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Infrared spectroscopic studies on photolysis of methyl iodide and its clusters in solid parahydrogen

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Methyl iodide is trapped as the monomer and as clusters in the parahydrogen, known as a quantum crystal, at temperatures below about 8 K. UV illumination of the deposited sample at about 5 K causes the dispersal of clusters and the production of the methyl radical, methane, and ethane as evidenced by their infrared absorption spectra. Thermal annealing of the photolyzed sample at temperatures up to 11 K results in the disappearance of the methyl radical, the enhancement of ethane, and the regeneration of methyl iodide. When the initial concentration of the iodide is small, the clusters in the deposited sample are suppressed. For such a sample the UV excitation produces the methyl radical and methane but the formation of ethane is negligibly small. Relevance of the present work to studies of photolysis in gaseous clusters of methyl iodide is discussed. © 1995 American Institute of Physics.

I. INTRODUCTION

Methyl iodide is one of the prominent molecules in molecular photophysics and chemistry because it has provided information on topics of fundamental importance such as the branching into two channels separated by the spin–orbit interaction,¹ the real-time dynamics of the C–I bond scission,^{2–4} and the internal energy distribution of the photodissociated methyl radical in the vibrational^{5–10} and the rotational energy regimes.^{11–14} Also, recent interest in possible new photochemical reactions in clusters¹⁵ has attracted attention to the methyl iodide cluster in molecular beams.^{16–24}

Meanwhile, a new high-resolution matrix-isolation spectroscopy using the solid parahydrogen as the matrix has been launched recently by Oka and co-workers. They have been studying relatively simple molecules such as orthohydrogen and deuterated hydrogens.^{25–31} The new matrix has several salient features favorable for high-resolution spectroscopy. We attempt to apply the new technique for the study of molecules of chemical interest such as methyl iodide. The present work is the first of a series of studies using the solid parahydrogen as a new matrix.

II. EXPERIMENT

Ultrahigh purity (>99.999 95%) normal hydrogen gas was transferred to a ferric oxide ortho-para converting catalyst at ~14.3 K for about 1.5 h to obtain parahydrogen with a purity of 99.9% as estimated by the intensity of the fundamental vibrational bands of orthohydrogen.³¹ Commercial methyl iodide (Nacalai tesque, Inc.) was used as received. The admixed gas of methyl iodide in parahydrogen with a concentration of 0.005%-0.01% was introduced into a copper cell which was attached to the bottom of a cryostat. The inner diameter and the path length of the optical cell were 2 and 3 cm, respectively. Slightly wedged CaF₂ windows of a thickness of ~2 mm were attached to both ends of the cell via indium gaskets. An optically transparent solid sample was grown in the cell by continuously flowing the gas into the cell at about 7.7 K, typically in 1 h. The optical measurement was performed by a Nicolet FTIR spectrometer (Magna 750) with a CaF₂ beamsplitter and a MCT (HgCdTe) detector with a resolution of 0.25 cm⁻¹. The measurements before and after the UV illumination described below were made at 4.80 ± 0.05 K. The UV illumination was carried out by using a 20 W mercury lamp which was placed directly in front of the outermost CaF₂ window of the cryostat. To see the effect of thermal annealing the photolyzed sample was kept at temperatures between 4.8 and 11.0 K for 15 min with an accuracy of ± 0.1 K, and then the optical measurement was carried out at each elevated temperature.

III. EXPERIMENTAL RESULTS

Spectra I–IV in Figs. 1 and 2 are for a relatively concentrated sample. Spectrum I was observed immediately after lowering of the temperature of the deposited sample to 4.80 K. Spectrum II is the same as I after a succeeding 150 min UV illumination at 4.80 K. Spectra III and IV are the same as II after successive elevation of temperature of the illuminated sample to 7.0 and 8.0 K, respectively. Spectral measurements were also made at other temperatures up to 11.0 K to obtain continuously changing spectra which are not shown in the figures to avoid congestion. The scales of the ordinate are arbitrary but are common to the four spectra in each figure. They are vertically displaced for clarity. All the numbers on the abscissa and in the text are in units of cm⁻¹ throughout the present paper.

