. Figure 8 displays a schematic correlation diagram for I, $I^* + RI \rightarrow I_2 + R$, where R is a structureless fragment with symmetry ²A' in the C_s point group. The symmetry labels are those of the double group, as exploited for Hund's case (c) molecules by Husain.³⁶ This diagram is strictly true for the HI₂ system, but is not expected to be significantly different in the present case. The important features to note are that the spin-orbit excited state of iodine correlates to electronically



FIG. 8. Correlation diagram for the reaction I, $I^* + RI \rightarrow I_2 + R$, where R is a structureless fragment with symmetry ${}^2A'$.

excited I_2 and that there are no avoided crossings which could make ground state I_2 accessible.

The correlation diagram certainly explains the very low reactivity of I* in the unclustered environment. If ground state I_2 is formed via reaction between I* and CH₃I, the cluster must somehow induce a nonadiabatic transition to the single reactive potential energy surface. This is certainly a possibility, but it leaves open the problem of the expected ineffectiveness of translational energy alone to promote the reaction with ground state iodine atoms. However, if this does take place, one would predict two different methyl translational distributions: one "hot," arising from the initial photolysis, and a second, "cold," from the $I^* + CH_3I$ reaction. This difference could provide a means to test the postulated mechanism. The observed energy disposal into rotation and vibration of the I₂ fragment becomes $f'_{int} \sim 0.12$ if we assume this mechanism. This is somewhat smaller than that reported for other I-atom transfer reactions,³⁷ such as

$$K,(Ba,F) + \frac{ICH_3}{ICF_3} \rightarrow KI(BaI,FI) + CH_3$$

in which $f'_{int}(XI) \sim 0.2-0.5$. It would be of interest to measure the translational energy distribution in the I₂ product as well.

Another possible mechanism for I_2 formation in this system is some form of "cooperative chemistry," in which interactions in the cluster change the fundamental photochemistry. If the CH₃I *cluster* is thought of as the chromophore, then it could, in principle, have quite a different photochemistry than its constituent monomers. This is true for instance in the $(NO_2)_2$ system, in which N_2O_4 is a photochemically distinct species. The potential energy surface in the excited state could be changed such that the monomer excited states are coupled to form new, mixed "exciplex" states. Although this type of coupling could be quite weak, a fundamental difference might be achieved; new bonds could result in the excited state species.

In fact, such a cooperative effect has been reported in matrix studies.^{38,39} Abrash and Pimentel³⁸ have reported ex-

periments which study the wavelength dependence of the photochemistry of HI·C₂H₂ complexes in solid krypton. Photochemical reactions are induced at wavelengths at which neither monomer absorbs. The authors of Ref. 38 attribute this result to new properties of the six-atom system, which they call the supramolecule. Moore and Andrews³⁹ report a study of the oxidation of phosphorus(III) halides in solid argon by long wavelength photolysis of its complex with ozone. They conclude that "the complex markedly increases the cross section for red photodissociation of ozone and suggest that this increase is due to the complex effectively lowering the barrier to dissociation by providing a strongly exothermic dissociation-recombination process."³⁹ In this vein, it is also interesting to note that Br₂ and Cl₂ are observed as products of a photoinduced four-center reaction: $2HX \rightarrow H_2 + X_2$, taking place on LiF surfaces.¹¹ In this case, the LiF surface might somehow act as a catalyst by introducing a cooperative interaction between the HX units. Very recently, Buntine et al.⁴⁰ have reported "slow" H₂ product molecules in an experiment probing the reaction $H + HI \rightarrow H_2 + I$. They suggest that the slow H_2 might be due to HI cluster photolysis, with a mechanism perhaps similar to that presented above.

These results all suggest that a cooperative chemistry occurring in clusters as small as the dimer is not impossible. This chemistry would involve the processes

$$(CH_3I)_2 \rightarrow CH_3 + CH_3 + I_2, \qquad (C)$$

and

$$(CH_{3}I)_{2} \rightarrow C_{2}H_{6} + I_{2}.$$
 (D)

These are exoergic by ~ 140 and ~ 520 kJ/mol, respectively, assuming a dimer binding energy of 12 kJ/mol.⁴¹ Our experimental result of very "cold" rotational and vibrational distribution of the I₂ product could be consistent with a fourcenter concerted reaction, such as that shown in reaction (D). Although ground state four-center exchange reactions are forbidden by the Woodward–Hoffmann rules, the excited electronic state reaction *is* allowed. It will be of great interest to determine whether C₂H₆ is a product of the dimer photolysis. The only reported²³ calculation of the dimer structure is similar to the crystal structure⁴² and predicts that the two iodines are not sterically hindered from reacting in this manner by the methyl groups.