The essential features of spectra I–IV are summarized as follows:

Spectrum I: The bands at 3060–3040, 2965–2940, 2850, and 2825–2815 in Fig. 1 and those at 1440–1420, 1410–1395, and 1250–1235 in Fig. 2 are comparable with the reported bands of methyl iodide in a neon matrix (Table I of Ref. 32) which are reproduced below with the qualitative description for the intensity as strong (s), medium (m), and weak (w); 3055 (m), 2965 (s), 2855 (w), and 2830 (m) for Fig. 1 and 1435 (s), 1409 (m), and 1249 (s) for Fig. 2. In



FIG. 1. Infrared absorption spectra of methyl iodide in solid parahydrogen, $3200-2750 \text{ cm}^{-1}$. (I) As deposited at 4.8 K. (II) Same as I after a 150 min UV illumination at 4.8 K. (III) Same as II measured at 7.0 K. (IV) Same as II measured at 8.0 K. We have measured the spectra at various temperatures up to 11 K to obtain intermediate spectral patterns but they are omitted to avoid congestion. The insets at the bottom and the top of the figure are for methane and ethane in solid parahydrogen at 4.8–4.9 K, respectively. The symbols, R, I, M, and E stand for the methyl radical, methyl iodide, methane, and ethane. They are indicated for convenience of identifying the absorption bands.

addition to the above seven absorption bands we observed a weak band at 2485–2465 which apparently corresponds to the one at 2496 reported for the neon matrix.³² This band, considered to be the first overtone of the band at 1250–1235, is omitted for the sake of space saving. The omission does not affect the essential argument which follows. The numerous downward spikes in the region of 1450–1360 of Fig. 2 are due to water vapor in the optical path and should be ignored. On account of the fair agreement of the bands in Figs. 1 and 2 with those reported for the neon matrix³² and of the internal consistency in the spectral analysis to be presented below all the band systems enumerated above are assigned to methyl iodide.

Spectrum II: The spectral changes upon the UV illumination are remarkable and extensive. They can be classified into the following three groups: R, M, and E. (These symbols stand for the methyl radical, methane, and ethane and these three spectral changes will be shown to be related to these three species.)

Group R: A new trio appears as a doublet at 3171.4/ 3170.6 (s), 2780.1/2779.3 (w), and 1402.7/1401.6 (s). They can be attributed to a common signal carrier because of their same behavior on warming (see spectra III and IV).

Group M: Richly structured bands newly appear at

3040–3000 and 1320–1295 which are found to behave in common upon photo and thermal treatments as described below.

Group E: Another new set of broad bands appears at 2985–2965 (s), 2960–2930 (weak and broad), 2923 (weak but relatively sharp), and 2890–2870 (medium and partially structured) in Fig. 1.

Besides the above three types of spectral changes we note that the bands assigned to methyl iodide in spectrum I and designated with I, which stands for the iodide, show a general tendency to be sharpened with the loss of the broad wing on the lower energy side. To be specific, the four bands of spectrum I in Fig. 1 change to those showing a sharp peak at 3057.6, 2965.2, 2853.1, and 2826.3. Similarly, the two bands of spectrum I in Fig. 2 change to a small peak at 1432.6 superposing on a low "terrace" at ~1440–1425 and another small peak at 1407.1. Finally, the partially structured bands at 1250–1235 of spectrum I in Fig. 2 collapse into the single feature at 1248.6. These spectral changes will be discussed in connection with the monomer and the cluster of methyl iodide (see Sec. IV B).

Spectra III and IV: The conspicuous doublet absorptions of group R diminish quickly with rising temperature while those of group M also decrease accompanying the growth of



FIG. 2. Infrared absorption spectra of methyl iodide in solid parahydrogen, $1450-1230 \text{ cm}^{-1}$. See caption for Fig. 1. The numerous signals except for the meaningful absorptions described in Sec. III are due to the irrelevant water vapor in the optical path. The "emissive" and absorptive patterns of the signals are due to the temporal fluctuation of the cancellation between the measurements of the background and the sample. The inset at the lower right corner is for a methane/parahydrogen system at 4.8–4.9 K.

a broad band in the lower energy region. The approximate maxima of the broad bands at the final stage of spectrum IV are at about 3015 and 1304. The absorptions of group E in spectrum II are enhanced slightly with the smearing of the structures seen for the bands at 2985–2965 and at 2890–2870.

Spectra I–III in Fig. 3 demonstrate representatively the spectral change observed for a relatively dilute sample. Spectrum I is for the sample immediately after the lowering of temperature to 4.80 K. Spectrum II is the same as I after a 240 min UV illumination at 4.80 K and measured at the same temperature. Spectrum III is the same as II after elevating the sample to 7.0 K and measured at the same temperature. Due to the reduction of the amount of the methyl iodide the overall spectral intensity in Fig. 3 is suppressed compared with the spectra in Figs. 1 and 2. However, the following spectral changes are notable:

Spectrum I: The absorption band corresponding to that at 2965–2940 in spectrum I of Fig. 1 is sharpened by losing the broad shoulder on the low energy side is compressed into a narrower range of 2965–2955. At the same time the multiplet structure is more pronounced than that on the band at 2965–2940 in spectrum I of Fig. 1.

Spectrum II: The doublet at 3171.4/3170.6 of group R and the band at 3040–3000 of group M observed in Figs. 1

and 2 also appear in Fig. 3 with the relative abundance of M over R. In contrast, the strong band at 2985–2965 of group E observed in Fig. 1 appears only feebly in the narrower region of 2985–2980. The other band of group R at 1402.7/1401.6 and the one at 1320–1295 of group M are also observed as in Fig. 2, but they are not shown to avoid redundancy. Notice that the band at 2965–2955 seen in spectrum I of Fig. 3 disappears almost completely in spectrum II.

Spectrum III: The doublets of group R are reduced remarkably as in Figs. 1 and 2 while the band at 2965–2955 in spectrum I of Fig. 3 seems to have recovered slightly as revealed by a small peak at about 2965.

IV. DISCUSSION

A. Spectral assignment

The spectra of group R are associated with the methyl radical because the two strong doublets at 3171.4/3170.6 and 1402.7/1401.6 are reasonably close to the absorptions of the methyl radical at $3162 (\nu_3)$ and $1396 (\nu_4)$ in a neon matrix [Table II of Ref. 32, apparently the number of 1398 in Table II should read 1396 in reference to Table VI] and at 3150 and 1385 in an argon matrix.³³ They should also be compared with the absorption of the radical in the gas phase. The band origin for the ν_3 (the in-plane-degenerate CH stretch) band is



FIG. 3. Infrared absorption spectra of methyl iodide in solid parahydrogen, $3200-2750 \text{ cm}^{-1}$. The spectra in this figure are for a sample in which methyl iodide molecules are better isolated than those for a sample giving the spectra in Figs. 1 and 2. (I) As deposited at 4.8 K. (II) Same as after a 240 min UV illumination at 4.8 K. (III) Same as II measured at 7.0 K.

determined to be 3160.8212(12) (Ref. 34) while the ν_4 band has not been detected. The very weak absorptions at 2780.1/ 2779.3 barely seen in spectrum II of Fig. 1 are regarded as the first overtone of the ν_4 band which has not been previously reported to our knowledge. The considerable blue shift of the absorptions in the solid hydrogen relative to the gas phase and their doublet feature are a most interesting subject to pursue. It is pertinent in this context to mention a recent report of the ESR detection of the methyl radical in photolyzed methyl iodide/parahydrogen mixture.³⁵

The spectra of group M are attributed to methane because we have observed quite comparable spectra for methane/parahydrogen mixtures as shown in the lower insets of Figs. 1 and 2. The characteristic structures on the two band systems are indicative of the quantization of the rotational levels of methane in the solid parahydrogen which will be investigated in detail.³⁶ At the moment it suffices to mention that the systems at 3040–3000 and 1320–1295 are assigned to the ν_3 (the asymmetric CH stretch) and the ν_4 (the degenerate CH bend) bands of the isolated methane molecule.³⁷