If this approach is correct, it implies that a remarkably small fraction of the available energy is channeled into the I₂ internal degrees of freedom. With 2.5 kJ/mol in the I₂ product internal degrees of freedom, less than 2% of the exoergicity appears as I₂ internal energy in the CH₃-producing reaction; even *less* if ethane is the product. This is a very small fraction to appear in a reaction product containing a new bond. In order to establish whether this is reasonable for the present system we have performed a surprisal analysis, using a prior distribution for the I₂ given by⁴³ $P^0(f_v) = 2/$ $9(1 - f_v)^{7/2}$. The surprisal plots $(-\ln[P(v)/P^0(v)] vsf_v)$ are linear for both reactions (C) and (D), and yield slopes $\lambda_v = +100$ and +400, respectively. Such large positive values imply a strongly nonstatistical disposal of the available energy into vibration. The same conclusion is reached on the basis of more realistic density of states calculations the I_2 internal energy disposal is very much smaller than any statistical outcome would predict.

It is possible that photoreactions of larger clusters also contribute to the I_2 signal. In this case, the newborn (perhaps very excited) I_2 could suffer several collisions with the surrounding solvent cage, and be vibrationally and rotationally deactivated. The energy lost by the I_2 would go into evaporation of the surrounding methyl iodine molecules, leaving an internally cool, isolated I_2 on the time scale of detection. However, our vapor pressure dependence results are strong evidence that the dimer is the dominant I2-generating species in the beam, at least in the low $p(CH_3I)$ regime. Furthermore, spectra measured in the low methyl iodide vapor pressure region (favorable for dimer formation) are the same as ones taken at higher vapor pressures where there is a greater possibility to form larger clusters. We interpret this as further evidence that I_2 signal due to contamination from larger clusters is negligible.

Partially due to the difficulties in quantitatively characterizing cooperative interactions, this phenomenon has not yet been considered widely in photochemistry. We think that cooperative interactions could play an important role in reactions taking place in clusters, in a matrix and also on a surface. We hope this work will stimulate more exciting studies in this direction.

CONCLUSIONS

 I_2 is formed in a one-photon excitation of methyl iodide clusters in a free jet expansion. The pressure dependence of LIF signal indicates that the I_2 is first formed under methyl iodide dimer conditions. The rotational and vibrational energies of the I_2 are each estimated to be 1.25 kJ/mol, obtained through spectral simulations. This energy distribution is the same for CH₃I seeded in CO₂, Ar, Xe, O₂, and He, as well as for neat expansions and for deuterated samples. The most reasonable mechanisms to account for the observed I_2 LIF signal postulates a cooperative effect introduced by clustering, suggesting that a new chemistry occurs in the photodissociation of methyl iodide dimers.

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- ²(a) P. Brumer and M. Shapiro, Acc. Chem. Res. 22, 407 (1989); (b) S. M. Park, S.-P. Lu, and R. J. Gordon, J. Chem. Phys. 94, 8622 (1991).
- ³A. Sinha, M. C. Hsao, and F. F. Crim, J. Chem. Phys. 94, 4928 (1991).

^{&#}x27;(a) See, for example, F. F. Crim, Science 249, 1387 (1990), and references therein; (b) C. X. W. Qian and H. Reisler, in Advances in Molecular Vibrations and Collisison Dynamics, edited by J. Bowman (JAI, Greenwich, 1990); (c) W. H. Miller, Laser Chem. 2, 243 (1983).

⁴I. Bar, Y. Cohen, D. David, T. Arusi-Parpar, S. Rosenwaks, and J. J. Valentini, J. Chem. Phys. **95**, 3341 (1991).

⁵M. J. Bronikowski, W. R. Simpson, B. Girard, and R. N. Zare, J. Chem. Phys. **95**, 8647 (1991).

⁶For recent review see R. Naaman, in Adv. Chem. Phys. 70, pt2, 181 (1988).