The new absorptions of group E are assigned to ethane because they are in fair agreement with those observed for ethane in a neon matrix at 2979 (s), 2947 (m), 2921 (w), 2888 (m), 2857 (w), and 2839 (w).³² Furthermore, they have general resemblance to the absorptions recorded in the

present work for an ethane/parahydrogen system which are shown in the upper insets of Fig. 1. It should be emphasized that ethane is already produced at the stage of the UV illumination at 4.8 K (see discussion on photochemistry below).

In concluding this subsection we can summarize that the spectral changes of R, M, and E in the previous section are associated with the production of the methyl radical, methane, and ethane, all being induced upon the UV illumination.

B. Photochemistry

In the present work the degree of isolation can be controlled by changing both the initial concentration of methyl iodide in the parahydrogen gas and the deposition temperature. A number of experiments with samples of varying degrees of isolation have led us to conclude that the samples giving the spectra in Figs. 1 and 2 correspond to the case of a medium degree of isolation which allows the coexistence of the monomer and clusters, while in the sample for Fig. 3 the iodide is mostly isolated. The cluster absorption bands at 2965–2940 and 1250–1235 are featureless and are always red shifted with respect to the sharp multiplets associated with the monomer absorption bands. As for the nature of the multiplets detailed analysis will be put forth following the planned investigation of a similar multiplet feature observed for the prototypical methane molecule.³⁶ It is interesting to note that the broad bands ascribed to the clusters transform drastically into the sharp multiplets as is seen from the comparison of spectra I and II in Figs. 1 and 2. The change indicates that the absorption of the UV photon by the clusters causes not only the photochemical processes to be discussed below but also efficient dispersal of the clusters to the monomer. The excess energy corresponding to the difference between the photon energy and the energy required for the chemical processes may be dissipated translationally to "boil" the clusters^{14,16} and spatter methyl iodide molecules into the bulk of the solid hydrogen which may be depicted as a temporary jellylike medium to accept the spattered molecules and confines each of them quickly. This may be a most unique property of the quantum solid of hydrogen.

A remarkable change upon the UV illumination common to Figs. 1–3 (cf. spectrum II against I) is that methyl iodide diminishes (in Figs. 1 and 2) or disappears completely (in Fig. 3) to yield the absorption bands of the methyl radical and methane which are denoted by R and M, respectively. Thus, it is obvious that some of the methyl radicals are sufficiently reactive to yield methane while the remainder are trapped. Since the feature of spectrum I in Fig. 3 indicates that methyl iodide is well isolated compared with the samples giving the spectra in Figs. 1 and 2, the hydrogen atom donor for the formation of methane must be among the hydrogen molecules surrounding the photolyzed iodide. At the same time, the concomitant appearance of the methyl radical implies that the thermalized methyl radical at 4.80 K does not abstract the hydrogen atom, at least appreciably, in the time scale of the present work. We can summarize the above statement by reactions (1)-(3) below where the asterisk indicates that the radical is epithermal and that the rate of reaction (3) is immeasurably slow, although the possibility of a slow tunneling reaction between the thermalized radical and a hydrogen molecule cannot be ruled out,

$$CH_3I + h\nu \rightarrow CH_3^* + I, \tag{1}$$

$$CH_3^* + H_2 \rightarrow CH_4 + H, \tag{2}$$

$$CH_3 + H_2 \rightarrow CH_4 + H.$$
 (3)

We note that the photon energy (\sim 4.9 eV) amply exceeds the dissociation energy of the C–I bond (\sim 2.3 eV) to permit the methyl radical being epithermal.

Another remarkable difference between Figs. 1 and 2 vs Fig. 3 is that the photo-induced production of ethane in the dilute sample is negligibly small (compare spectrum II of Fig. 1 with spectrum II of Fig. 3). This indicates that the formation of ethane is closely related to the initial clustering of methyl iodide dominant in the concentrated sample.