- ⁷(a) S. Buelow, G. Radhakrishan, and C. Wittig, J. Phys. Chem. **91**, 5409 (1987); (b) G. Radhakrishan, S. Buelow, and C. Wittig, J. Chem. Phys. **84**, 727 (1986).
- ⁸S. Buelow, G. Radhakrishan, J. Catanzarit, and C. Wittig, J. Chem. Phys. 83, 444 (1985).
- ⁹O. Cheshnovsky and S. Leutwyler, Chem. Phys. Lett. 121, 1 (1985).
- ¹⁰(a) C. Jouvet and B. Soep, Laser Chem. 5, 157 (1985); (b) Chem. Phys. Lett. 96, 426 (1983); (c) C. Jouvet, M. Boivineau, M. C. Duval, and B. Soep, J. Phys. Chem. 91, 5416 (1987).
- ¹¹(a) C.-C. Cho, J. C. Polanyi, and C. D. Stanners, J. Chem. Phys. **90**, 598 (1989); (b) E. B. D. Bourdon, C.-C. Cho, P. Das, J. C. Polanyi, C. D. Stanners, and G.-Q. Xu, *ibid.* **95**, 1361 (1991).
- ¹²T. D. Mark and A. W. Castleman, Jr., in Advances in Atomic and Molecular Physics (Academic, New York, 1985), Vol. 20, p. 65.
- ¹³(a) D. Ray, N. E. Levinger, J. M. Papanikolas, and W. C. Lineberger, J. Chem. Phys. **91**, 6533 (1989); (b) J. M. Papanikdas, J. R. Gord, N. E. Levinger, D. Ray, V. Vorsa, and W. C. Lineberger, J. Phys. Chem. **95**, 8028 (1991).
- ¹⁴N. F. Scherer, C. Sipes, R. B. Bernstein, and A. H. Zewail, J. Chem. Phys. **92**, 5239 (1990); J. J. Breen, L. W. Peng, D. M. Willberg, A. Heikal, P. Cong, and A. H. Zewail, *ibid.* **92**, 805 (1990).
- ¹⁵Y. Chen, G. Hoffmann, S. K. Shin, D. Oh, S. Sharpe, Y. P. Zeng, R. A. Beaudet, and C. Wittig, Adv. Photochem. 16, 249 (1991).
- ¹⁶J. P. Visticot, B. Soep, and C. J. Whitham, J. Phys. Chem. **92**, 4574 (1988); W. H. Brickenridge, C. Jouvet, and B. Soep, J. Chem. Phys. **84**, 1443 (1986).
- ¹⁷D. A. Prinslow and V. Vaida, J. Chem. Phys. **93**, 1836 (1989).
- ¹⁸W.-B. Tzeng, H.-M. Yin, W.-Y. Leung, J.-Y. Luo, S. Nourbakhsk, G. D. Flesch, and C. Y. Ng, J. Chem. Phys. 88, 1658 (1988).
- ¹⁹N. Sivikumar, G. E. Hall, P. L. Houston, J. W. Hepburn, and I. Burak, J. Chem. Phys. 88, 3692 (1988).
- ²⁰See, T. Suzuki, H. Kanamori, and E. Hirota, J. Chem. Phys. 94, 6607 (1991), for a brief review of the current knowledge on CH₃I photodissociation.

- ²¹S. P. Sapers, V. Vaida, and R. Naaman, J. Chem. Phys. 88, 3638 (1988);
 V. Vaida, D. J. Donaldson, S. P. Sapers, and R. Naaman, J. Chem. Soc. Faraday Trans. 86, 2043 (1990).
- ²²J. A. Syage and J. Steadman, Chem. Phys. Lett. 166, 159 (1990).
- ²³P. G. Wang, Y. P. Zhang, C. J. Ruggles, and L. D. Zeigler, J. Chem. Phys. 92, 2806 (1990).
- ²⁴Y. B. Fan and D. J. Donaldson, J. Phys. Chem. 96, 19 (1992).
- ²⁵S. P. Sapers, N. Andraos, and D. J. Donaldson, J. Chem. Phys. 95, 1738 (1991).
- ²⁶E. Bishenden and D. J. Donaldson (unpublished results).
- ²⁷C. Fotakis and R. J. Donovan, J. Chem. Soc. Faraday Trans. 2 74, 2099 (1978).
- ²⁸K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure*, Pt. IV (Van Nostrand Reinhold, New York, 1979).
- ²⁹J. Tellinghusen, J. Quant. Spectrosc. Radiat. Transfer 19, 149 (1978).
- ³⁰R. O. Loo, G. E. Hall, H.-P. Haerri, P. L. Houston, J. Phys. Chem. **92**, 5 (1988).
- ³¹S. Baughcum and S. R. Leone, J. Chem. Phys. 72, 6531 (1980), and references therein.
- ³²D. L. McFadden, E. A. McCullough, Jr., F. Kalos, and J. Ross, J. Chem. Phys. **59**, 121 (1973).
- ³³L. J. Kovalenko and S. R. Leone, J. Chem. Phys. 80, 3656 (1984).
- ³⁴J. C. Polanyi, Acc. Chem. Res. 5, 161 (1972).
- ³⁵P. J. Dagdigian and M. L. Campbell, Chem. Rev. 87, 1 (1987).
- ³⁶D. Husain, Ber. Bunsenges. Phys. Chem. 81, 168 (1977).
- ³⁷J. C. Whitehead, in *Chemical Kinetics*, edited by C. H. Bamford and C. F. H. Tipper (Elsevier, New York, 1983), Vol. 24 and references therein.
- ³⁸S. A. Abrash and G. C. Pimentel, J. Phys. Chem. **93**, 534 (1989).
- ³⁹B. W. Moore and L. Andrews, J. Phys. Chem. 93, 1902 (1989).
- ⁴⁰M. A. Buntine, D. P. Baldwin, R. N. Zare, and D. W. Chandler, J. Chem. Phys. **94**, 4672 (1991).
- ⁴¹D. J. Donaldson, V. Vaida, and R. Naaman, J. Chem. Phys. 87, 2522 (1987).
- ⁴²T. Kaweguchi, M. Hijikigawa, Y. Hayafuji, M. Ikeda, R. Fukushima, and Y. Tomiie, Bull. Chem. Soc. Jpn. 46, 53 (1973).
- ⁴³E. Zamir and R. D. Levine, Chem. Phys. Lett. 54, 239 (1979).