Despite the difference of the present system of the solid parahydrogen from the familiar system of jet-cooled molecular beams,^{16–24} we note some relevance between the two systems from the viewpoint of the photochemical reactions therein; studies of the valence excitation of gaseous methyl iodide clusters in the molecular beam have disclosed "new" chemistry²³ in which the iodine molecule is supposed to be produced from the photoexcited dimer by an unusual concerted mechanism as summarized in reactions (4) and (5),

$$(CH_3I)_2 + h\nu \rightarrow CH_3 + CH_3 + I_2, \tag{4}$$

and/or

(

$$CH_3I)_2 + h\nu \rightarrow C_2 + H_6 + I_2.$$
(5)

The major reasoning for reactions (4) and (5) is that the iodine molecule is produced within 10 ps,¹⁷ carrying only a very small fraction of the exoergicity of the reaction.²² However, direct evidence for either product, the radical or ethane, has not been given. Contrastingly, the present work has provided definite spectral evidence for both of them. The formation of ethane by reaction (5) seems to be substantiated because the bands of group E are already observed at 4.8 K for the UV illuminated sample containing the methyl iodide clusters (see spectrum II of Figs. 1 and 2) but only negligibly for the sample containing no clusters (see spectrum II of Fig. 3).

C. Thermochemistry

The changes from spectrum II to III and IV in Figs. 1 and 2 and the change from II to III in Fig. 3 plainly indicate the thermally induced disappearance of the methyl radical (R) and the increase of ethane (E). Although the absorption line shape of ethane is deformed with temperature, the integrated intensity of the absorption of E continues to increase. Thus, one may add the following recombination reaction which proceeds between the near-lying radicals formed by reaction (4):

$$CH_3 + CH_3 \rightarrow C_2H_6. \tag{6}$$

The necessity of the proximity of the two radicals is supported by the fact that the formation of ethane in the dilute sample, where reaction (4) is prohibitive, is negligibly small (cf. spectrum II of Fig. 3). The thermal acceleration of the recombination implies that the reaction is not completely barrier-free, which is reasonable in view of the possible cage effect in the solid matrix.

Meanwhile, the small recovery of methyl iodide in spectrum III of Fig. 3 may be attributed to the geminate recombination of the iodine atom of reaction (1) with the counterpart radical which has failed to induce reaction (2). Thus, we add the following recombination also:

$$CH_3 + I \rightarrow CH_3I.$$
 (7)

It is to be noted that the methyl radical survives at 4.8 K for longer than 10 h. Thus, the recombination reactions (6) and (7) must be immeasurably slow at 4.8 K but start to be observed at temperatures higher by only a few kelvins. Such a sensitivity of the reactions to the temperature is quite remarkable.

The three stable species, i.e., methyl iodide, methane, and ethane, present in the photolyzed sample are considered to be susceptible to aggregation by thermally induced diffusion as revealed by the loss of the band structures and/or by the red shift of the newly appearing broad bands (see Figs. 1 and 2). We note that the thermal expansion of the solid parahydrogen increases sharply at temperatures above about 7 K.³⁸ The stress caused by the increase in the thermal expansion may ease the diffusion of the molecules for aggre-

gation. In the case of ethane, however, both the loss of the structure and the spectral shift are small compared with methane and methyl iodide. It is also noted that the absorptions ascribed to ethane in spectra II–IV of Fig. 1 are considerably different from the absorptions of the ethane/ parahydrogen system shown in the inset of Fig. 1. In this latter system ethane is not considered to be well isolated, whereas the ethane giving the absorptions in spectra II–IV of Fig. 1 should be isolated from another ethane molecule by virtue of the mechanism of reaction (5). This difference of the environment of ethane in the two systems is regarded as responsible for the difference of the spectral line shape.

It must be stressed that the above argument is based on the presumption that the reactions in the gaseous and in the solid parahydrogen are essentially the same. To endorse the assumption it is desirable to detect iodine molecules produced simultaneously with ethane and the methyl radical in our system. We are now planning such experiments.

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